Polymer 44 (2003) 19–24

polymer

www.elsevier.com/locate/polymer

Surface modification of halogenated polymers. 4. Functionalisation of poly(tetrafluoroethylene) surfaces by diazonium salts

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Received 8 June 2002; received in revised form 19 September 2002; accepted 27 September 2002

Abstract

Reduced PTFE can be grafted by nitro and bromo-phenyl diazonium tetrafluoroborate salts in a manner similar to that used for carbon, except that no application of a reductive potential during grafting was required. Grafting was evidenced by cyclic voltammetry, X-ray fluorescence or ToF-SIMS. Nitro- and bromo-phenyl moieties were covalently linked to the PTFE material and could be eliminated only by abrasion.

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Keywords: PTFE; Surface modification; Diazonium salts

1. Introduction

Fluoropolymers are widely used in applications, where their low chemical activity, elevated resistivity, low friction coefficient and high temperature resistance, make them primary choices as far as durability is concerned [1,2]. However, the very same properties can prove disadvantageous when the fluoropolymer is required to be in contact with another material. Therefore, surface modification of PTFE has to be carried out prior to any of the applications like bonding, painting, printing or metallisation [3–5]. Suitable surface pre-treatments modify the superficial properties of the polymer, without altering the bulk properties to any significant extent. The various pre-treatments, which are recognised, include photochemistry [6], γ irradiation, ion bombardment [7] and reduction [8,9]. They result in the reduction of the polymeric surface and generally in its carbonisation [8,9].

Besides such treatments, few other types of modifications have been reported. Among the latter, grafting of reducing agents under photochemical inducement [10] and electro-induced radicalar nucleophilic substitution of PTFE surfaces [11] are worth mentioning. In both cases, functionalisation is performed during a reductive and competitive treatment.

In this paper, we present another approach dealing with the functionalisation of the polymeric carbonaceous layer obtained by reduction treatment of a PTFE surface. Grafting of carbon electrodes by organic groups derived from diazonium salts, under reductive conditions has already been reported [12,13]. We have used a similar grafting procedure, except that no external electric potential was applied since reduction of PTFE leads to a *n*-doped conductive carbonaceous material [8,9]. Indeed, it is well known that (i) charged carbon can reduce spontaneously various species [14,15] such as iodine or dioxygen [16] and (ii) polyacetylene, which can intervene as an intermediate in the reduction of PTFE, behaves as a semi-conductor when charged or discharged [17].

2. Experimental

All the chemical reagents were purchased from Aldrich (Saint-Quentin Fallavier, France) and used without further purification. Teflon plaques were supplied by Goodfellow

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PII: S0032-3861(02)00736-X

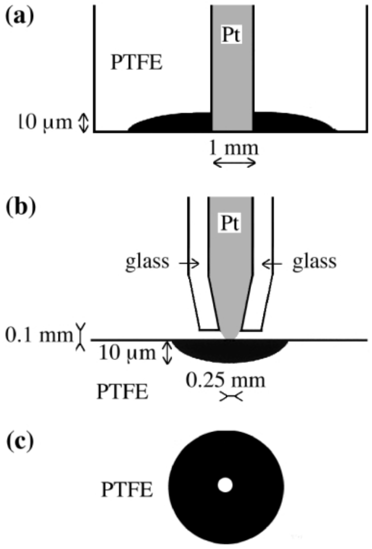

Fig. 1. Scheme of reduction processes on PTFE surfaces. Cross section of: (a) a PTFE coated platinum disc electrode, (b) a PTFE plaque, (c) top view of the PTFE plaque. Black regions represent carbonaceous zones.

(Lille, France). Before treatment, the samples (diameter: 2 cm, thickness: 3 mm) were polished (abrasive paper P4000, Presi, Grenoble, France), rinsed in acetone under sonication for 5 min and dried in an oven (80 °C overnight).

2.1. X-ray fluorescence analysis

Elemental profiles were obtained with a Pentafet Link ISIS Oxford analyser coupled to a JEOL JSM-5200 scanning electron microscope (SEM) operating at an accelerating voltage of 10 kV.

2.2. ToF-SIMS analysis

The time of flight secondary ion mass spectrometry (ToF-SIMS) measurements were performed at PCPM (UCL, Louvain-la-Neuve, Belgium) using a Phi-Evans TFS-4000MMI (TRIFT) spectrometer. The sample was bombarded with a pulsed $^{69}Ga^+$ ion beam (15 keV, 1 nA d.c.). The secondary ions were accelerated to ±3 keV by applying a bias on the sample. The initial kinetic energy spreading of the secondary ions was compensated by a 270° deflection in three electrostatic analysers. In order to increase the detection efficiency of high-mass ions, a 7 keV post-acceleration voltage was applied to the detector entry. The analysed area was 260 µm × 260 µm. With a 5-min data acquisition time, the fluence was $<5\times 10^{11}$ ions/cm^2, ensuring static analysis conditions. Charge neutralisation was achieved using a pulsed electron beam of 20 eV. With these experimental conditions, the practical mass resolution ($m/\Delta m$) obtained with this ToF-SIMS spectrometer is ~3000 at m/z 28 onto a silicon wafer. A minimum of three areas was analysed on each sample. ToF-SIMS data were treated using ‘Cadence’ software (Phi-Evans), which determine peak mass from well-defined reference peaks.

2.3. Surface modification

Our procedure consisted of two steps: first, the surface was locally reduced into a carbon material by an electrode, which was in contact with the polymer [18] and second, diazonium salts were made to react with the carbonaceous surface. Nitro- and bromo-phenyldiazonium tetrafluoroborate salts (NO_2-PD and Br-PD, respectively) were chosen as synthons since their grafting is easy to prove: by studying the electrochemical response of the grafted function by cyclic voltammetry (in the case of the nitro derivative) and by detecting grafted fragments containing the Br atom or the NO_2 group by ToF-SIMS or X-ray fluorescence (in the case of the bromo derivative).

The PTFE samples we have used were (i) a platinum disc electrode embedded in a piece of PTFE insulating material for the voltammetric study and (ii) PTFE plaques or skived tapes for surface analysis. Reduction of PTFE was achieved in a solution of DMF + 0.1 M NBu_4BF_4 by applying for 200–400 s a potential of −2.2 to −2.4 V/Ag/AgCl to a platinum working electrode in contact with the PTFE surface (Fig. 1a–c). The working electrode was either the disc electrode itself in case (i) or a tip in case (ii). A platinum counter electrode was used in both cases. Reduction of PTFE resulted in the growth of carbonaceous zones as depicted in Fig. 1a–c. In the case of the PTFE plaques, the imprint of the tip on the material surface remained unmodified (the white zone on Fig. 1c) since there was no electrolytic solution between the tip and the surface.

Modification of PTFE samples was carried out at the end of the surface reduction by adding the diazonium salt into the electrolysis solution up to a 20 mM concentration. The system was then left to react for 5–10 min under nitrogen or argon without any applied potential, rinsed in DMF under sonication for 5–10 min or in methanol under magnetic stirring for 12 h.

3. Results and discussion

3.1. Cyclic voltammetry measurements of the NO_2-PD grafted PTFE sample

The electrochemical characterisation of the grafting by Br-PD was not performed because (i) the Br-PD redox system is irreversible due to the reductive cleavage reaction of the bromide anion and (ii) at the reduction potential of Br-PD, which is highly negative, PTFE carbonisation occurred. The support used to characterise the grafting of PTFE by NO_2-PD was the platinum disc electrode embedded in PTFE (Fig. 1a).

The first problem encountered was due to the electrical

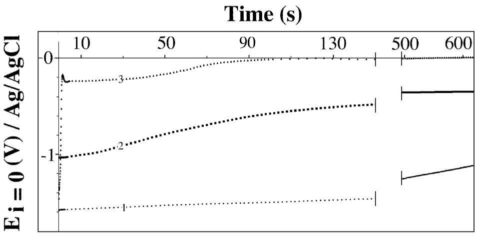

Fig. 2. Variations of the zero current potential of the carbonaceous zone obtained under the conditions described in Fig. 1b, with time. Solvent: DMF. Time: 0 refers to the end of the reduction. PTFE reduction: (1) and (3), 400 s; (2), 25 s; (1) and (2), no diazonium salt added; (3), in the presence of 20 mM nitro-phenyldiazonium tetrafluoroborate.

discharge of the carbonaceous zone, once the reduction of PTFE was over. Such a phenomenon could be evidenced by the increase of the zero current potential with time (Fig. 2, curves 1 and 2). Since this discharge phenomenon was more important in old solutions and depended on the water content of the DMF solution, we assumed that it resulted from the redox reaction of the *n*-doped carbonaceous zone with H_2O, O_2 or impurity traces and led to the surface passivation and decrease of the conductive area of the material [16]. The modified PTFE layer was able to reduce compounds whose reduction potential was higher than its zero current potential (~ − 1 V/Ag/AgCl for a 25 s PTFE reduction and lower for longer reduction times, Fig. 2, curves 1 and 2). Since reduction of diazonium salts occurs at ~0 V/Ag/AgCl, [12,13] we expected diazonium salts to be reduced by the modified PTFE surface. Actually, in the presence of a diazonium salt, it was observed that the zero current potential almost instantaneously stabilised at the reduction potential of the diazonium salt (~ − 0.2 V/Ag/AgCl) and finally reached the former equilibrium value of the platinum electrode in a much lesser time (Fig. 2, curve 3). This reductive process was limited by the discharge phenomenon and it occurred at both the conductive carbonaceous zone and the platinum electrode.

Once derivatised, the electrode was carefully rinsed and then immersed into a DMF + NBu_4BF_4 solution. Fig. 3 presents the dependence of the voltammograms obtained in this solution with time. We could notice: (i) on the first voltammogram (1) an increase of both the faradaic and capacitive currents compared to that of platinum (6), (ii) on the second voltammogram (2) a decrease of the faradaic current with the capacitive current remaining constant, (iii) on the following voltammograms a concomitant decrease of both the faradaic and capacitive currents (3, 4) until a curve (5) analogous to that of platinum was reached (6) and there was a shift of the new peak towards positive potentials.

These observations are consistent with the grafting of the nitrophenyl group on PTFE which resulted in the appearance of its electrochemical signal on (1) at approximately the same potential as for a carbon electrode (~ − 1.2 V/Ag/AgCl), and the increase of the conductive surface area which explained the increase of the capacitive current. The poor reversibility observed on each cycle should result from the decrease of the area of the conductive carbonaceous zone as time went on and from the background current corresponding to bulk PTFE reduction. The faradaic current decreased on (2) because of the elimination of adsorbed NO_2-PD species on the level of (1); such an elimination should result from the charge change of adsorbed NO_2-PD on scan (1). These observations were also made on carbon electrodes, where both faradaic and capacitive currents were higher since grafting of the carbon electrode occurred on the entire electrode surface. The proportional decrease of the faradaic and capacitive currents observed on cyclic voltammograms (3)–(6) should result from the decrease of the area of the conductive surface and not from the elimination of the grafted species that would have decreased mainly the faradaic current. Moreover, the proportionality between capacitive and faradaic currents indicated the homogeneity of the grafting on the whole conductive carbonaceous zone.

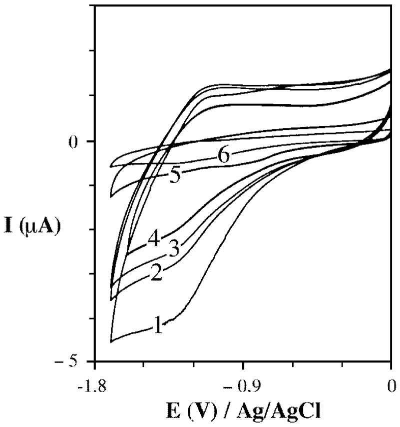

Fig. 3. Cyclic voltammograms of a reduced PTFE coated platinum disc electrode (Fig. 1a) subjected to reaction with 20 mM nitro-phenyldiazonium tetrafluoroborate in DMF, then rinsed into DMF for 5 min under sonication and characterised in DMF + 0.1 M NBu_4BF_4. Platinum counter electrode, Ag/AgCl reference, room temperature. Time elapsed after the rinsing: (1), 0; (2), 1 min; (3), 3 min; (4), 11 min; (5), 52 min. (6), Pt.

In agreement with previous work by other authors, [19] grafting also occurred at platinum. That was confirmed by a blank experiment performed on a platinum electrode embedded in glass instead of PTFE. When submitted to reduction and addition of NO_2-PD in the same conditions as above, the Pt electrode remained unchanged. However, when it was set at a reductive potential lower than − 0.5 V during immersion in the diazonium solution, grafting of the platinum surface occurred and a voltammogram analogous to (6) was obtained, with a faradaic contribution at ~ − 1.2 V/Ag/AgCl. In our case with a Pt electrode embedded in PTFE, grafting could occur despite the absence of applied potential because of the negative charge in the PTFE material after the reduction step. We have estimated grafting on Pt to be about seven times less important than on carbon.

These results were confirmed by differential pulse voltammetry, for which a new peak corresponding to

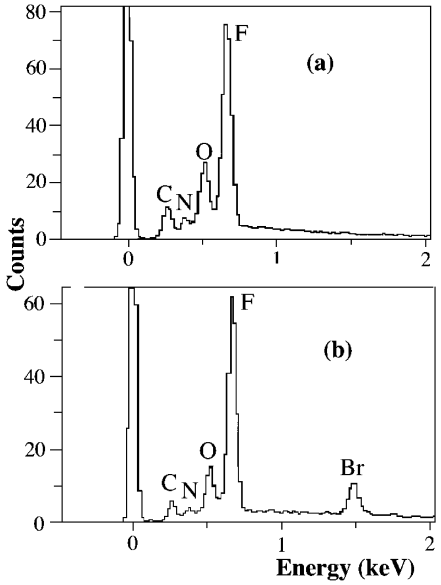

Fig. 4. X-ray fluorescence spectra of locally carbonised PTFE plaques (Fig. 1b) submitted to grafting with 20 mM of bromo-phenyldiazonium tetrafluoroborate in DMF. Reaction started (a) more than 1 h after the end of PTFE reduction, (b) once PTFE reduction was over. The reaction time was 5 min followed by 12 h rinsing in methanol under magnetic stirring at room temperature.

~ -1.2 V/Ag/AgCl was also observed when PTFE was reacted with NO_2-PD and which varied linearly with time. Due to the variation of current with time, it was difficult to study the variation of the peak current with the sweep rate.

3.2. X-ray fluorescence of the Br-PD-grafted PTFE sample

The supports used for X-ray fluorescence analyses were locally carbonised PTFE plaques or skived tapes (Fig. 1b and c) submitted to grafting with the diazonium salts. For comparison, spectra of samples treated with Br-PD and NO_2-PD, under conditions impossible for grafting to occur (treatment performed more than 1 h after the end of PTFE reduction when the carbonaceous zone was believed totally passivated), were also considered. In the case of Br-PD, the Br characteristic peak absent on the X-ray fluorescence spectrum of ungrafted PTFE, was observed on the spectrum of a PTFE sample submitted to grafting by Br-PD (Fig. 4a and b). Such a study could not be performed to characterise the grafting of PTFE by NO_2-PD because of the presence of a contamination peak of nitrogen on all the spectra.

3.3. ToF-SIMS characterisation of the Br-PD- and NO_2-PD-grafted PTFE samples

We have also studied the SIMS spectra of the same samples. The ToF-SIMS technique presents several advantages, compared to X-ray fluorescence: first, it is more sensitive (detection threshold: $\sim 1-10$ ppm instead of $\sim 100-1000$ ppm for fluorescence) and second, the explored material thickness is lower (X-ray fluorescence: ≥ 1 μm and ToF-SIMS: ≤ 1 nm for molecular ions), which results in a less important part of unreacted carbon and/or virgin PTFE explored than with X-ray fluorescence.

We have studied the SIMS spectra of grafted carbon electrodes to determine which peaks were characteristic of the grafting by Br-PD and NO_2-PD. In the case of Br-PD, the peaks of Br^- ($m/z = 79$) and its isotope ($m/z = 81$) as well as Br_2^- ($m/z = 158, 160, 162$) were observed in the negative mode, whereas the positive mode underlined the presence of phenyl fragments: $C_7H_7^+$ ($m/z = 91$) and $C_7H_6Br^+$ ($m/z = 169, 171$). Unfortunately, some of these peaks were also present on the spectra of reduced PTFE: $Si_2O_2C_5H_{15}^-$ (negative, $m/z = 163$, contamination), $C_3F_7^+$ (positive, $m/z = 169$). The positive peak at $m/z = 91$, which was weak for carbon samples, could not be detected on PTFE samples. Therefore, in the case of Br-PD, we have focused mainly on Br^-. In the case of NO_2-PD, because of the abundance of the fragments, only NO_2^- ($m/z = 46$) could be observed clearly both on carbon and PTFE samples.

The supports were the same as those used for X-ray fluorescence. We have reported in Fig. 5a and b, the negative spectra of an ungrafted PTFE zone and of a Br-PD-grafted PTFE sample, respectively. We were able to observe that there was a residual Br^- peak on the spectrum of ungrafted PTFE. It should result from the adsorption of Br-PD on carbonised PTFE. The absence of the bromine peak on X-ray fluorescence spectra of the same samples should result from the higher sensitivity and the smaller explored material thickness with ToF-SIMS. The intensity of the peak relative to Br^- increased when PTFE was submitted to grafting conditions (note the difference in the scales and in the total number of counts). In the case of NO_2-PD, similar trends were observed on the peak relative to NO_2^- (not shown). Once normalised relatively to the total number of counts, Br^- and NO_2^- peaks were at least about 10 times higher than those observed for ungrafted PTFE and about 20% lower than those observed for carbon sample, whatever the sample.

ToF-SIMS and X-ray fluorescence analyses of platinum electrodes embedded in PTFE and submitted to grafting by Br-PD were performed. They showed that grafting was not homogeneous all over the carbonaceous zone and was primarily near the platinum electrode, where the accumulated charge was the highest. Bromine atoms could also be detected at the platinum surface, due to the grafting of the platinum electrode by diazonium salts, as expected from the voltammetric study in the case of NO_2-PD.

We have not carried out XPS analysis since (i) a quantitative analysis of the grafting was out of the scope of this paper; (ii) in the case of the grafting by NO_2-PD, XPS would not have been sensitive enough due to presence of NBu_4^+ from the electrolyte and; (iii) we wanted to perform an analysis that could also be used for smaller grafted zones (100 μm diameter) that we expect to make in the future; in

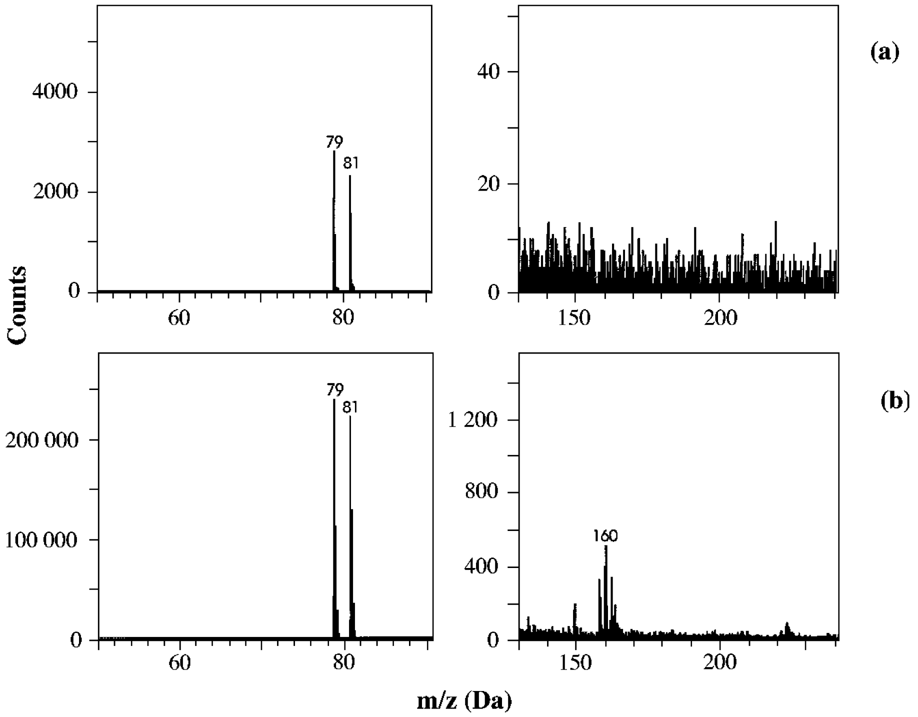

Fig. 5. Negative ToF-SIMS spectra of the samples described in Fig. 4.

that context ToF-SIMS is more sensitive than XPS that cannot be used for samples diameters lower than 1 mm.

3.4. Suggestion of a mechanism for surface functionalisation

From the above results, we can propose a mechanism for functionalisation of PTFE.

First, the reduction of the PTFE surface by the electrode into polymeric carbon (reaction (1)) is followed by the injection of an excess of negative charge into the material (reaction (2)):

$$-(CF_2-)_n + 2n\,e^- + 2n\,NBu_4^+ \rightarrow -(C-)_n + 2n[NBu_4^+, F^-] \quad (1)$$

$$-(C-)_n + \delta' n\,e^- + \delta' n\,NBu_4^+ \rightarrow [-(C^{\delta'-}-)_n, \delta' n\,NBu_4^+] \quad (2)$$

with NBu_4^+, the cation of the electrolyte and $\delta' n$, the average negative charge borne by the carbon atoms in the whole carbonaceous zone.

Next, reduction of the diazonium salt is achieved by the negatively charged carbon material at the material surface:

$$[-(C^{\delta-}-)_n, \delta n\,NBu_4^+] + \delta n\,X{-}Ph{-}N_2^+ \rightarrow [-(C-)_n] + \delta n\,X{-}Ph^{\cdot} + \delta n\,N_2 + \delta n\,NBu_4^+ \quad (3)$$

with δn, the average negative charge borne by the carbon atoms at the material surface, X = NO_2 or Br, Ph = phenyl ring.

Other deactivation reactions of the charged polymer may occur so that the stoichiometry of reaction (3) may be different, with a number of reacted diazonium salt moles lower than δn.

Then the formed aryl radical adds to the carbon polymeric material [13,20]:

$$[-(C-)_n] + \delta\,X{-}Ph^{\cdot} \rightarrow [-(C(Ph{-}X)-]_{n\delta}[-(C-)_{n(1-\delta)}] \quad (4)$$

In the absence of other deactivation reactions of the negatively charged carbon intermediate, this sequence can therefore be represented by the following balance:

$$-(CF_2-)_n + (2+\delta)n\,e^- + \delta n\,X{-}Ph{-}N_2^+ \rightarrow [-(C(Ph{-}X)-]_{n\delta}[-(C-)_{n(1-\delta)}] + \delta n\,N_2 + 2n\,F^-. \quad (5)$$

4. Conclusion

We have shown that it was possible to graft reduced PTFE by nitro and bromo-phenyl diazonium tetrafluoroborate salts in a manner similar to that used for carbon; it was not necessary to apply a reductive potential during grafting owing to the intrinsic conductivity of the *n*-doped carbonaceous polymer obtained when reducing PTFE. Grafting could be evidenced by cyclic voltammetry, X-ray fluorescence or ToF-SIMS. Nitro- and bromo-phenyl moieties were covalently linked to the PTFE material and could be eliminated only by abrasion.

We are currently trying to decrease the size of the carbonaceous zones from 1 mm to 100 μm by reducing

PTFE in the vicinity of an ultramicro-electrode. Our long-term objective is the design of a multisensor consisting of selectively modified regions disseminated on the virgin inert perfluorinated surface. For that purpose, advantage should be taken of some qualities of PTFE like its hydrophobicity and chemical inertness, which would avoid any undesired adsorption on the unmodified inert virgin surface and its low dielectric constant [21], which is well adapted for microelectronics. Keeping in mind this objective, we are working on the grafting of metals as well as other organic synthons.

Acknowledgements

The authors are indebted to R. Ollitrault for her assistance in X-ray fluorescence.

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