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Graft-polymerization of a hydrophobic monomer onto PAN textile by low-pressure plasma treatments

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Abstract

In order to confer a good and durable water and oil repellence to polyacrylonitrile (PAN) fabrics, the fluorinated monomer 1,1,2,2, tetrahydroperfluorodecyl acrylate (AC8) was graft-polymerized onto PAN samples using a low-pressure microwave (MW) plasma process. The property was achieved by creating covalent bonding between the PAN fabrics and the fluorinated polymer. The grafting and the polymerization processes were followed by weighing measurements, XPS, IR(ATR) spectroscopies and SEM. The impermeability of the fabrics and the durability of the coating were investigated by Schmerber tests. Moreover, these tests allowed us to appreciate the effect of a reorientation of the fluorinated chains at the surface and also the role played by the addition of a small amount of a cross-linking agent on the surface properties.

Keywords: Microwave plasma; Graft-polymerization; Hydrophobic coating; Schmerber pressure; Fluorinated acrylate

1. Introduction

Fluorine liquids, because of their weak intermolecular interactions, have very low surface tensions. Therefore, it is not surprising that fluorinated polymers exhibit also low surface tensions, which render these polymers extremely difficult to wet with aqueous or organic liquids [1]. These surfaces are not adhesive with a low friction coefficient and consequently are oil- and water-resistant. For that reason, fluorine derivatives—monomers, oligomers or polymers—are widely used for the coating of substrates such as textiles, papers, leather, wood, etc. in order to obtain oil- and water-repellent surfaces. For this purpose, fluoroalkyl compounds and particularly the perfluoalkyl(meth)acrylates, as their homo and copolymers, are actually the most effective [2,3].

Previously, several wet treatments have been made, but the increase in industrial applications prompted the search for more profitable and environmentally clean processes, such as low-pressure plasma techniques. Moreover, the effect of the plasma treatment has the advantage of being mostly limited to the surface of the material.

Here we present a fast and convenient synthetic method involving a low-pressure plasma process to waterproof polyacrylonitrile fabrics with AC8 (1,1,2,2, tetrahydroperfluorodecyl acrylate).

2. Experimental

2.1. Materials and reagents

PAN fabrics were kindly supplied by the Dickson–Constant Society and the monomer (AC8) used for graft polymerization onto this fabric was donated by Elf Atochem. The monomer is stabilized with hydroquinone (<100 ppm). It was used either as received or the stabilizing agent was extracted twice with 10% aqueous NaOH, and the separated organic phase was dried over anhydrous magnesium sulfate prior to use. The photo-initiator 2-hydroxy-2-methylpropiophenone (Darocur 1173) and the cross-linking agents EGDMA (Ethylene glycol dimethacrylate), BPEDA [bisphenol A ethoxylate

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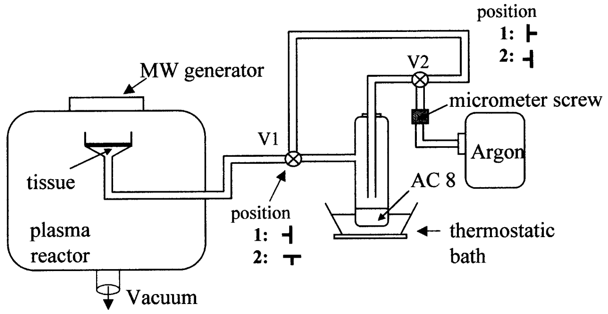


Fig. 1. Experimental set-up for the vaporization of AC8.

(4 EO/phenol) diacrylate], TTEGDA [tetra(ethyleneglycol)diacrylate] were purchased from Aldrich. Chloroform, petroleum ether and 1,1,2-trichloro-1,2,2-trifluoroethane (freon 113) were obtained from SDS and/or Prolabo. They were utilized as received. Argon (99.998%) was obtained from Air Liquide.

2.2. *Low-pressure plasma process*

A Europlasma set-up composed of three parts generates the microwave plasma. (i) A microwave generator (2.46 GHz) with a tunable power ranging from 0 to 600 W provides the excitation, (ii) a glow-discharge, which is generated at the top of the chamber (volume: 27 l), and (iii) a pumping system composed of a primary pump (E2M28 PFPE, Edwards). 'Unit mass flow controllers' regulate the gas flow.

2.3. *Graft-polymerization procedure*

2.3.1. *Plasma induced graft-polymerization of AC8*

In a first step, pieces of textile fabrics (14×18 cm) were pre-activated by an Ar plasma (flow rate: $F_{\mathrm{Ar}}=$ 0.5 l/min; $P=100$ W, $t=10$ min), and subsequently the samples were immersed at room temperature for one minute in 50 ml of a petroleum ether solution containing 5–200 g/l of AC8 in the presence of 2.5% by weight of the initiating agent (Darocur 1173) and various amounts of a cross-linking agent. After the immersion step, these impregnated fabrics were pressed to evacuate the excess of the solution and submitted to a MW Ar-plasma ($F_{\mathrm{Ar}}=0.5$ l/min; $P=100$ W, $t=10$ min). The treated fabrics were finally washed-in some cases up to 24 h at room temperature or in a soxhlet using various solvents and dried under different conditions.

2.3.2. *Plasma polymerization of AC8*

Because AC8 has a low volatility (<1.3 hPa at $T=$ 298 K), we used the experimental set-up depicted in Fig. 1 to perform the direct plasma polymerization of AC8 on virgin PAN. This set-up allows us also to avoid problems of polymerization inside the mass flow controller. The monomer (which contains 1% wt. of hydroquinone to prevent its homopolymerization) was kept in a thermostatic bath between 25 and 80 °C. The vapor of AC8 was introduced directly into the plasma chamber by passing an argon flow over the surface of the liquid monomer. The flow was not regulated by the mass flow controller of the plasma set-up, but controlled by the pressure measured inside the reactor. The valves V1 and V2 permit either to pass pure argon (for the purpose of pre-activation) or AC8 loaded argon into the plasma chamber.

The tissue was spanned into a polypropylene funnel (diameter: 13.2 cm) which was connected directly with the gas inlet in such a way that the employed gases had to go through the sample. The tissue was pre-activated ($t=3$ min, $P=100$ W, $P=93$ Pa) with argon (valves V1, V2 in position 1). Subsequently, the valves V1 and then V2 were changed into position 2 in order to introduce the monomer/argon gas mixture. Various experiments were performed by changing the treatment time, the working pressure, and the temperature of the thermostatic bath.

2.4. *Surface characterization*

[^{1}H] NMR spectra were recorded in Cl_2FCCF_2Cl with C_6D_6 as external lock or $CDCl_3$ using a Bruker WP 300 NMR spectrometer.

Infrared spectra were recorded with a Bruker IFS 48 spectrometer using a Graseby Specac, continuously variable-angle ATR accessory equipped with a KRS-5 crystal.

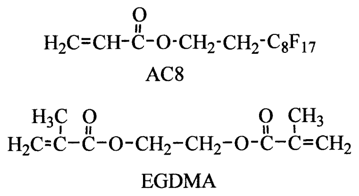
The XPS analyses were performed with a LHS 10 system (Leybold AG). The X-ray source was operated at 13 kV, 20 mA using AlKα radiation (1486.6 eV). Vacuum during analyses was in the 10^{-6} Pa range. All the experiments were carried out at the normal incidence relative to the plan film surface.

Weighing measurements were used to monitor the grafting and polymerization processes. The degree of grafting was determined as follows:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

Where, W_0 and W_g are the weights of the PAN fabric samples before and after grafting, respectively.

Considering the irregularity and the capillarity of the surface the commonly used contact angle measurements were not reliable for the investigation of the wettability of the tissues and the durability of the coating and were replaced by Schmerber tests (Norm NFG 07057 or Schopper DIN 53886). The principle is the following: A column of water is connected from below to a piece of textile stretched on a frame. Water is added progressively to the column, whereby the textile is exposed to an increasing pressure of water. The Schmerber value noted corresponds to the height of water (cm) reached when three drops of water went through the fabric. The



$$H_2C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}C_8F_{17}$$

AC8

$$H_2C{=}\overset{H_3C}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2$$

EGDMA

Scheme 1. Structure of AC8 and EGDMA.

height of the water column is directly transformed to the water pressure, in our case, 1 cm of water $=0.01$ N/cm^2. The textile is regarded as a succession of capillaries with a radius R. For a given liquid L, the capillary pressure is given by the following Eq. (1):

$$P=(2\gamma_L/R)\cos\theta \qquad (1)$$

In which γ_L and R are determined by the nature of the textile and the liquid used, θ is the contact angle. When the values of the surface tension are used, for water at 25 °C, ($\gamma_L=72.8$, $\gamma_L^d=21.8$ and $\gamma_L^p=51.0$ mN/m), Eq. (1) becomes:

$$P=(145.6/R)\cos\theta \qquad (2)$$

With P (mN/m^2) and R (m).

3. Results and discussion

In order to investigate the behavior of AC8 in polymerization reactions induced by an microwave Ar plasma, we have studied the kinetics of the homopolymerization under the influence of different parameters like the presence or absence of a stabilizing agent, an initiator and its concentration, the power of the plasma generator and the thickness of the monomer films. The results were presented in a previous paper [4]. These experiments allowed us to find the optimal conditions for AC8 homopolymerization, i.e. $P=100$ W, 2.5% wt. Darocur and were applied for the treatment of the PAN fabric samples. As outlined in the experimental section, we developed a simple four step process for the PAN surface coating with AC8 consisting of (i) a short pre-activation of the PAN surface, (ii) an impregnation of the pre-activated PAN textile in a AC8 bath solution, (iii) a plasma induced graft polymerization, and (iv) a washing and drying routine.

3.1. Influence of the concentration of monomer AC8

A series of experiments was performed with a petroleum ether solution of the monomer AC8 at various concentrations, 20, 100 and 200 g/l with 2.5% wt. of Darocur 1173 and 3.5% wt. of cross-linking agent (EGDMA) (Scheme 1).

In each case the fabrics were weighed initially (W_i), after pre-treatment (W_0), after plasma treatment (W_g), after washing (soxhlet with $CHCl_3$ and/or freon 113) and drying (1 h at 60 °C) (W_g'). The grafting yield was evaluated from the increase of the weight of dried polymers based on the weight of the pre-treated textile fabrics (W_0). Fig. 2 shows the effect of the concentration of monomer AC8 on the degree of grafted compound on PAN fabric samples.

As shown in Fig. 2, the amount of deposited perfluoroacrylate compound increases almost linearly with the concentration of monomer in the bath solution. However, the amount of grafted product does not follow this pattern. After washing with chloroform, which is a solvent for the monomer only, the weight loss is very high in any case independently on the concentration of the monomer. With the most concentrated solution (200 g/l) the weight loss reaches 90%. When the PAN fabric samples are washed with freon 113 which is a solvent for the monomer and the polymer, the amount of residual product deposited on the textile (25, 62 and 7% compared to the deposited amount before washing for AC8 concentrations at 20, 100 and 200 g/l, respectively) is even lower. Note that the weight loss of PAN fabric samples after activation followed by washing with $CHCl_3$ or freon 113 is below 1% indicating little ablation from the PAN surface under the plasma conditions we used.

[^{1}H]-NMR experiments of the washing solution allowed us to confirm the loss of polymer in the case where the most diluted solution (20 g/l) was used for the grafting process. Indeed, the [^{1}H]-NMR spectrum reveals only the presence of signals corresponding to the polymer. Contrarily, when a PAN fabric sample is immersed in pure AC8, treated in the MW plasma as above, and washed with freon 113, only the signals of the monomer are noticed in the [^{1}H]-NMR spectrum. We conclude that the product, which remains on the PAN fabric and resists the washing procedure with freon (soxhlet) corresponds to the part of polymer which is

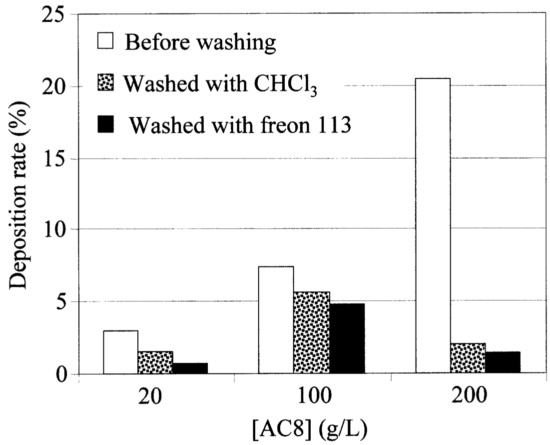


Fig. 2. Effect of the concentration of AC8 on the degree of grafting on PAN tissue treated by a MW Ar plasma ($F_{Ar}=0.5$ l/min; $P=100$ W, $t=10$ min), before and after washing in $CHCl_3$ and freon 113.

Table 1
Schmerber pressures of impregnated PAN tissue samples in various solution of monomer containing 2.5% of darocur +3.5% of EGDMA and then treated by a MW Ar plasma ($F_{Ar}=0.5$ l/min; $P=100$ W, $t=10$ min) before washing

[AC8] (g/l)	$P_{Sch.}$ (N/cm^2)
0	0.00
20	0.39
100	0.31
200	0.24

covalently grafted on the surface of the fabric. This amount of grafted polymer depends on the concentration of the impregnation solution and is highest for a AC8 concentration of 100 g/l.

In Table 1, the Schmerber pressures of the treated textile samples before washing are given.

As can be clearly seen, the Schmerber value decreases when the AC8 concentration in the impregnation solution is increased indicating an increase of the surface tension. This somewhat unexpected result is probably due to the higher amount of deposited monomer on the fabric and/or a more disorganized layer of the deposited polymer using high AC8 concentrations. Because surface coatings with the most diluted solution gave satisfying results, i.e. a high Schmerber pressure, we choose a concentration of 20 g/l AC8 in the bath solution for the following investigations.

3.2. Effect of the cross-linking agent

To evaluate the effect of the cross-linking agent and its concentration, three different tests were performed on pre-treated PAN fabric samples impregnated in a petroleum ether solution containing 20 g/l of AC8, 2.5% by weight of Darocur and various amounts of EGDMA.

3.2.1. XPS analyses

Fig. 3 shows the XPS wide scan spectra and the atomic ratios for PAN fabric samples (a) untreated, (b) impregnated in a monomer solution without and (c) with 3.5% wt. of EGDMA. All the fabric samples were washed in a soxhlet freon and dried during 1 h at 40 °C. For both types (b) and (c) of impregnated textiles, the spectra exhibit the F1s component indicating the presence of grafted fluoropolymer on the surface of the textile.

The disappearance of the N1s component gives information about the depth of the grafted polymer, which is higher or equal to the analyzed depth (50 Å). Moreover, the atomic ratios are consistent with the formation of polyAC8. Note that the untreated PAN presents a nN/nC ratio lower than the expected one (0.27) and a higher nO/nC ratio. These differences can be attributed to the presence of methyl polyacrylate, which is constitutive to the PAN fiber and organic impurities on the surface of the textiles.

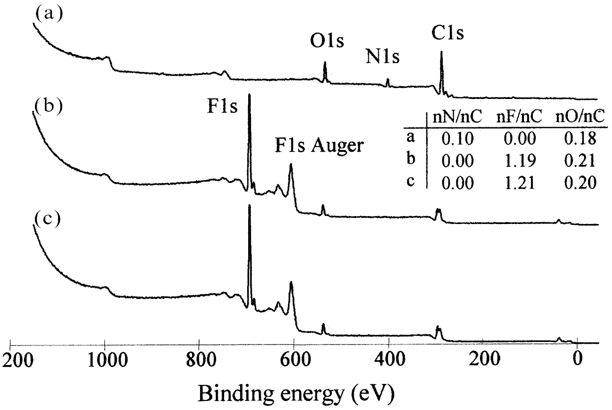


Fig. 3. XPS spectra and atomic ratios of PAN tissue samples (a) not treated; (b) pre-treated and immersed in a solution in petroleum ether containing 20 g/l of AC8, 2.5% wt. of darocur, Ar-plasma exposed, washed in a soxhlet freon and dried 1 h at 40 °C; (c) same condition as (b) plus 3.5% wt. of EGDMA.

3.2.2. IR(ATR)

The presence of polyAC8 on the surface of the treated PAN fabric samples has been also identified by IR(ATR) spectroscopy, as shown in Fig. 4.

In both cases, for the treated PAN fabric samples with or without EGDMA, the characteristic absorption bands at $\nu=1200$ cm^{-1} and $\nu=1150$ cm^{-1} appear corresponding to the asymmetric and symmetric CF stretching vibrations, respectively. These bands are missing in the IR-spectra of non-treated PAN textile. In the case of fabrics treated in presence of a cross-linking agent, these absorption bands are more intense than without EGDMA. However, in both cases the absorption band characteristic for the C=N stretching vibration at $\nu=2240$

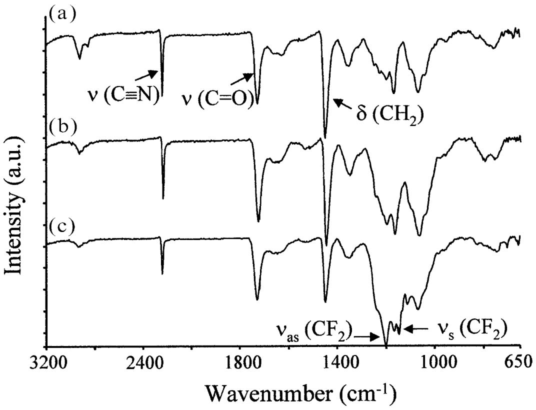


Fig. 4. IR(ATR) spectra of PAN tissues (a) not treated; (b) pre-treated and immersed in a solution in petroleum ether containing 20 g/l of AC8, 2.5% wt. of darocur, Ar-plasma exposed, washed in a soxhlet freon and dried 1 h at 40 °C; (c) same condition as (b) plus 3.5% wt. of EGDMA.

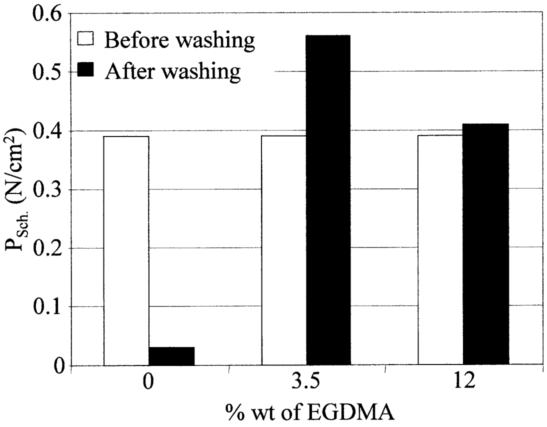


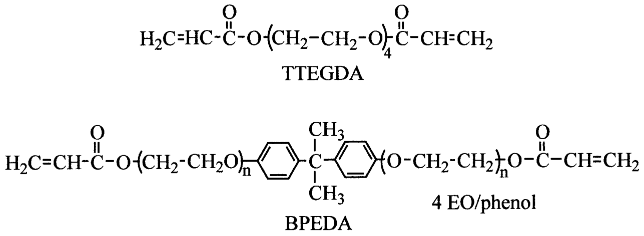
Fig. 5. Dependence of the% wt. of EGDMA on Schmerber values of polyAC8 grafted PAN tissues (a) before and (b) after washing in freon 113 (soxhlet).

cm^{-1} is still visible which indicates that the depth of the deposited layer is lower that the analyzed depth (≈ 1 μm).

3.2.3. Schmerber tests

The effect of the amount of cross-linking agent on the Schmerber pressures ($P_{Sch.}$) obtained for polyAC8-grafted samples before and after washing in freon (soxhlet, 24 h) and drying during 1 h at 40 °C are presented in Fig. 5.

The Schmerber pressure drops dramatically (0.03 N/cm^2) without EGDMA as a cross-linking agent, contrarily to the cases where this compound is present. Indeed, a maximum of 0.56 N/cm^2 is reached for 3.5% wt. of EGDMA. However, with 12% wt., the pressure is still high, but less pronounced as in the previous case. The Schmerber pressure gives information about the surface energy of the textile and the higher its value, the lower is the surface energy. The cross-linking agent participates actively to the grafting of the polyAC8 on the PAN textile, which helps to confer good hydrophobic properties to the fabric.



Scheme 2. Structure of TTEGDA and BPEDA.

3.2.4. SEM

The grafting could be visualized also by comparing SEM pictures of treated PAN fabric samples with untreated ones (Fig. 6).

As shown on Fig. 6a, the surface morphology along the fiber of the untreated PAN tissue is rough and scaly. On the contrary, the surface of the polyAC8-grafted sample (Fig. 6b) is completely surrounded by the grafted polymer, which covers the irregularities. Note that only the surface of the fiber is sheltered, the space between the fibers stays free of polymer.

3.2.5. Effect of the nature of the cross-linking agent

The effect on the polymerization of two other cross-linking agents BPEDA and TTEGDA (Scheme 2), which differ by the nature or the length of the spacer between the two (meth)acrylate functions was investigated and compared with the results obtained with EGDMA.

In all cases the Schmerber pressures obtained are exactly the same and equal to 0.39 N/cm^2. The nature of the cross-linking agent has no effect on the $P_{Sch.}$ and consequently, on the surface energy. The following investigations have been pursued with EGDMA.

The combination of the results discussed so far, allows us to conclude that the polyAC8 on the surface of the treated PAN fabric samples, which resists even several washing cycles in a soxhlet with freon, is covalently grafted and not only deposited. When the AC8 monomer is subjected to a bulk Ar-plasma polymerization, a

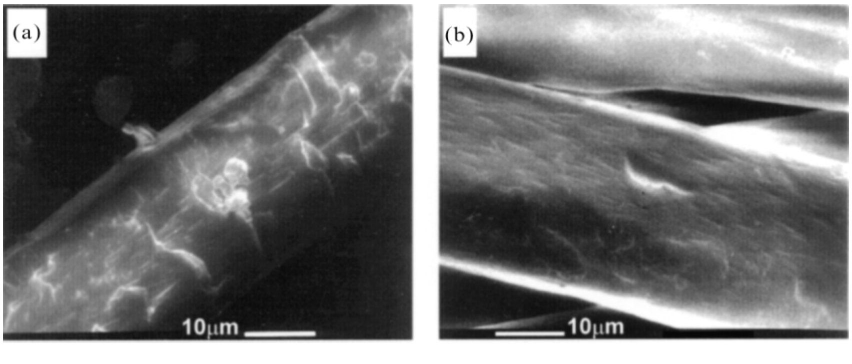
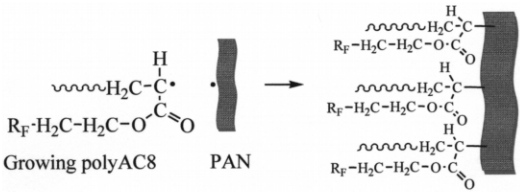
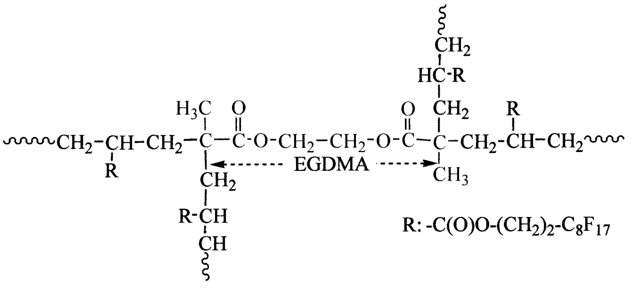


Fig. 6. SEM images of PAN tissue samples (a) not treated; (b) pre-treated and immersed in a solution in petroleum ether containing 20 g/l of AC8, 2.5% wt. of darocur and 3.5% wt. of EGDMA, Ar-plasma exposed, washed in a soxhlet freon and dried 1 h at 100 °C.



Scheme 3. Schematic representation of the grafting of the growing polyAC8 on the surface of the PAN tissue.



Scheme 4. Illustration of the insertion of EGDMA in the polyAC8.

Table 2
$P_{\mathrm{Sch.}}$ values (N/cm^2) of polyAC8 grafted PAN tissue samples obtained initially and after 7 months of aging

Fabrics	$P_{\mathrm{Sch.}}$ (N/cm^2)	
	Initial	After 7 months of aging
n°1	0.45	0.44
n°2	0.42	0.47
n°3	0.42	0.50

soluble polymer (not cross-linked) is obtained. This indicates that the grafting may proceed via the coupling between an acrylate radical of a growing polyAC8 chain and a PAN surface radical (Scheme 3).

Moreover, the presence of EGDMA is crucial for a sufficient grafting. This agent can serve as a cross-linking agent between the polyAC8 chains (Scheme 4) and as a coupling agent between the polyAC8 and the PAN surface.

This effect can be explained by its higher polarity compared to the fluorinated acrylate, which provokes its migration to the PAN-monomer interface in order to minimize the interfacial tension between the substrate and the monomer or the growing polymer and consequently assists the grafting. However, when the concentration of the cross-linking agent is too high, the surface tension of the grafted polymer film increases and therefore its wettability. This is indicated by the decrease of the $P_{\mathrm{Sch.}}$ values with higher amount of cross-linking agent.

The repellent properties of the PAN fabric are visualized in the following pictures (Fig. 7).

The droplets of water roll onto the surface with an apparent contact angle of 132°, which confirm the water repellent character of the treated fabric (Fig. 7a). Moreover, the low surface energy render the modified fabric also to be stain resistant (Fig. 7b).

In order to test the resistance of the grafting under out-door conditions, three polyAC8 grafted PAN fabric samples which were independently synthesized but under the same conditions were exposed outside of the laboratory during 7 months. The aging of the coating was evaluated by $P_{\mathrm{Sch.}}$ measurements. The results are presented in Table 2.

As can be seen, the three samples exhibit almost the same initial pressure, which attests the reproducibility of the treatment and the reliability of the measurement. After 7 months of exposition outside, the pressure is almost the same in the case of sample *n*°1 and even slightly higher for the others. This demonstrates the durability of the coating due to the formation of covalent bonds between the PAN surface and the polyAC8. It is well known that the surface properties of polymers are time, temperature and environment dependant[5]. Our aging experiments indicated that the grafted polymer chains at the surface do re-orientate according to the atmospheric conditions to minimize the interfacial tension between the polymer and the environment which may lead to a slight increase of the Schmerber pressures.

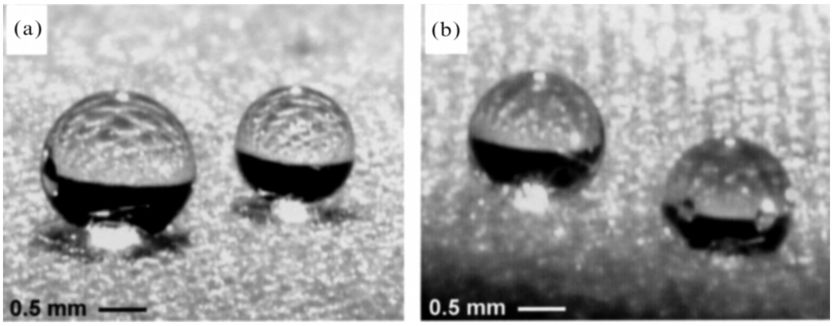


Fig. 7. Repellent properties of polyAC8-grafted PAN tissue samples towards water (a) and olive oil (b).

Table 3
Bragg spacings (nm) obtained at room temperature for polyAC8 and polyMAC8 films

Sample	Diffraction maxima					Ref.
	d_1	d_2	d_3	d_4	d_5	
PolyAC8	3.32	1.61	1.08	0.65	0.50	[9]
	3.33	1.62	1.07		0.50	[8]
	3.20	1.60				[6]
	3.20	1.60			0.50	Our results
PolyMAC8	3.00	1.55	1.03		0.52	[9]
	3.01	1.55	1.04		0.53	[8]
	3.20				0.50	[7]
	3.20	1.60				[6]

In order to demonstrate the dynamic behavior of the surface, various experiments have been performed with the treated PAN fabric samples.

3.3. Dynamic of the surface

Fluorinated poly(meth)acrylates are comb-shaped polymers having fluorocarbon segments in the side chains orientated perpendicularly to the longitudinal axis of the macromolecule. It was already described that these fluorocarbon side chains give crystalline domains within the amorphous hydrocarbon skeleton [6–9].

Table 3 reports the Bragg spacing obtained from X-ray diffraction measurements at room temperature of polyAC8 and polyMAC8 extracted from the literature. Our values found for a polyAC8 film (the monomer was previously coated on a glass support) obtained by Ar-plasma induced polymerization ($F_{\mathrm{Ar}} = 0.5$ l/min; $P = 100$ W, $t = 10$min, thickness$= 190$ μm) are also given.

The Bragg spacings of a polyAC8 film (resulting from Ar-plasma polymerization of AC8) are comparable to those mentioned for polyAC8 films obtained by other techniques. The innermost diffraction d_1 (3.20 nm), which is twice as long as the expected chain length (≈ 1.62 nm), indicates the presence of a double layer. The distance between each fluorocarbon groups (within one layer) is given by d_5 (0.5 nm) and is also in accordance with the results previously described. For the bi-layer formation two models can be proposed, one with an eclipsed double-comb organization A the other one with an alternating orientation of the fluorocarbon chains as schematized in B in Fig. 8.

We favor the model B in view of the steric hindrance of the substituents [10,11]. The glass substrate, which has a higher affinity with the relatively polar polymer backbone, orientates the first layer in such a way that the C_8F_{17} units point away from the substrate. This induces an alternation of C_8F_{17} chain double layers and of polymer backbone. Finally, the surface tension of the polyAC8 film (14.7 mN/m) is in accordance with a surface covered by CF_3 groups.

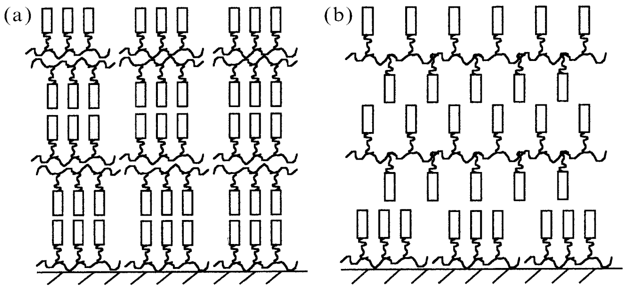


Fig. 8. Two-dimensional scheme illustrating the principal arrangements of alternating layers of the fluorocarbon chains and the polymer hydrocarbon skeleton. (a) double comb organization and (b) alternating orientation of the side chains [7].

3.3.1. Effect of the drying temperature

It is known [6–9,12] that the chain mobility increases with the temperature provoking re-orientations of deposited polymer chains. This effect was evaluated for the polyAC8 grafted PAN fabric samples by measuring the Schmerber pressures of unwashed samples after drying at various temperatures for either 1 h or 3 days. The pressures were taken after gradual cooling to room temperature in air (Fig. 9).

This graphic clearly shows that for a constant time of drying, a linear increase of the pressure with the temperature occurs. This variation from 25 to 100 °C is more pronounced when a long drying period was applied (3 days: $\Delta P = 0.22$ N/cm^2, 1 h: $\Delta P = 0.07$ N/cm^2). Note that at room temperature, no surface motions are observed.

In all cases the samples were slowly cooled to room temperature. Thermal transitions determined by DSC on polyAC8 films obtained by Ar-plasma have indicated no glass transition temperature (from −100 to 120 °C) but an endothermic peak at 62 °C (the corresponding enthalpy change is estimated to be 12.5 J/g) indicating the melting of the crystalline part (fluorocarbon chains) of the polymer. During the slow cooling process from 100 to 25 °C, a re-crystallization of the C_8F_{17} chains of

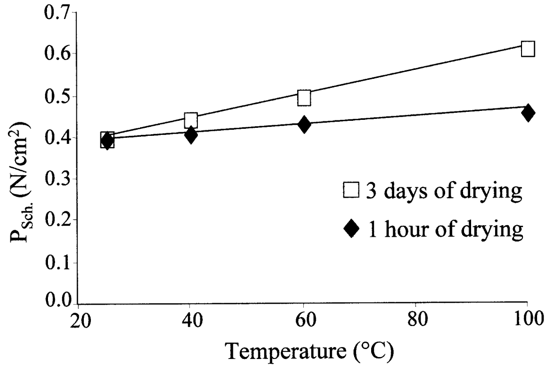


Fig. 9. Dependence of the drying temperature on the $P_{\mathrm{Sch.}}$ (N/cm^2) of unwashed grafted PAN tissue samples.

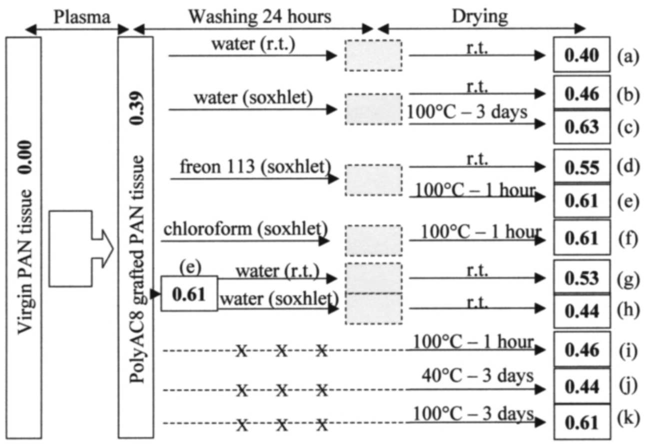


Fig. 10. Effects of the washing and drying conditions on the Schmerber pressures (N/cm^2).

the polyAC8 may occur. To verify this, fabric samples identically treated and dried at 100 °C for 3 days were immersed in liquid nitrogen for 30 min and then kept in the deep freezer until the measurements. The pressure obtained in that case was 0.43 N/cm^2 against the 0.61 N/cm^2 previously observed. The initial pressure, taken immediately after the Ar-plasma treatment was 0.39. This indicates that even in the molten state [13], the fluorocarbon chains maintain a certain degree of order, which is higher than the one obtained in the case of samples measured directly after their exit from the plasma chamber.

3.3.2. *Effect of the washing solvent*

In order to evaluate the effect of the polarity of the washing solvent on the surface properties of polyAC8-grafted PAN fabric samples, three solvents with different surface tensions were taken: freon 113 ($\gamma c = 12–15$ mN/m), chloroform ($\gamma c = 27$ mN/m) and water ($\gamma c = 72.2$ mN/m). The samples were washed with these solvents and dried under different conditions as depicted in Fig. 10.

Immediately, two predominant and independent effects are seen in Fig. 10: the surface tension of the solvent and the temperature of drying. For textiles washed first in a solvent with a low γL like chloroform and freon 113, and subsequently dried for one hour in air at 100 °C (e and f), very high $P_{\text{Sch.}}$ values are found (0.61 N/cm^2). This finding cannot be attributed neither to the drying temperature nor to washing procedure alone. An unwashed tissue dried under the same conditions exhibits a $P_{\text{Sch.}}$ of 0.46 N/cm^2 only (i). For a freon extracted (soxhlet) tissue which was dried in air at room temperature, the pressure [0.55 N/cm^2 (d)] is higher than before washing but still lower than in cases (e) and (f). For textiles which were washed with a solvent with a high surface tension like water and dried at room temperature, (a) no change of the initial pressure is observed. On the contrary, there is a moderate increase of the $P_{\text{Sch.}}$ value when the coated tissue is washed at the soxhlet temperature and dried at room temperature (b). Note that although water does not wet the tissue at the beginning of the washing procedure (85 °C), this is not the case after several hours in the soxhlet (not observed at room temperature). One has already explained this effect by the mutual variation of the surface tension of both counterparts with varying temperatures [6]. Indeed, when the temperature of the water augments from 25 to 80 °C, the surface tension decreases from 72.8 to 62.6 mN/m. Exactly the inverse phenomenon happens for the polyAC8 film; γS increases from 14.3 (25 °C) to 29 mN·m^{-1} (86 °C) [14]. This effect explains the pressure obtained in entry (b) but not in (c) where the pressure reaches 0.63 N/cm^2. This significant variation is mainly a consequence of the conditions used for drying because almost the same value is obtained for the unwashed textiles (k). Water is a non-solvent for the monomer and the polymer and the results obtained in (d) and (e) with freon may result from the dissolution of unbound monomer and polymer. In order to verify whether this hypothesis is correct or not, further tests were performed with a sample prepared as indicated in entry (e). Two samples were washed again in water at two different temperatures and finally dried at room temperature. Interestingly, after the treatment with water in a soxhlet the $P_{\text{Sch.}}$ drops from 0.61 to 0.44 N/cm^2 (h) comparable to the result reported in entry (b) where the same conditions were employed. When the washing procedure with water is performed at room temperature, the PSch. drops also but to a lesser extend (g). The system is reversible, i.e. applying to the tissue obtained after treatment (h) the procedure (e) will lead to an increase of the $P_{\text{Sch.}}$ to the original value of 0.61 N/cm^2. In a third experiment, the tissue was exposed a second time to the washing procedure with freon followed by drying, which, however, does not affect the Schmerber value.

All these tests clearly demonstrate dynamic motions at the surface of the grafted PAN tissue and this behavior is due to the mobility of the perfluorinated chains at the interface polymer film/air or polymer film/solvent. When immersed in a liquid (water, $CHCl_3$, freon) the predominant factor is the interfacial tension between the two counterparts. As seen, in hot water, the fluorinated chains tend to migrate in the direction of the substrate increasing the surface tension of the fabric. In a freon or chloroform medium, the opposite behavior is observed.

When exposed to air, the chain mobility is mostly affected by the temperature. It was already described for this type of polymers carrying fluorine chains that small tilts disturb the parallel comb-shaped organization of the chains, causing noticeable changes of the surface properties. Indeed, when the orientation of the fluorocarbon chains is perfectly parallel, the outermost surface of the substrate is completely covered by CF_3 groups, which lowers considerably the surface energy. But reorientation may occur according to the surrounding atmospheric conditions making the polar groups of the polymer accessible which leads to an increase of the surface energy and concomitantly to a decrease of the Schmerber pressure. However, by varying again the environmental conditions, these phenomena are completely reversible.

3.4. Plasma polymerization of AC8

Although not the objective of this work but for comparison, we studied in preliminary form the direct plasma polymerization of AC8 on virgin PAN. Because AC8 has a low volatility (<1.3 hPa at $T=298$ K) we used the set-up described in more detail in the experimental section. An argon stream was loaded with AC8 by passing the stream over the surface of the liquid monomer which was kept at a temperature between 25 and 80 °C. The gas flux into chamber was regulated such that different working pressures between 50 and 120 Pa were maintained. In a number of experiments the treatment time, the working pressure, and temperature of the heating bath containing the monomer container was varied. As is shown in Fig. 11, the amount of the deposited polymer increases with increasing values of each of these parameters.

XPS analyses (Table 4) confirm the deposition of a fluorocarbon polymer on the surface of the PAN fibers. The deposit is slightly reduced after washing and drying and the nF/nC and nN/nC ratios given in entry (2) of Table 4 indicate the amount of the remaining grafted polymer.

Table 4
XPS analyses and Schmerber pressures of PAN tissues treated by an (AC8+Ar) plasma ($p=93$ Pa, $P=100$ W, $T_{bath}=25$ °C, $t=10$ min). (1) before washing, (2) after washing (soxhlet freon) and drying (1 h, 100 °C)

(AC8+Ar) treated PAN tissues	XPS analyses		$P_{Sch.}$ (N/cm^2)
	nF/nC	nN/nC	
(1)	1.27	0	0.32
(2)	0.98	0.05	0.29

However, the Schmerber values are inferior to all values obtained with the plasma induced polymerization procedure described above. They increase slightly with the treatment time (i.e. $P_{Sch.}=0.28$ N/cm^2 at 0.3% deposition rate and $P_{Sch.}=0.35$ N/cm^2 for 1.4% deposition rate) but they decrease after washing with freon 113 (soxhlet) and drying at 100 °C for one hour (Table 4). Interestingly, this contrasts the behavior we have observed previously for the samples, which have been treated by the plasma induced polymerization process of AC8. In this case, the Schmerber pressure increased from 0.39 to 0.61 N/cm^2 when the coated sample was washed and dried under the same conditions [see entry (e) in Fig. 10].

We interpret these results as follows: It is well established that classical plasma polymerization procedures whereby the deposition process proceeds via a gaseous monomer lead to highly cross-linked polymers. This causes the loss of the chain mobility and impedes the 'comb shaped' orientation of the fluorocarbon chains on the surface. As a result, a high surface tension and low impermeability is obtained as is indicated by the low Schmerber pressures. Using the plasma induced

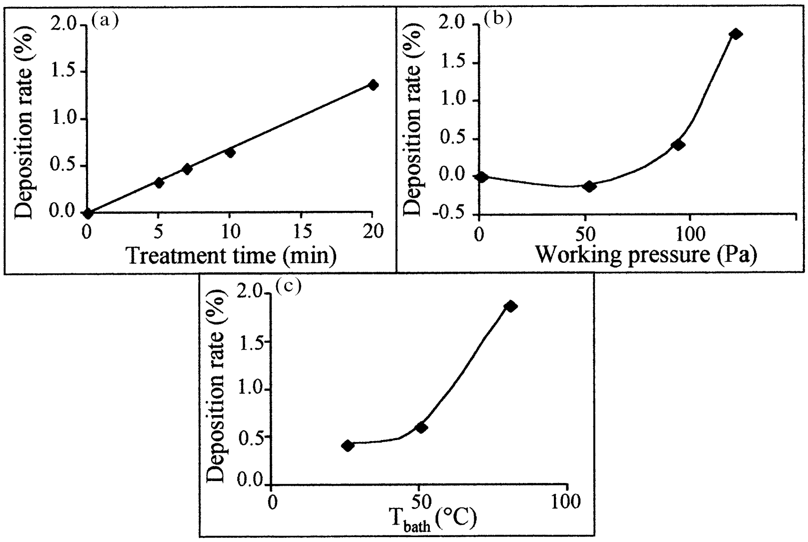


Fig. 11. Dependence of (a) the treatment time ($P=93$ Pa, $P=100$ W, $T_{bath}=25$ °C), (b) the working pressure ($P=100$ W, $T_{bath}=25$ °C, $t=10$ min) and (c) the temperature of the thermostatic bath ($P=93$ Pa, $P=100$ W, $t=10$ min) on the deposition rate of polymer on virgin PAN treated under (AC8+Ar) plasma.

polymerization grafting procedure which we described here, obviously gives polymer deposits which have only a low degree of cross-linking. Thereby a sufficient degree of flexibility of the fluorocarbon chains is maintained which allows their 'comb shaped' orientation, which is the 'key-point' for a good repellent character.

4. Conclusions

This work demonstrates that PAN textiles can be made water and oil repellent in a very efficient and simple way using a low-pressure plasma process which induces simultaneously the grafting and the polymerization of monomers on the surface of the substrate in one working-step. To achieve this, a PAN tissue is impregnated with a solution of a fluorinated methacrylate (AC8), in presence of an initiator (Darocur) and a cross-linking reagent. The excess of reactant is removed by pressing and the remaining material polymerized. In comparison to procedures using plasmas created with gaseous fluorinated reactants, or the AC8 monomer, the Ar plasma induced graft-polymerization of a monomer of low volatility and in direct contact with the substrate surface gives a superior performance concerning the water and oil repellency. This result is due to the fact that with this procedure the structure of the monomer is largely maintained in the repeating units of the monomer which in turn determines the macromolecular properties of the polymer chains (comb-shape orientation of the fluorocarbon residues), which in this case is the 'key-point' for a good repellent character. Furthermore, the method described here uses much smaller amounts of fluorinated reactant to achieve the desired effects. Indeed, it turned out that already small concentrations of AC8 in the bath solution (20 g/l) are sufficient to make PAN tissues highly water- and oil repellent. Hence, the method presented here is a cost-, energy and waste saving process. We are currently investigating the scope of this procedure, especially, the possibility of creating polyfunctional surfaces.

Acknowledgments

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