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Surface modification of halogenated polymers. 2. Chloro- and fluoropolymers

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Solutions of solvated electrons in the presence of magnesium make possible the surface modification of halogenated polymers such as PVDF, Viton®, PCTFE, PVC or PVDC. The magnesium treatment which is milder than that using solutions of solvated electrons in the presence of alkali metals results in defluorination and/or dechlorination of the halogenated polymers. In the case of PVDF, it was demonstrated that (i) the surface free energy and consequently the hydrophilic character of the surface increased slightly with defluorination; (ii) anion radicals could also be used as reducing species; and (iii) copper or nickel metallization of magnesium treated samples could be achieved with the electroless procedure. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: PTFE; PVDF; Viton®)

INTRODUCTION

Halogenated polymers, and especially fluoropolymers, are generally used because of chemical inertness, high temperature stability and low dielectric constant[1,2]. Due to their low surface free energy, surface modification of fluoropolymers has to be carried out prior to any application that requires a good bondability to other materials[3–9]. Different methods of treatments can be used such as photochemistry[10], γ irradiation, ion introduction[11] and reduction[12]; we will focus only on reductive treatments. Reductive reagents may be classified in two categories: strong reactants such as alkali metals whose reaction with the polymer is very fast but poorly controlled[12–17] and mild ones such as the benzoin dianion which have to be reacted for several hours and leave some PTFE unreacted. In Part 1 of this work, we showed that magnesium solutions offered an interesting alternative for the surface treatment of PTFE[18]. Such solutions which can be obtained by an indirect electrochemical procedure (and not by direct reduction)[19,20] present many advantages for the surface treatment of PTFE when compared to the classical solutions of solvated electrons in the presence of alkalis: the polymer remains white instead of black, its surface is not destroyed and presents a controlled hydrophilic character. The extension of the magnesium treatment to another fluoropolymer such as Nafion®, which is frequently used in cationic exchange membranes, has also shown some interest since it resulted in an increase of the permselectivity of the membrane[21]. Here, the method is described in the case of other fluoropolymers such as PVDF, Viton® and PCTFE and also for some chlorinated ones (PVC, PVDC) in order to corroborate the tendencies observed. The results are analysed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and the measurement of wettability of the polymer surface.

EXPERIMENTAL

The experimental conditions relative to the treatment by solutions of solvated electrons and to the analysis of the samples have already been given in Part 1[18] and will only be summarized here. PVDF, PVC and PVDC were supplied by Goodfellow Ltd., PCTFE by 3P Ltd. and Viton® by Weber Métaux Ltd. Before treatment, the samples (2–3 cm^2 and 1 mm thick) were pretreated in order to decrease surface contamination. This consisted in washing them for 2 h in refluxing isopropanol and then drying them in an oven (100°C). PVC and PVDC plaques were used as received. After treatment, the samples were washed sequentially with aqueous HCl (0.1 M) and distilled water for 30 min, while being agitated in an ultrasound bath. If the work to be carried out in the solution was to be for a duration of more than 30 min, a constant current density of 3×10^{-2} A cm^{-2} was applied to the cell during the treatment.

Treatment by solutions of solvated electrons

The solvated electron solutions in the presence of magnesium (referred to as the $(e_{s,Mg^{2+}})$ solutions) were obtained via an electrochemical procedure which consisted of the electrolysis of a solution of ammonium tetrafluoroborate (2.52 g, 24 mmol, 0.3 M) under conditions of controlled current (10^{-1} A cm^{-2}) using a stainless steel cathode (10 cm^2, 156 mesh per cm^2) and a magnesium anode. The solutions of solvated electrons in the presence of sodium and magnesium were obtained via a similar procedure as for the $(e_{s,Mg^{2+}})$ solutions with the addition of $NaBF_4$ (2.6 g, 24 mmol) after the electrolysis. These solutions are referred to as the (e_{s,Na^+}) solutions. Solutions of solvated electrons in the presence of sodium only were

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Table 1 Concentrations in the solutions of solvated electrons

	$e_{s,Mg^{2+}}$ (M)	e_{s,Na^+} (M)
[e^-, NH_3]	0.15	0.15
[$Mg(BF_4)_2$]	0.15	0.15
[$NaBF_4$]	0	0.30

prepared by dissolution of metallic sodium (0.55 g, 24 mmol, 0.3 M).

The treatment consisted of immersing the samples in the solution of solvated electrons for 30 min. After treatment, they were washed sequentially with aqueous HCl (0.1 M) and distilled water.

The concentrations used are given in *Table 1*.

Treatment by solutions of anion radicals

The electrolysis of an aromatic compound (A) in liquid ammonia between a stainless steel cathode (10 cm^2, 156 mesh per cm^2) and a magnesium anode and in the presence of potassium bromide (5.95 g, 50 mmol) as the electrolyte leads to the corresponding anion-radical:

$$A \xrightarrow[Mg]{e,\,K^+Br^-} A^{\bullet-},K^+ + \underset{\downarrow}{MgBr_2}$$

This method allowed the preparation of 0.0625 M solutions of naphthalene and benzonitrile radical anions into which the samples were immersed for 30 min.

Nucleophilic substitutions

Untreated PVDF samples were immersed in a cell containing 100 ml of liquid ammonia and potassium *tert*-butoxide (6.5 g, 50 mmol) for 1 h. In the case of ethoxide solutions, ethanol (2.3 g, 50 mmol) was added to the previous solution.

Metallization

Treated PVDF samples were metallized according to the electroless procedure.

Prior to metallization, the treated samples were dried in an oven at 100°C for 30 min to remove water traces from the surface. In a first step, the surface was sensitized with a 0.1 M HCl aqueous solution of stannous chloride, $SnCl_2$, $2H_2O$ (2 g, 8.9 mmol) for 30 min, then washed in distilled water in an ultrasound bath for 20 min. In a second step, the sensitized sample was activated with a 0.1 M HCl aqueous solution of palladium chloride, $PdCl_2$, for 30 min, then washed as in the previous step. In the last step, the sample was metallized with copper or nickel.

Metallization by copper. The sample was immersed in a 30 ml aqueous solution containing formaldehyde (5 ml, 180 mmol), sodium hydroxide to ensure a pH higher than 11, and copper sulfate, $CuSO_4$, $5H_2O$ (1.5 g, 6.0 mmol) for 15 min. The characteristic blue colour of copper sulfate had by then disappeared. The sample was later washed in distilled water in an ultrasound bath for 30 min.

Metallization by nickel. The sample was immersed for 10 min at 95°C in a 30 ml aqueous solution containing

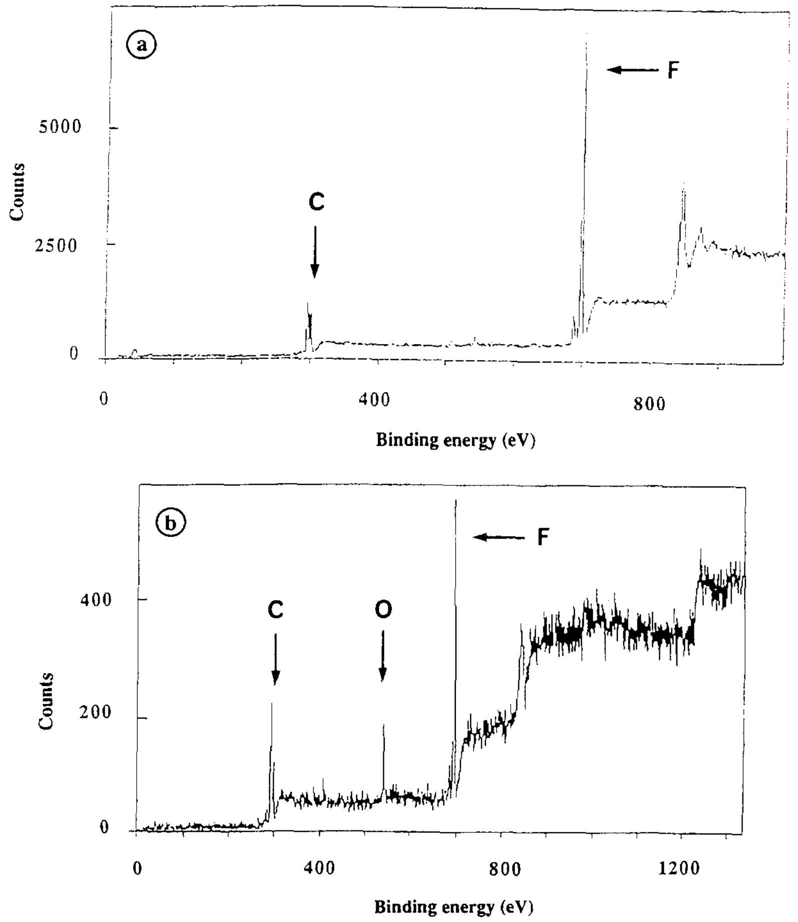

Figure 1 See text for details

nickel chloride, $NiCl_2$, $6H_2O$ (650 mg, 2.7 mmol), NaH_2PO_2 (200 mg, 2.3 mmol), $Na_3C_6HO_7$ (2 g, 5.6 mg), ammonium chloride, NH_4Cl (1 g, 19 mmol) and NaOH to ensure a pH of 8. The sample was later washed as in the case of metallization by copper.

Analysis of the samples

Images of the samples were obtained by scanning electron microscopy (SEM).

The chemical composition of a superficial layer (about 5 nm) of the samples was determined by XPS which made possible the calculation of the fractional atomic concentrations of one element relative to carbon 1s. For each polymer, the sensitivity factors of oxygen, fluorine and chlorine relative to carbon were consistent with those in the literature: $S_O = 3.1$ (reference value for various oxygenated polymers), $S_F = 3.4$ (reference value for PTFE) except for PVDF for which $S_F = 3.7$, $S_{Cl} = 2.8$ (reference value for PVC)[23]. The accuracy of the XPS measurements is between 10% and 20%.

The surface free energy of the samples were deduced from the measurement of equilibrium contact angles of small sessile drops of probe liquids of various surface tensions deposited on the surface of the samples.

RESULTS AND DISCUSSION

Polyvinyldifluoride (PVDF, $-(CF_2-CH_2)_n$)

Treatment by solvated electrons

XPS analysis[22,23]. Before treatment, the appearance of PVDF was translucent and after treatment by the different solutions of solvated electrons (in the presence of magnesium, sodium and magnesium, or sodium only) there was no visible change.

X-ray photoelectron spectra of untreated PVDF plaques consist mainly of two elemental peaks relative to carbon and fluorine atoms (cf. *Figure 1a*). The intensity of these two peaks are in agreement with: (i) the formula of PVDF ($-(CF_2-CH_2)_n$; and (ii) the sensitivity factor of fluorine relative to carbon ($S_F = 3.7$). The peak of carbon can be divided into two main elementary peaks corresponding to CH_2 (I) and CF_2 (III); two secondary elementary peaks are also present (cf. *Figure 2a*). That at the lowest binding energy (*I'*), which is present for untreated samples only and is also mentioned in the literature should correspond to CH_2 groups not bonded to CF_2 groups; the binding energy of the second one (II) is typical of either carboxyl groups in an adventitious hydrocarbon environment, or oxygenated or monofluorinated carbon atoms {COH, C=O, CHF} within the PVDF chain. The spectra of treated samples are quite

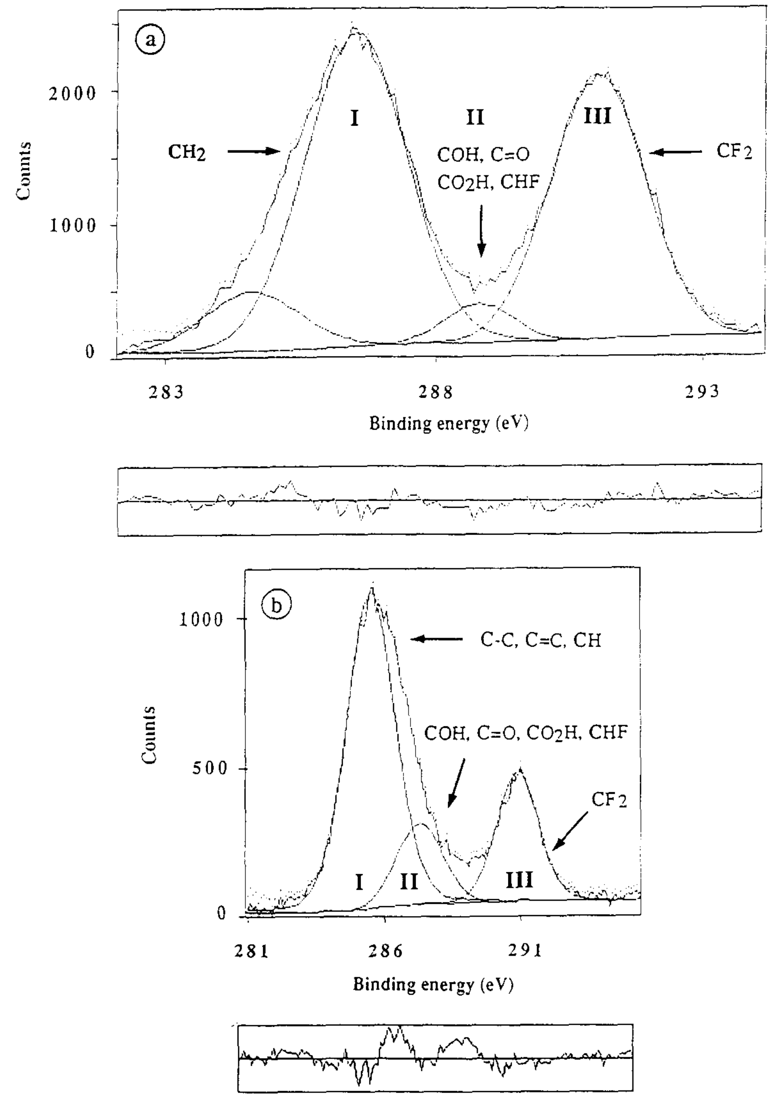

Figure 2 See text for details

different (cf. *Figure 1b* and *Figure 2b* in the case of a 1 h Mg treatment). The main peak relative to CH_2 (I) has increased and its binding energy has slightly decreased, which is in agreement with a less electronegative vicinity; the secondary peak at the lowest binding energy (*I'*), has disappeared and become included in the main one (I), that relative to CF_2 (III) has decreased, and the peak relative to oxygenated or monofluorinated carbon atoms (II) has increased. These observations are consistent with the replacement of difluorinated carbon atoms by hydrogenated, monofluorinated and oxygenated carbon atoms.

The variations observed with sodium/magnesium treatments are significantly higher than those observed with magnesium alone. We have checked that there was no significant difference between a sodium treatment in the presence of magnesium and a treatment by sodium alone (in the latter case the solvated electrons were obtained chemically by dissolution of sodium). Oxygenation attains about 10%–15% with both magnesium or magnesium/sodium treatments and does not change with the time of treatment. This is in agreement with an oxygenation phenomenon occurring after the treatment when the samples are removed from the cell and exposed to room atmosphere; the reactive sites generated by the reductive treatment can then be oxidized by oxygen. Oxygenation cannot occur during the reductive treatment since oxygen cannot exist in the presence of solvated electrons in liquid ammonia because of the high driving force of the reaction between solvated electrons and oxygen (the difference between the redox potentials of the two systems is higher than 2 V). The percentage of defluorination (100(1 − F/C ratio)) reaches about 45% with the magnesium treatment and about 75% with the sodium treatment. Defluorination increases with the time of treatment: the maximum of defluorination is obtained after 1 h of the magnesium treatment and only 0.5 h of the sodium treatment. Sodium is therefore more reactive than magnesium for the treatment of PVDF.

No inclusion of magnesium or sodium was observed at the surface of the treated plaques: these elements were not detected by XPS.

Analysis of the samples at different emission angles was performed with the 1 h treated Mg samples. Defluorination increases very slightly on going from the bulk (emission angle, 0°) to the surface (emission angle, 45°). The same tendency was observed with PTFE but the variations were greater. Larger effects would be expected when increasing the emission angle, an angle slightly lower than 90° being the best adapted. Unhappily such angles could not be attained with our XPS device.

Wettability[24–27]. The surface free energy of the untreated PVDF was found to be higher than values given in the literature (30.3 mJ m^{-2}). The wettability of PVDF increases with treatment time of the material in solutions of solvated electrons either in the presence of magnesium or sodium/magnesium. Since no physical roughening of the surface can be observed after both treatments, this effect was attributed to chemical changes only. The dispersive component of the surface free energy of PVDF increases with treatment time from 32.5 mJ m^{-2} for the untreated sample to 38.6 mJ m^{-2} for the sample treated for 2 h in the magnesium solution and to 39.0 mJ m^{-2} for the sample treated for 2 h in the sodium solution. At the same time, the polar component increases with treatment time from 5.1 mJ m^{-2} for the untreated sample to 10.1 mJ m^{-2} for the sample treated for 2 h by the magnesium solution and to 11.4 mJ m^{-2} for the sample treated for 2 h by the sodium solution. In all cases, the surface free energy and consequently the hydrophilic character of the surface increase slightly with defluorination. The order of magnitude of the highest values obtained can be compared to those of 6-6 nylon or polyvinylchloride (44.7 and 42.9 mJ m^{-2}, respectively)[28]. SEM has shown that surface rugosity is unaffected. This observation is relevant in the context of wettability since rugosity can modify measured contact angles. We can therefore attribute modifications in wettability directly to chemical changes.

The changes between the untreated and the treated samples are weak compared to what was observed with PTFE since first untreated PVDF is more polar than untreated PTFE. This is illustrated by both the higher dispersive and polar components of the surface free energy of PVDF than PTFE. The values of the dispersive component of 2 h Mg or Na treated PVDF are about the same as those observed with treated PTFE (respectively, 40.1 and 43.3 mJ m^{-2} for the 32 min treated Mg and Na PTFE samples). However, the polar component increases to higher values with PVDF than PTFE (7.0 and 7.8 mJ m^{-2} for the 32 min treated Mg and Mg/Na PTFE samples, respectively).

Scanning electron microscopy. The SEM images of PVDF samples treated by the magnesium and sodium solutions are not significantly different from the images of untreated samples. By analysing the X-rays emitted from a slice through the irradiated sample, it is possible to analyse how the chemical composition of the sample varies with depth. F/C increases from 25% at the surface to 78% at about 1 μm from the surface and to 100% in the bulk. Since (i) the size of the X-ray probe is about 2 μm, and (ii) the sample had been immersed in a resin which contains no fluorine atoms, this means that defluorination is not homogeneous throughout the sample and that the depth of attack is less than 2 μm. The sodium treatment leads to the same result.

Treatment by anion radicals

Defluorination and oxygenation of PVDF can also be achieved by anion radicals $A^{\bullet -}$. XPS analysis of the treated samples shows that the efficiency of the treatment increases when the standard reduction potential, $E°$ of the redox system $A/\dot{A}^-$ decreases ($E°_{\mathrm{benzonitrile}} = -1.78_5$ V and $E°_{\mathrm{naphthalene}} = -2.02_5$ V *versus* Ag/Ag^+), i.e. when the anion radical is a stronger reducing agent (cf. *Table 2*). The efficiency obtained with the stronger reducing agent (the naphthalene radical anion) is only a little lower than that obtained with magnesium/sodium solutions but higher than that corresponding to magnesium solutions.

An increase of the wettability of the surface is observed with the treatment by radical anion solutions, but the effect is smaller than with the solvated electron solutions. The effect is about the same for both anion radicals: the dispersive component of the surface free energy increases to 35.3 mJ m^{-2} for the benzonitrile radical anion and to 37.1 mJ m^{-2} for the naphthalene radical anion whilst the polar component increases to 7.1 mJ m^{-2} for the benzonitrile radical anion and to 6.2 mJ m^{-2} for the naphthalene radical anion.

Nucleophilic substitutions

The immersion of PVDF samples into solutions of either *tert*-butoxide or ethoxide results in a change of colour of the

Table 2 XPS analysis of samples of PVDF plaque: influence of the reducing agent (Mg, Na or anion radicals)

Sample	Proportion of C at binding energy, E_b (%)			Relative proportions of O and F (%)	
E_b (eV)[a]	286.5 ± 0.5 C–C, C=C, CH	289.0 ± 0.5 COH, C=O, CO_2H, CHF	291.0 ± 0.5 CF_2	O/C ($S_O = 3.1$)	F/C ($S_F = 3.7$)
Untreated	57[e]	4	39	4	100
Mg–5 min[b]	59	9	32	11	78
Mg–30 min[b]	60	8	32	7	73
Mg–1 h[b]	67(72[c])	8(9[c])	25(19[c])	12(13[c])	55(56[c])
Mg–2 h[b]	59	17	24	8	53
Mg/Na–5 min[d]	76	9	15	13	38
Mg/Na–30 min[d]	76	15	9	17	23
Mg/Na–1 h[d]	74(74[c])	15(17[c])	11(9[c])	16(17[c])	24(19[c])
Mg/Na–2 h[d]	67	17	16	10	31
Benzonitrile	68	10	22	11	48
Naphthalene	72	12	16	14	33

[a] Binding energy
[b] $[NH_4BF_4] = 0.3$ M; $[e_{s,Mg^{2+}}] = 0.15$ M
[c] Photoelectron emission angle: 45° instead of 0°
[d] $[NaBF_4] = 0.3$ M added to the latter solution
[e] Contribution of peak *I'*: 8% among 57%

Table 3 XPS analysis of samples of halogenated polymers plaques: influence of the reducing agent (Mg or Na)

Sample	Proportion of the element at binding energy E_b (%)					Relative proportions of O, F, Cl (%)		
	Viton®					(–(CF(CF_3)–CF_2)$_x$(CF_2–CH_2)$_y$)		
	285 C–C, C=C CH	287 CF_2–CH_2 COH	288.5 CF_2–CH_2 C=O	292.5 CF(CF_3)–CF_2 CF(CF_3)–CF_2	295 CF(CF_3)–CF_2	O/C ($S_O = 3.1$)	F/C ($S_F = 3.4$)	
Untreated		23	24	38	15	40	147	
Mg–30 min[b]	68		19	5	8	45	48	
Na–30 min[c]	71		11	8	11	48	46	
	PCTFE					(–(CF_2–CFCl)$_n$)		
	285 C–C, C=C CH	288 CHF, COH C=O, CO_2H	291 CF_2 CFCl			O/C ($S_O = 3.1$)	F/C ($S_F = 3.4$)	Cl/C ($S_{Cl} = 2.8$)
Untreated	30	8	62			10	110	57
Mg–30 min[b]	77	19	4			21	14	2.2
Na–30 min[c]	61	27	12			40	23	6.4
	PVDC					(–(CH_2–CCl_2)$_n$)		
	285 C–C, C=C CH	286.5 CHCl COH	288 CCl_2, C=O CO_2H			O/C ($S_O = 3.1$)		Cl/C ($S_{Cl} = 2.8$)
Untreated	74	0	26			8		50
Mg–30 min[b]	77	6	17			17		25
Na–30 min[c]	83	3	14			18		20
	PVC					(–(CH_2–CHCl)$_n$)		
E_b (eV)[a] peak assignment	285 C–C, C=C CH	286.5 CHCl COH	288 C=O CO_2H			O/C ($S_O = 3.1$)		Cl/C ($S_{Cl} = 2.8$)
Untreated	61	39	0			9		20
Mg–30 min[b]	76	21	3			13		16
Na–30 min[c]	71	25	4			10		15

[a] Binding energy
[b] $[NH_4BF_4] = 0.3$ M; $[e_{s,Mg^{2+}}] = 0.15$ M
[c] $[NaBF_4] = 0.3$ M added to the latter solution

samples which become slightly brown. The F/C ratio decreases to about 15% whilst the O/C ratio increases to about 25% in both cases. Such effects were also observed when treating PVDF or PVF with aqueous KOH or LiOH[29]. The high increase of the oxygen peak can be considered as the direct result of the substitution by the oxygenated nucleophile, but the results must be considered with care since it is well-known that, in the presence of a strong base, PVDF undergoes elimination reactions.

Metallization [30,31]

Metallization of untreated PVDF samples does not take place. On the contrary the samples of PVDF which had been treated for 1 h in a magnesium solution could be metallized by copper or nickel with the electroless procedure. However, in the case of copper, the deposited layer was not uniform and some places were not metallized. XPS spectra exhibited the characteristic peaks of both PVDF and copper which means that the deposition was either heterogeneous or thinner than the analysed depth. The situation was even worse in the case of nickel since the deposited layer could easily be pulled off the material, simply by scratching it, for instance.

Various polymers

The various polymers were treated by magnesium or sodium solutions for 30 min. The results of the XPS analyses of untreated and treated samples are given in *Table 3*.

Viton® $(-(CF(CF_3)-CF_2)_x(CF_2-CH_2)_y)$

The appearance of Viton® is black and quite porous even before treatment. Since the pure polymer should be translucent white, this means that the polymer used was an impure commercial material. After treatment, in both cases, no change was visible to the naked eye.

The intensities of the carbon elementary peaks of untreated Viton® are consistent with the theoretical chemical formula with $x = y$. The F/C ratio should then be equal to 500/8 = 160%, which is close to the experimental value (147%). Unexpectedly, the O/C ratio is rather high (40%); this should be due to the impurities contained in the polymer which could retain a large amount of water in high vacuum.

The modifications obtained with both treatments are very similar: the relative proportion of each type of fluorinated carbon atom (CF, CF_2, CF_3) decreases largely whilst the proportion of apolar carbon atoms (C–C, C=C, CH) increases up to about 70%. Degree of oxygenation remains approximately constant with a very slight increase: it was already high for the untreated polymer.

PCTFE $(-(CF_2-CFCl)_n)$

The colour of PCTFE, which is white when untreated, changes after both treatments: it becomes light brown after the magnesium treatment and brown after the sodium treatment. In the case of the sodium treatment, the surface has visibly been attacked to a larger extent.

The untreated sample presents some surface contamination: the relative proportion of halogenated carbon atoms is only 62% instead of the expected 100%. The F/C and Cl/C ratios are not too far from the expected values (110% for F/C instead of 150%, 57% for Cl/C instead of 50%).

Both magnesium and sodium treatments make the (**C**–C, **C**=C, **C**H) and the (**C**HF, **C**OH, **C**=O, **C**O$_2$ H) proportions increase and the (CF_2, CFCl) proportions decrease. Oxygenation is more important with the sodium treatment although the increase of the unpolar carbon atoms and the decrease of halogenated carbon atoms are lower; this observation is not easy to explain since the surface of the plaque has been strongly affected by the sodium treatment and some places of untreated polymer can also be present at the surface.

PVDC $(-(CH_2-CCl_2)_n)$

The transparent appearance of PVDC did not change after either treatment.

The amount of chlorine of the untreated sample is only equal to half the theoretical amount (50% instead of 100%) and some oxygen is also present. The Cl/C proportion of 50% is in agreement with the intensity of the elementary peak of chlorinated carbon atoms (26%).

Both treatments make oxygenation and dechlorination increase by a factor greater than 2, whilst the (**C**–C, **C**=C, **C**H) proportions increase slightly. The variations of the elemental peaks intensities at 286.5 and 288 eV are difficult to rationalize since each peak is relative to both oxygen and chlorine (**C**HCl and **C**OH at 286.5 eV and **C**Cl$_2$, **C**=O and **C**O$_2$H at 288 eV). The effects are always a little greater for the sodium treatment.

PVC $(-(CH_2-CHCl)_n)$

Before treatment the sample was opaque and white; no change was observed after treatment in either solution.

As already observed for PVDC, the amount in chlorine of the untreated sample is rather low: 20% instead of 50%. Since for the untreated sample (i) the proportion of oxygen relative to carbon is 9%, (ii) oxygenated carbon atoms are COH elements only, and (iii) the proportion of (**C**HCl and **C**OH) is 39%, the proportion of **C**HCl can be estimated at about 30%, which is in rough agreement with the 20% proportion of chlorine relative to carbon. The variations observed after both treatments are moderate: the increase of the amount of oxygen and the decrease of the amount of chlorine are only a few percent with both magnesium and sodium treatments.

Comments

In all cases, magnesium or sodium treatments cause defluorination and/or dechlorination of halogenated polymers. The carbon–halogen bonds are replaced by carbon–hydrogen or double bonds and some oxygenation is also present.

Dechlorination is almost total for PCTFE $(-(CF_2-CFCl)_n)$ because of the electron-withdrawing character of the fluorine atoms which make the reduction easier when compared to the reduction of PVDC $(-(CH_2-CCl_2)_n)$ or PVC $(-(CH_2-CHCl)_n)$ for which Cl/C is about 20% after both treatments. In the same way, reduction becomes more difficult on going from PTFE $(-(CF_2-CF_2)_n)$ to Viton® $(-(CF(CF_3)-CF_2)_x(CF_2-CH_2)_y)$ and to PVDF $(-(CH_2-CF_2)_n)$: after a 30 min Mg treatment F/C = 23% for PTFE, 48% for Viton® and 73% for PVDF. Since defluorination is higher for PTFE than PVDF, we may conclude that PVDF is not an intermediate in the reduction of PTFE and that reduction of PTFE involves the simultaneous expulsion of two vicinal fluorine atoms. Defluorination is about the same for PTFE and PCTFE which means that reduction of both may involve the same first intermediate radical: $-CF_2-\dot{C}F-$ which in turn yields $-CF=CF-$. In the case of PVDF being modified by basic agents (KOH, LiOH) the same type of intermediate $(-CH=CF-)$ was postulated[29,32]. The existence of such intermediates is in good agreement with the higher defluorination observed with PTFE than with PVDF since $-CF=CF-$ is easier to reduce than $-CH=CF-$ because of the higher electron-withdrawing character of fluorine than hydrogen.

Oxygenation is important with porous polymers such as Viton® (40% for the untreated polymer, a little higher after both treatments) or PCTFE after the sodium treatment (40%). The results must be considered with care since elimination of water prior to the XPS measurements is very difficult to perform with porous polymers. In the other cases oxygenation is between 10% and 20% and should occur after the treatment when the samples are taken out of the electrochemical cell and put in the ambient air. Control of oxygenation involves control of the medium after treatment.

In the case of non-halogenated polymers such as polystyrene $(-(CH(C_6H_5)-CH_2)_n)$ the treatment does not cause any significant chemical change since no reducible elements are present. In the case of polyethylenenaphthalate

$(-((C_{10}H_6)(CO_2)(CH_2)_2(CO_2))_n)$, treatment by the magnesium solution leaves the polymer unchanged. However, after being treated by the sodium solution, the sample became brittle and slightly opaque, a yellow residue was recovered from the surface of the polymer and a green colour appeared in the solution close to the sample. The colour is probably that of an anion radical, such as naphthyl—or a derivative—which is green in liquid ammonia. We may therefore assume that the backbone structure of the polymer has been severely damaged. Reduction of the ester groups by a Bouveault-Blanc reaction resulting in cleavage of the carbon–oxygen bonds to yield diols[33,34] may have occurred.

CONCLUSION

Surface modification of halogenated polymers such as PVDF, Viton®, PCTFE, PVC or PVDC can be achieved by solvated electrons in the presence of magnesium. The magnesium reactant is milder than the well-known solutions of solvated electrons in the presence of alkali metals. Generally the appearance of the polymers is not modified by the treatment except in the case of PCTFE which changes from white to light brown. The change observed when PCTFE is treated by solvated electrons in the presence of alkalis is greater and some porosity appears. This behaviour can be compared to that of another perhalogenated polymer, PTFE: this polymer remains white after a magnesium treatment but becomes black and porous after a sodium treatment.

XPS analyses show that magnesium or sodium treatments cause defluorination and/or dechlorination of the halogenated polymers. The degree of dechlorination and defluorination increases as the electron-withdrawing character of the substituents on the polymeric backbone increases: (i) dechlorination which is almost total for PCTFE is lower for PVDC and PVC; and (ii) defluorination decreases from PTFE and PCTFE to Viton® and to PVDF. The carbon–halogen bonds are replaced by carbon–hydrogen or double bonds. Some oxygenation occurs after the treatment when the samples are removed from the cell and exposed to room atmosphere.

The case of PVDF has been more thoroughly studied. The order of magnitude of the depth of attack could not be estimated by scanning electron microscopy but should be less than 2 μm. The wettability of PVDF increases with treatment time of the material in solutions of solvated electrons either in the presence of magnesium or sodium. The surface free energy and consequently the hydrophilic character of the surface increase slightly with defluorination. Differences between the untreated and the treated samples are relatively small when compared to what was observed with PTFE. This is mainly because untreated PVDF is more polar than untreated PTFE. Anion radicals can also be used as reducing species. The efficiency of the treatment can be related to the standard reduction potential of the reducing agent: as expected it increases when the standard reduction potential of the reducing agent decreases, i.e. when the anion radical is a stronger reducing agent. An increase of the wettability of the surface is observed with the treatment by radical anions solutions, but the effect is smaller than with the solvated electrons solutions. Copper or nickel metallization of magnesium-treated PVDF samples could be achieved with the electroless procedure.

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