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Fluorinated-plasma coating on polyhydroxyalcanoate PHBV Effect on the biodegradation

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Abstract

Poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) (PHBV) was covered with an hydrophobic layer from plasma polymerization of tetradecafluorohexane, octadecafluorooctane, 3,3,4,4,5,5,6,6,6-nonafluoro-hex-1-ene and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-oct-1-ene. The water contact angle increased from 74° for untreated films to 98° for the treated films and the surface energy decreased from 40.9 to 18.8 mJ m^{-2}. XPS analysis showed the introduction of 54% fluorine and 3–7% oxygen, the binding energies were assigned to chemically differently bonded carbon atoms. CF_2/CF_3 molar ratio in plasma layers was lower than that in the monomers due to molecular fragmentation, however the extent of monomer structure retention in PFH, PFO saturated chains is higher than in NFH, TDFO unsaturated chains. Biodegradation tests under aerobic conditions showed that the fluorinated plasma layer inhibited the biodegradation of the PHBV film underneath.

Keywords: Fluorinated monomers; Plasma polymerization; X-ray photoelectron spectroscopy; Polyhydroxyalcanoate; Biodegradation

1. Introduction

Plasma polymerization is a powerful technique to modify the surface of materials by changing the chemical nature of the groups. The process results in depositing a 10–500 nm thick layer, which is generally compact and cross-linked. During the two past decades, plasma polymerization led to the development of fundamental researches and applications; such as microelectronic devices, protective layers against corrosion, selective layers for ultrafiltration and gas or liquid separation membranes, biocompatible and hemocompatible coatings for biomaterials, dressings, medical tubings and catheters [1,2].

The technique involves an electrical discharge, created from a 13.56 MHz rf generator, in low-pressure gas or monomer vapours. The excited species resulting from the activation of the gaseous media through energetic collisions, combine to form oligomers then polymers which deposit on the surface of the materials. The plasma-polymerized layer is generally covalently and permanently bonded to the macromolecular chains of the surface which is also activated during the plasma discharge. The polymerization in fluorocarbon plasmas has been widely studied. Among the fluorinated molecules used to modify a large range of polymer surfaces, tetrafluoromethane, perfluoroethane and perfluoropropane were the most investigated (for example [3–6]). More recently, sulfur hexafluoride plasma was employed [7].

Biodegradation of polymers is also related to the surface properties, because the surface is the entrance to the bulk for enzymes from the microbial flora. Depending on the nature of the surface, the onset of biodegradation of the material underneath could be delayed or initiated. Surprisingly, there are few examples of modification of the surface of biodegradable polymers by the plasma technique, in order to deposit a film with specific properties.

The polyalcanoates, well-known thermoplastic polymers, are of particular interest because of low environmental impact [8]. Improvement of the biodegradation of polyalcanoates can be achieved by increasing the hydrophilicity of the surface to facilitate diffusion of the enzymatic aqueous media towards the

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bulk. Argon and oxygen plasma for grafting polar groups and acrylic acid plasma for depositing an hydrophilic layer, were most widely investigated [9,10]. However, modification of the polyalcanoate surface did not lead to a more rapid biodegradation.

For the use of polyalcanoates in packaging, their poor barrier properties against water and their susceptibility to hydrolysis, are major obstacles for their possible replacement of traditional packaging materials such as polyethylene, polyethylene terephthalate. The surface modification of polyalcanoate based materials by a thin waterproof layer could make them more attractive.

In this article, attempts are described to cover polyalcanoate film by a hydrophobic and protective plasma layer and to evaluate its possible effect for delaying biodegradation. For this purpose, poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) (PHBV) was selected. PHBV films were prepared by the cast-evaporation technique and plasma polymerizations of various fluorinated monomers were carried out. The layers deposited were characterized by XPS, FTIR-ATR and by the contact angle method to determine the wettability and the surface energy. Biodegradation of untreated and plasma treated PHBV films was measured under aerobic conditions and the oxygen consumption was compared to estimate the involvement of the fluorinated surface layer on the biodegradation.

2. Results and discussion

2.1. Characterization of the fluorinated plasma-deposited layer

Four fluorinated monomers: CF_3–$(CF_2)_4$–CF_3 (tetradecafluorohexane, perfluorohexane PFH), CF_3–$(CF_2)_6$–CF_3 (octadecafluorooctane, perfluorooctane PFO), CF_3–$(CF_2)_3$–$CH{=}CH_2$ (3,3,4,4,5,5,6,6,6-nonafluoro-hex-1-ene NFH), CF_3–$(CF_2)_5$–$CH{=}CH_2$ (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-oct-1-ene TDFO) were plasma polymerized to obtain hydrophobic layers with slightly different properties.

These monomers were selected for their availability and because their structures bear linear chains of varying lengths and varying fractions of CF_2 and CF_3 groups.

2.1.1. XPS analysis

The atomic percentage (at%) of carbon and oxygen present on the surface of the untreated film were 69.1 and 30.9, respectively, which is in reasonable agreement with the PHBV theoretical composition (67.2 and 32.8) (Table 1). Significant amounts of fluorine were detected on treated films. They are close to values expected for the various monomers, ranging from 53 to 56%.

The oxygen incorporated into the plasma layer came from the combination of gaseous oxygen or water, which could be present in the reactor in the form of adsorbed molecules, and the activated species present as radicals produced from the fluorinated monomers by glow discharge. Oxygen incorporation also occurred during aggressive plasma treatment, through the degradation of the superficial layer of the untreated surface which is often composed of short macromolecular chains and contaminating adsorbed molecules. Consequently, oxygenated groups are volatilized and could be recombined with fluorinated excited species. The main possibility is that the presence of oxygen was the result of interactions between radicals remaining in the polymers and dioxygen from air, when the samples were removed from the reactor vessel after finishing the plasma treatment. The oxidation of plasma treated films is generally observed and can be avoided with difficulty.

Oxygen content is slightly higher for PFH and PFO (about 7.4 at%) than for NFH and TDFO (about 3.4 at%) (Table 1). The greater reactivity of PFH and PFO plasma layers with dioxygen can be attributed to the presence of a large amount of residual activated species with long life time.

Typical high resolution spectra, C1s, from PFH plasma and PFO plasma films are reproduced in Figs. 1 and 2. They are also representative of NFH plasma and TDFO plasma, respectively. C1s envelopes reveal complex signals. For PFH and PFO 8 chemically differently bonded carbon atoms (Fig. 1a) and 7 for NFH and TDFO (Fig. 2a), are indicated according to the curve-fitting procedures and optimization of the analysis. The additional peak for both saturated monomers was situated at a high binding energy.

The curve fits for C1s spectra usually discussed in the literature are classified in terms of 5 types: CF_3, CF_2, CF, $\underline{C}$–CF

Table 1
Atomic percentage (at%) of elements for untreated and plasma treated PHBV film: averaged value from 3 spots with take-off angle 45° for each sample

at% of elements	Untreated PHBV	Plasma treatment			
		C_6F_{14}	C_8F_{18}	C_4F_9–$CH{=}CH_2$	C_6F_{13}–$CH{=}CH_2$
C	69.1	37.1	38.2	42.9	42.4
O	30.9	7.4	7.1	3.4	3.2
F		55.5	54.7	53.7	54.4
F/C					
Monomer		2.3	2.2	1.5	1.6
Plasma layer		1.5	1.4	1.3	1.3
CF_2/CF_3					
Monomer		2	3	3	5
Plasma layer		0.9	1.2	1.1	1.3

Typical values for C_6F_{14} (PFH), C_8F_{18} (PFO), $C_4F_9CH{=}CH_2$ (NFH) and $C_6F_{13}CH{=}CH_2$ (TDFO) plasma-polymerized monomers.

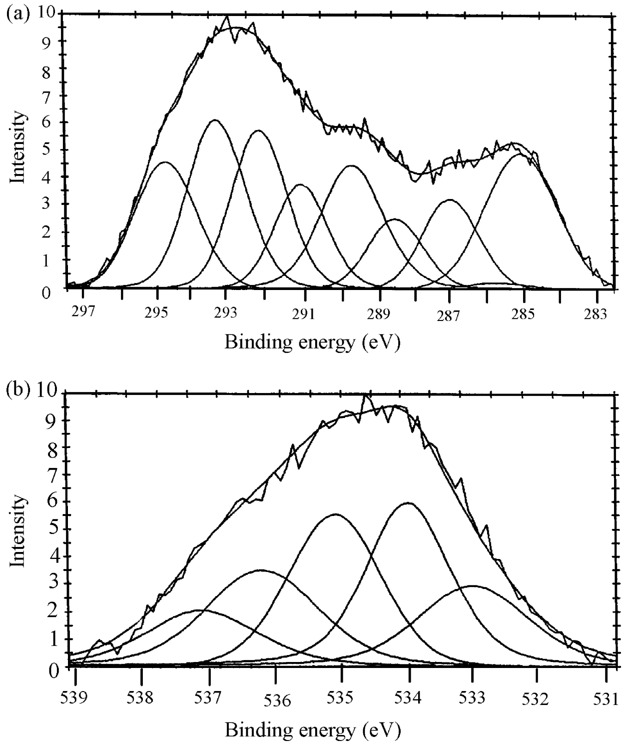

Fig. 1. C1s (a) and O1s (b) XPS spectra of C_6F_{14} (PFH) plasma-polymerized layer on PHBV film (binding energies are corrected to 285 eV for aliphatic carbon).

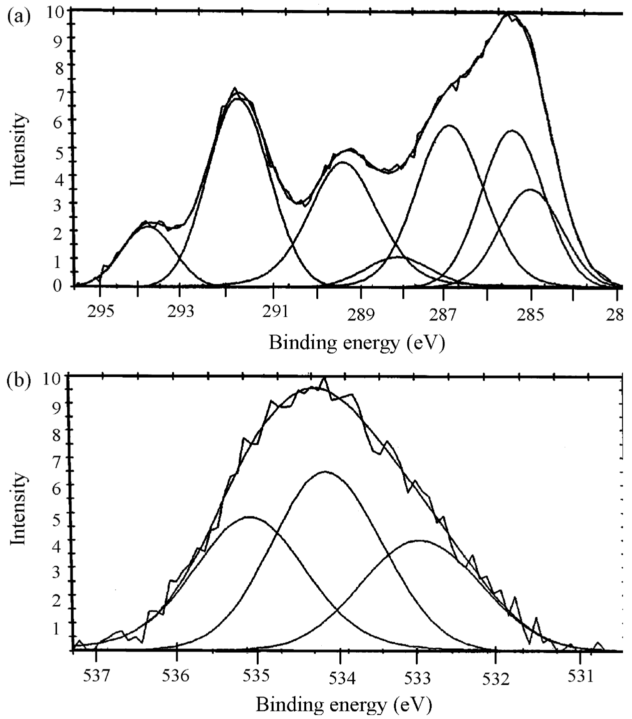

Fig. 2. C1s (a) and O1s (b) XPS spectra of $C_4F_9CH{=}CH_2$ (PFO) plasma-polymerized layer on PHBV film (binding energies are corrected to 285 eV for aliphatic carbon).

and C–C. The complete assignment of each binding energy to a functional group of such a random structure is not easy; for this situation the curves have to be interpreted very cautiously (Table 2) by using well-known data bases [11,12] containing fluorinated polymers and related species, for example poly(vinylidene fluoride), poly(tetrafluoroethylene), poly(vinyl trifluoroacetate), poly(vinyl trifluoroacrylate), and data from fluorine modified-polymer surfaces [13–17]. All binding energies have been charge-corrected to 285.0 eV for polymeric aliphatic carbon.

The peak at 294.8 eV that is present only in PFH and PFO plasma coatings can be attributed to carbon of the trifluoromethyl group in perfluoroalkyl chains $\underline{C}F_3–(CF_2)_x$, $CF(\underline{C}F_3)–(CF_2)_x$ or $\underline{C}F_3–O–(CF_2)_x$ with $x \geq 1$. Such a high binding energy has been found [13–17] but it is not an unequivocal assignment. The origin of these functional groups can be connected with the nature of the fragments made by the glow discharge from the single or double bonded structure of the monomers.

The O1s features reveal also complex signals. For PFH and PFO 5 chemically differently bonded oxygen atoms (Fig. 1b) are found and 3 for NFH and TDFO (Fig. 2b). The PFH and PFO plasma coatings show high BE at 536.4 and 537.3 eV that could be correlated with the presence of the C1s peak at 294.8 eV (Table 2). These binding energies were assigned to oxygen in the following perfluorinated structures $CF_3–O–(CF_2)_x$ and $CF_2–O–(CF_2)_x$. O1s situated at 535.2 eV was detected in the curve fits of PFH, PFO, NFH and TDFO plasma coatings and attributed to oxygen in O–CF and $CF_3–C–O$ groups.

2.1.2. Comparison of F/C and CF_2/CF_3 ratios in monomers and plasma layer

The F/C and CF_2/CF_3 ratios may be an important indicator not only of the functional chemistry of the coating, but also of the extent of retention of monomer structures in the plasma-deposited film. Table 1 shows the ratios of the outer coatings obtained from the monomers in comparison with that of the original compound. CF_2/CF_3 ratio was deduced from at% of CF_2 and CF_3 peaks at 291.3 eV, 292.6 eV and 293.6 eV, 294.8 eV, respectively.

It can be seen from this data that saturated and unsaturated compounds show a similar trend of ratios in the coating allowing the assumption that similar chemistry of the various coatings was obtained whatever the ratios in the starting monomer. It is not surprising that the coating has significantly lower ratios than the original molecule because the plasma is expected to cause fragmentation of the monomer in such processing conditions, power 40 W and pressure 60 Pa [1]. However, the $CF_3–(CF_2)_x/(CF_3 + CF_2)$ ratio equal to 0.5 (as 7.9 /4.5 + 6.2 + 5.0 in Table 2) for coating from saturated monomer, indicates that, qualitatively speaking, the extent of monomer structure retention in PFH, PFO saturated chains is higher than in NFH, TDFO unsaturated chains. This indicates that the unsaturated monomer tends to fragment at more sites than the comparable chain that have saturated bonds.

2.1.3. Wettability of the surface

Contact angle value (θ_{H_2O}) changed from 74° for the untreated PHBV film to $98 \pm 2°$ after treatment (Fig. 3), θ_{H_2O} values being close to 98° whatever monomer was used. The

Table 2
Binding energies (BE) and C1s, O1s and F1s atomic percentage (at%) for untreated and plasma treated PHBV film: averaged value from 3 spots with take-off angle 45° for each sample

	BE (eV)	Untreated PHBV (at%)	Plasma treatment		Functional groups	
			C_6F_{14} (at%)	$C_4F_9–CH=CH_2$ (at%)		
C_{1s}	294.8 ± 0.1		7.9	–	$\underline{C}F_3–(CF_2)_x$	$\underline{C}F_3–O–(CF_2)_x$
	293.6 ± 0.4		4.5	4.9	$\underline{C}F_3–CF$ $\underline{C}F_3–C–O$	$\underline{C}F_2–O$
	292.6 ± 0.3		6.2	5.3	$\underline{C}F_2–CF_2$	
	291.3 ± 0.3		5.0		$\underline{C}F_2–CF$	$CF_2–\underline{C}FO$
	289.6 ± 0.1		3.7	10.9	$CF_2–\underline{C}F–CF_2$	$O–\underline{C}O–CF_3$
	289.3	15.6			$C=O$	
	288.3 ± 0.3		3.6	6.9	$\underline{C}F–C$	$\underline{C}F–CF$
	286.9	18.0			$O–C$	
	286.6 ± 0.2		4.3	10.5	$\underline{C}–CF_2$	$\underline{C}–CF$
	285.6	17.5		2.7	CH_2	$\underline{C}–C=O$
	285	18	1.9	1.7	$C–C$	
%C total		69.1	37.1	42.9		
O_{1s}	537.3		1.3	–	$CF_3–O–(CF_2)_x$	
	536.4		1.6	–	$CF_2–O–(CF_2)_x$	
	535.2		1.7	1.5	$O–CF$	$CF_3–C–O$
	533.9	14.9	1.3	1.2	$\underline{O}–C=O$	$\underline{O}–COCF_3$
	532.8	16.0	1.5	0.7	$O–C=\underline{O}$	$O–C\underline{O}CF_3$
%O total		30.9	7.4	3.4		
F_{1s}	689.4 ± 0.2		55.5	53.7		

Typical values for C_6F_{14} (PFH) and $C_4F_9CH=CH_2$ (NFH) plasma-polymerized monomers, close values were obtained for C_8F_{18} (PFO) and $C_6F_{13}CH=CH_2$ (TDFO), respectively (BE are corrected to 285 eV for aliphatic carbon).

different plasma-polymerized layers have similar wettability, probably due to similar surface chemistry, close fluorine content and cross-linked structure. The hydrophobicity ($\gamma_s = 18.8$ mJ m^{-2}) for such fluorinated coating is moderate in spite of the presence of CF_3 and $CF_3–(CF_2)_x$ groups. It can be related to the presence of oxygen in the plasma layer leading to more hydrophilic groups but FTIR-ATR did not enable the oxygenated groups to be distinguish unequivocally. A strong band at 1210 cm^{-1} was assigned to covalent C–F bonds, its broad shape resulted from superimposition of several contribution, i.e. CF_3, CF_2 and CF groups [18].

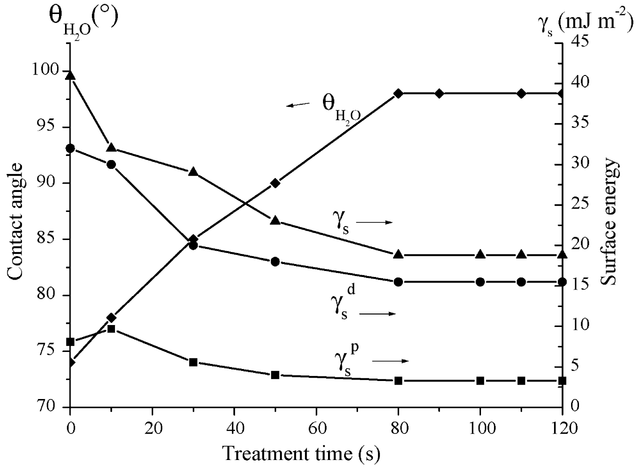

Fig. 3. Typical evolution of contact angle ($\theta_{H_2O} \pm 1°$), dispersive (γ_s^d) and polar (γ_s^p) components of surface energy ($\gamma_s \pm 1$ mJ m^{-2}) of PHBV film coated with fluorinated plasma-polymerized layer (PFH, PFO, NFH and TDFO).

In all cases, the θ_{H_2O} value increased with the treatment time. The deposit of a non-homogeneous layer for treatment time less than about 80 s was responsible for the slow change in θ_{H_2O} observed. Nevertheless, the polymerization time to obtain these hydrophobic coatings remains very short [19].

The decrease in surface energy (γ_s) from 40.9 to 18.8 mJ m^{-2} (Fig. 3) was due mainly to the decrease of the dispersive component (γ_s^d); the polar component did not change to any extent. The same experimental values of θ_{H_2O} and $\gamma_s = \gamma_s^d + \gamma_s^p$, were found after 20 days storage showing the permanent modification and stability of the plasma coating.

The treatment time was increased to 60 min for a better mass-determination of the deposit. The deposition rate was in the range from 2 to 10 μg min^{-1} cm^{-2} for PFH and PFO, and from 5 to 30 μg min^{-1} cm^{-2} for NFH and TDFO. The more rapid deposition of the unsaturated monomers can be partly due to the high reactivity of the double bond [19].

2.2. Biodegradation of plasma treated PHBV films

Aerobic biodegradation tests in microbial flora were carried out to evaluate possible differences between untreated PHBV films and PHBV films treated on both sides by PFH, PFO, NFH and TDFO plasma. Among all the test methods currently available for testing polymer degradability [20], the traditional and highly sensitive respirometric method was selected. The oxidation curves versus days (Fig. 4) show the oxygen consumption in % of the oxygen amount for the complete mineralization of the polymer in carbon dioxide and water

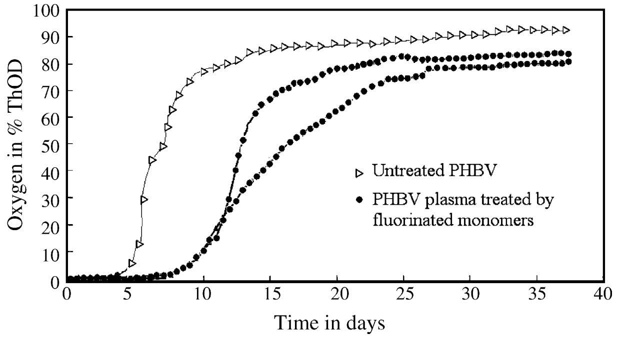

Fig. 4. Representative curves of biodegradation in % of theoretical oxygen demand (%ThOD) under aerobic conditions of untreated PHBV and plasma treated PHBV (similar curves were obtained for PFH, PFO, NFH and TDFO, only one symbol (●) was used).

(%ThOD in mg O_2 per mg polymer). The curves give the degradation level and the adaptation time or lag-phase defined as the incubation time until 10% of the ThOD is reached. Untreated PHBV showed a rapid biodegradation with a lag-phase of 5 days that conforms to the literature results [21]. For treated PHBV films the lag-phase covered a scale of time from 8 to 14 days and the consumption at the end of incubation time reached 70–80%. Only representative curves are presented (Fig. 4) because longer lag-times, slightly smaller extents of degradation and slower rate of oxygen consumption were observed whatever the fluorinated monomer used. The fluorinated layer greatly changed the biodegradation of PHBV films but no real difference between the type of monomer and the effect on biodegradation was apparent.

2.3. Correlation between the fluorinated surface and delayed biodegradation of PHBV

The plasma layer corresponding to the general formula CxFyOz was probably not biodegraded. Fluorinated synthetic resins and polymers, for example polytetrafluoroethylene (PTFE), show an inherent resistance to attack by biological agents. Limited moisture absorption and surface smoothness also lead to biological inertness due to the absence of enzymatic systems capable of action on such chemical compositions [8,22]. The plasma layer was cross-linked and covalently bond to the film; in such rigid structure the tensile stress led to the formation of cracks, particularly for plasma layer thickness greater than about 50 nm. The increase of the lag-phase from 5 to 8–12 days, corresponds with the required time for the enzymes of the microbial flora to go through the plasma layer via structural defects and to reach the surface of the PHBV film underneath.

3. Conclusion

Plasma polymerization of PFH, PFO, NFH and TDFO led to the deposition of a hydrophobic layer on PHBV films. In the given plasma power, pressure and time studied, the plasma layers were similar in composition. However, PFH/PFO plasma layers contained trifluoromethyl groups in perfluoroalkyl chains as a result of the higher structure retention of saturated monomers.

Biodegradation of plasma-treated PHBV films was delayed then slowed down. These results indicate that monomers can be quite effectively applied to elaborate protective coatings in order to prevent hydrolysis for a given period and control the properties of PHBV for packaging.

4. Experimental

4.1. Materials

Bacterial poly(3-hydroxybutyric acid-co-3-hydroxyvaleric acid) (91:9 wt%), P(HB-co-9% HV), [–OCH(CH_3)–CH_2–CO–/–OCH(C_2H_5)–CH_2–CO–]$_n$ abbreviated PHBV in this article, weight-average molecular weight M_w = 564,000 g mol^{-1} 1 (determined by Gel Permeation Chromatography) was supplied by I.C.I (England). It was used after purifying by dissolution in chloroform ($CHCl_3$) and precipitation in diethyl ether.

Fluorinated monomers were kindly supplied by Dr H. Blancou from the laboratory UMR 5073, Université Montpellier II, France.

4.2. Film preparation and plasma treatment

A 10 wt% polymer solution in $CHCl_3$ was cast on a glass plate. After solvent evaporation, films were dried at 100 °C for 48 h and kept in a dry atmosphere. The dense and smooth face of cast film which was on the glass plate, was selected to be modified by plasma treatment. Thickness of films was about 50 μm.

The experimental set-up used for plasma treatment has been schematically illustrated previously [23]. The reactor contains a pair of parallel aluminium coupled with a rf generator (13.56 MHz). Dried samples of about 10 cm^2 set on the bottom electrode, then the vacuum was established, the initial pressure was about 3 Pa. Gas flow was monitored with a Pirani gauge regulated to obtain the desired pressure. PHBV samples were pretreated by argon plasma (5 W, 40 Pa, 60 s) to clean the surface and to graft more easily the polymer coating.

In order to operate in suitable conditions for all the monomers and to standardize the process, the samples were arranged symmetrically on the bottom circular electrode, then the rf power was turned on and plasma treatment with PFH, PFO, NFH and TDFO monomers was conducted at a level of 40 W power and 60 Pa pressure for 10, 30, 50, 80, 100, 110, 120 s. The system was pumped down for 15 min before the reactor was opened.

Care was taken to ensure that the experimental configuration, the gas flow and the operating parameters, led to a stable and homogeneous glow discharge. Plasma polymerization deposition is related to the energy level of the discharge and the relative position of the polymer samples placed into the reactor. In the literature, the W/FM parameter is used for the evaluation of the discharge power, where W, F and M are the input electric power (W), flow rate (standard cubic centimetre, Sccm) and molecular weight of monomer (kg mol^{-1}), respectively. This parameter indicates an apparent input energy per unit of monomer introduced into the plasma [24]. A 20–60 W generator forward power was appropriate for a 50–65 Pa monomer pressure. This pressure range yielded a regular and controlled vaporization of each monomer at ambient temperature. The discharge was steady, that is the volume of the plasma phase stayed localized between the two electrodes and the uniformity of the colour of the glow discharge was similar for PFH, PFO, NFH and TDFO monomers.

4.3. X-ray photoelectron spectroscopy (XPS)

XPS were recorded using a Perkin-Elmer Physical Electronics Model 5400 spectrometer equipped with a hemispherical capacitor analyzer. The Mg Kα X-ray source (non-monochromatic) used to irradiate the samples operates at 15 keV and 400 W. The resolution for the main Ag peak (3d 5/2) at a pass energy of 35.37 eV using this source is 1.04 eV. The background observed is Bremsstrahlung radiation due to electrons which have experienced in elastic energy losses emerging from the sample. A Shirley function was used to correct for the background of all spectra. Each analysis was performed with 3 spots per sample, and spectra were acquired with XPS take-off angle 45°. All binding energies have been charge-corrected to 285.0 eV for aliphatic carbon.

4.4. Wettability

Contact angles were measured with a Kruss G1, immediately after plasma treatment and after 20 days storage under ambient conditions. The measurements were made 5 s after the drop was deposited. Water, diiodomethane, heptane and hexadecane were used. Surface energy (γ_s), dispersive (γ_s^d) and polar (γ_s^p) components were calculated with the Owens and Wendt method [25] based on the following formula:

$$(1+\cos\theta)\gamma_L = 2(\gamma_s^d\gamma_L^d)^{1/2} - 2(\gamma_s^p\gamma_L^p)^{1/2}$$

θ is the contact angle of the polar or non polar liquid, $\gamma_{L,}$ γ_L^d and γ_L^p are the superficial tension, dispersive and polar component, of the liquids.

4.5. Biodegradation under aerobic conditions in water

Equipment consisted of an automatized BOD (Biochemical Oxygen Demand) measuring device (BSG-Digi/Sapromat), a manostatic closed system for aerobic screening purposes. It allowed the determination of the biodegradation by following oxygen consumption during aerobic degradation in water. An electrolytic oxygen generator provided oxygen to replace that consumed in the reaction vessel. Carbon dioxide produced was absorbed by sodalime pellets. The decrease of the pressure in the flask started the oxygen electroforming then the measured electrical charge (C) was proportional to the oxygen consumed.

The polymer sample was the sole source of carbon and energy in the medium and microbial flora (inoculum) consisted of activated sludge from a sewage treatment factory that treated mainly municipal wastewater. This inoculum represented a close approximation to environmentally appropriate conditions.

Untreated PHBV films were used as reference or control substance. Plasma treatment time was increased to 15 min for each side of films in order to obtain a plasma layer thickness about 200 nm. Scanning Electron Microscopy allowed to verify the thickness range. All biodegradation tests of PHBV films treated with fluorinated monomers were carried out in triplicate.

Acknowledgements

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