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Surface modification of poly(tetrafluoroethylene) by magnesium amalgam

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Mg amalgam reacts with PTFE (foil or oriented film on Si) to give a thin surface layer containing MgF_2 in a mixture with complicated, air-sensitive, carbonaceous product containing large amount of residual C-F bonds. The reaction does not propagate into the bulk polymer, which, consequently, retains its white color even after hundreds of hours of reaction at 150 °C. These findings contrast with the reactivity of PTFE with amalgams of alkali metals, Li, Na, K. The differences are interpreted, in terms of the electrochemical model of amalgam carbonization, as blocking of charge (e^-/Mg^{2+}) propagation through the modified layer. AFM patterns show that the Mg-treatment increases the surface roughness. The molecular-level ordering of PTFE films is strongly perturbed by the action of Mg-amalgam; the treated surface shows only small proportion of organized macromolecules. *© 2001 Kluwer Academic Publishers*

1. Introduction

A low surface energy of poly(tetrafluoroethylene) (PTFE) impedes applications, where bonding of PTFE to other materials and to itself is required; such applications comprise, e.g., adhesive bonding, lamination, painting, and metallization. This problem was first addressed in 1957 by duPont and 3M in their patents aimed at promotion of bondability of PTFE by surface treatment [1]. Chemical or electrochemical methods of the PTFE treatment are usually based on reductive defluorination, where the most popular reagents are sodium dihydronaphthyllide in tetrahydrofuran or ammonia solutions of alkali metals [1]. Defluorination by these agents is usually not quantitative, and the reaction is complicated by breakdown of solvents and/or impurities. The side reactions, e.g. with NH_3, provide hydrogen atoms, which are rapidly attached to the defluorinated intermediates [1]. Consequently, the products are poorly defined, and their composition varies in broad limits between that of elemental carbon, fluorinated "carbonaceous" materials up to even poly(ethylene) [1, 2].

Combellas *et al.* [3, 4] have shown that a solution of Mg in liquid NH_3 offers certain practical advantages over the ammonia solutions of alkali metals: the modified PTFE surface is less damaged, while even its color remains white. The same reagent was successfully employed also for surface treatment of Nafion [5], and some other chloro-and fluoropolymers [6]. The thickness of the modified surface layer was only about 10–1000 nm, but its chemical composition was again complicated and variable. The Mg/NH_3 solution was generated electrochemically by dissolution of Mg anode, since magnesium is normally insoluble in NH_3 [3, 4]. A similar strategy was employed by Kawase *et al.* [7]; they have carbonized PTFE electrochemically in tetrahydrofuran medium by using a sacrificial Mg anode, which dissolved in the electrolyte solution. Also in this case the layer thickness was only 1 μm, but it contained, according to IR and Raman spectra, a significant amount of conjugated polyyne, -$(C{\equiv}C)_n$-. The same group [8–10] has later demonstrated that the ex-PTFE polyyne can be transformed by heating to 800 °C at simultaneous electron irradiation into nanoscale carbon tubules of a diameter 10–50 nm and length ca. 1000 nm.

Reductive defluorination of PTFE and other perhalogenated polymers can also be carried out by the action of alkali metal amalgams [1]. In contrast to the treatment with dihydronaphthyllide or ammonia solutions of alkali metals, the amalgam-driven defluorination gives simple products, and the reaction mechanism and kinetics are known in detail [1]. The reason for this favorable behavior is, that the amalgam-defluorination is not perturbed by any side reactions with solvents or impurities, which complicate the reactions, e.g. in ammonia or tetrahydrofuran media [1]. The defluorination of PTFE by alkali metal (M = Li, Na, K) amalgams leads quantitatively to a mixture of n-doped elemental carbon with a stoichiometric amount alkali metal fluoride ($C^{\delta-} + 2MF$). The mechanism has been interpreted assuming a spontaneous formation of an interfacial galvanic cell:

$$\text{M(Hg)|C-MF|C, PTFE} \qquad \text{(Scheme 1)}$$

whose thermodynamic cell voltage equals 3.251 V (for M = Li at 25 °C). C-MF denotes the reaction product, i.e. a conducting (e^-/M^+) mixture of carbon with the alkali metal fluoride [1]. According to this electrochemical model, the interfacial film (C-MF) grows as a result of self-discharge of the cell. Consequently, its thickness (L) varies with time (t) according to the kinetic equation:

$$L = \sqrt{\frac{\Delta E M \sigma_e \sigma_i t}{a F \rho (\sigma_e + \sigma_i)}} = K \cdot t^{1/2} \qquad (2)$$

where ΔE is the cell voltage, M is molar mass of CF_2 unit, σ_e and σ_i are electronic and ionic conductivities, respectively, a is thickness ratio of C-MF and that of consumed PTFE, F is Faraday constant and ρ is density of PTFE. The actual value of rate constant (K) is controlled by the M^+ conductivity of C-MF (σ_i) [11]. The Equation 2 is valid also for the amalgam carbonization of some other perhalogenated polymers; the rate constants, K do not vary much with the polymer type, but they decrease significantly with increasing atomic number of the alkali metal [1, 11].

Whereas the reductive carbonization of PTFE and other perhalogenated polymers by alkali metal amalgams has been studied carefully in the past, there is no relevant report about magnesium amalgam. This paper scrutinizes the first results obtained on this system.

2. Experimental section

PTFE foils (20 × 10 × 0.3 mm, from Goodfellow, UK) were purified and outgassed before use as described elsewhere [11]. Oriented PTFE films were prepared by friction deposition (hot-dragging) [12, 13] method on Si wafers (10 × 5 mm, OKMETIC Finland). During the PTFE deposition, the substrate temperature was 270°C, load ≈15 N/cm^2 and speed 0.6 mm/s (see Ref. [13] for further preparative details).

Magnesium chips (Aldrich, 99.98%, impurities content (in ppm): Zn (35), Mn (30), Fe (25), Al (20), Ni (20), Na (5)) were dissolved in polarographic grade mercury (Služba výzkumu, CR, 99.9999+ %), and the prepared liquid amalgam was filtered through a glass capillary in vacuum. The amalgam concentration was determined by acidimetric titration as 3036 ppm (w/w). The PTFE foils or films were contacted with the amalgam at 25, 100 and 150 °C for a desired reaction time. After the reaction was finished, the samples were washed with pure mercury to remove the non-reacted magnesium. All operations were carried out under high vacuum in a sealed, all-glass apparatus. The consumption of Mg was determined by chemical analysis of the amalgam before and after the reaction. The modified PTFE was also analyzed for F^-. The sample of reacted PTFE was mineralized by boiling with 5 ml of 30% hydrogen peroxide and 1 ml of 0.1 M KOH for 30 min in a Teflon beaker. The solution was evaporated and the dry residue dissolved in water. Fluoride was determined spectrophotometrically by Zr-alizarine or by potentiometric titration with fluoride-ion sensitive electrode. Further details are given elsewhere [11].

Atomic force microscopy (AFM) studies were carried out on Scanning Probe Microscope TMX 2010 Discoverer (TopoMetrix, USA), with pyramidal Si_3N_4 AFM tip (1520 Standard, TopoMetrix). All measurements were made at the ambient atmosphere and temperature. Static charge formation and accumulation on the sample surface during AFM scanning was prevented by an ionizer ^{241}Am (α, 50 MBq).

X-ray photoelectron spectra (XPS) were measured on a VG Scientific ESCA 3 Mk II electron spectrometer with pressure of residual gases lower than 0.1 μPa. Spectra were excited by Al K_α radiation ($h\nu = 1486.6$ eV). The hemispherical electron analyzer operated in the fixed transmission mode with a band-pass energy of 20 eV, giving the width of 1.1 eV for the Au $4f_{7/2}$ spectral line. The measurement was carried out at three photoelectron take-off angles: 5°, 55° and 75°. Static sample charging was corrected by assigning the value of 284.8 eV to the CH_x (C 1s) peak from hydrocarbon impurity. The peak area was calculated after removal of the satellite lines $K\alpha_{34}$ and non-linear background, while the overlapping peaks were resolved numerically [14] The surface concentrations were determined by using the subshell photoionization cross-section [15] and corrected for the attenuation electron lengths [16]. The surface concentration of Mg was determined from the most intense Auger KLL line. The intensity callibration of Mg 2s vs. Mg_{KLL} was carried out by several external standards. The samples were installed into the spectrometer after a short contact (minutes) to air.

3. Results and discussion

3.1. Sample preparation

In contrast to the amalgams of alkali metals (Li, Na, K), the magnesium amalgam showed significant “wetting” of the PTFE surface as well as of the walls of the reaction vessel (made from Pyrex glass), which indicates some interaction with both materials. These surfaces are immediately covered by a thin, firmly-adhering film of the amalgam. (Alkali metal amalgams do not show any apparent “wetting” of PTFE or glass; they behave like pure mercury in contact to these materials). However, the reaction of Mg amalgam with glass (if any) is restricted only to a thin surface layer; blank experiments have confirmed that there was no measurable change of the Mg concentration even after 400 hours of contact with Pyrex glass at 150 °C

The reaction of PTFE with Mg amalgam is also significantly different from that with alkali metal amalgams. The magnesium amalgam does not cause any blackening of the PTFE surface, even after several weeks of contact at 150 °C. This resembles the behavior of magnesium in ammonia solution, which also leaves the PTFE surface white [3, 4]. (On the other hand, blackening of PTFE was observed in tetrahydrofuran-electrolyte solution with anodically dissolved Mg anode; this is, reportedly, caused by the presence of highly reactive Mg^+ species [7–10].

Assuming a 1 : 1 stoichiometry of the reaction of Mg amalgam with PTFE:

$$Mg + \text{-}CF_2\text{-} \rightarrow \text{-}C\text{-} + MgF_2 \qquad (3)$$

the thickness of chemically modified PTFE can simply be determined from the consumption of Mg and/or by the content of F^- in the product. The latter method is more sensitive; it allows to measure layer thickness down to about 100 nm [11]. (The measurement of thick layers is also limited by low solubility of MgF_2).

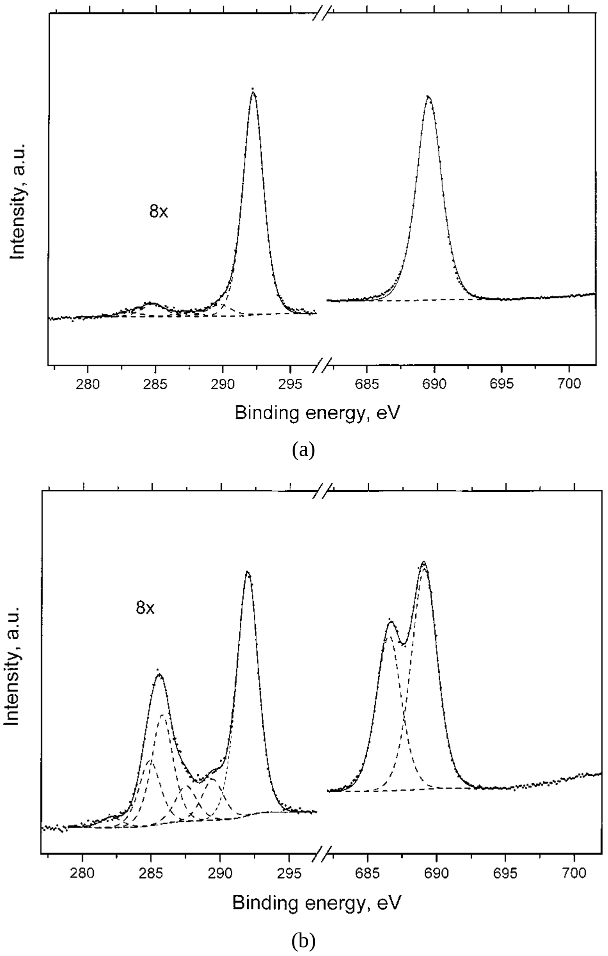
The reaction (3) was monitored analytically at varying conditions (reaction time 1–400 hours, temperature 25–150 °C). The results were poorly reproducible, and the estimated layer thicknesses were usually close to the detection limit of analytical methods used ($\approx$100 nm). Hence, the reaction of Mg-amalgam with PTFE seems to be restricted only to a thin surface layer, and does not propagate into the bulk polymer as in the case of alkali metal amalgams (cf. Equation 2). The striking difference between alkali metals and Mg can hardly be explained in terms of the reaction thermodynamics. Actually, the standard potential of Mg amalgam equals -2.09 V [17], which is even more negative than the standard potentials of Na- or K-amalgams. (The standard potentials of alkali metal amalgams equal as follows [17]: -2.195 V (Li), -1.959 V (Na), -1.975 V (K)).

The blocking of the PTFE-Mg(Hg) reaction should be connected to some perturbation of the reaction propagation (valid for alkali metals, cf. scheme 1 and Equation 2). In all cases, the reaction is triggered by a chemical reduction of PTFE, producing a thin layer of products (C-MF). Such a thin layer is formed also in the case of Mg(Hg) (*vide infra*). This is in accord with the expected high driving force of the reaction, which is derived from the corresponding redox potentials. However, the magnesium-formed layer does not grow electrochemically, because the interfacial film is insulating for electrons, Mg^{2+} cations or both the charge carriers. In analogy to systems with alkali metals, we may speculate that the blocking effect is connected to the transport of Mg^{2+}.

Generally, all reactions producing a compact solid film (which is impermeable to the reactants) must propagate by an alternative mechanism, e.g. by an independent transfer of electrons and cations through the growing film (scheme 1) [1]. If the interfacial layer is not conducting for e^-/M^+, the layer propagation stops as soon as the direct “chemical” contact (e.g. through casual cracks in the film) is hindered. Analogous interpretation might be suggested also for the reaction with Mg/NH_3.

3.2. XPS spectra

Fig. 1a and b show XPS spectra in the C1s and F1s regions of the PTFE foil before (Fig. 1a) and after (Fig. 1b) the treatment with Mg amalgam for 96 hours at 25 °C. Similar spectra were obtained also for Si/PTFE films and for samples treated at elevated temperatures. The binding energies and surface concentrations are summarized in Table I. The starting PTFE, both in the form of foil or Si-supported film, show the expected surface stoichiometry: $C^{\delta}F_{2.1}(C_{0.1}^{\alpha-\gamma}O_{0.03})$ or $C^{\delta}F_{2.1}(C_{0.7}^{\alpha-\gamma}O_{0.03})$, respectively. Small amounts of carbonaceous impurities ($C^{\alpha-\gamma}$) are created during the measurement by X-ray induced cross-linking [18]. The F1s level is not very sensitive to this effect, but there appear several new low-binding-energy C1s peaks assigned to CF_x ($x = 0$–3) species [18].



(a)

(b)

Figure 1 (a) XPS spectra (C1s, F1s) of the PTFE foil. Note different intensity scales. (b) XPS spectra (C1s, F1s) of the PTFE foil (as in Fig. 1a) treated by Mg amalgam at 25 °C for 96 hours. Note different intensity scales.

Fig. 1b and Table I demonstrate that the PTFE treated by Mg amalgam displays only a partial disappearance of the fluoropolymer’s C1s (292 eV) and F1s (689 eV) peaks. This contrasts with the XPS spectra of PTFE treated by alkali metal amalgams, both ordinary PTFE foil [19] and oriented PTFE film [13]. The PTFE surface treated by alkali metal amalgams shows no residual C-F bonds, i.e. the conversion of PTFE to carbon and alkali metal fluoride, is complete [1, 13, 19].

The Mg-treated surface contains the expected by-product, i.e. MgF_2, although not in the stoichiometric proportion to carbon. (Crystalline MgF_2 showed the following values: F1s 685.6 eV, Mg_{KLL} 1177.5 eV). The inorganic fluoride (686 eV, F^{α}) forms only a smaller part of the total fluorine in the treated samples. The rest is present in C-F bonds (689 eV, F^{β}) which are not much different from those in PTFE. Analogous behavior occurs also for Mg/NH_3 treatment [4].

The C1s region exhibits considerable amount of carbon other than elemental or CH_x impurity (285 eV, C^{α}) and residual C-F (292 eV, $C^{\delta}/C^{\varepsilon}$). These carbon peaks correspond to surface oxides, which are formed during a short contact (minutes) of the sample with air oxygen and humidity. This contact is unavoidable in our set-up, since the preparation of samples (manipulations with

TABLE I Results of XPS analysis of PTFE films. E_b are binding energies of photoelectrons and E_A are kinetic energies of Auger electrons (cf. also Fig. 1a and b). PTFE-foil is a commercial material from Goodfellows; Si/PTFE-film denotes a highly-oriented film deposited on silicon wafer by a hot-dragging method (see Experimental Section for details)

		C1s			F 1s		Mg (KLL)		O 1s	
		E_b (eV)	C/C^α		E_b (eV)	F/C^α	E_A (eV)	Mg/C^α	E_b (eV)	O/C^α
PTFE-foil	C^α	284.8	1.00		689.5	34.2	—	0	531.9	0.55
Virgin	C^β	287.3	0.33							
	C^γ	289.7	0.95							
	C^δ	292.2	15.9							
PTFE-foil	C^α	284.8	1.00	F^α	686.5	5.03	1177.4	3.94	532.6	1.51
After treatment	C^β	285.7	2.57	F^β	689.1	7.39				
	C^γ	287.4	0.79							
	C^δ	289.4	3.50							
	C^ε	291.9	3.50							
Si/PTFE-film	C^α	284.8	1.00		689.5	6.30	—	0	532.2	0.10
Virgin	C^β	285.2	0.98							
	C^γ	288.5	0.20							
	C^δ	292.5	2.95							
Si/PTFE-film	C^α	284.8	1.00	F^α	685.6	0.12	1177.3	0.13	532.5	0.41
After treatment	C^β	286.6	0.20	F^β	689.0	0.60				
	C^γ	288.5	0.17							
	C^δ	292.0	0.28							

mercury) *in situ* is excluded technically. Generally, the C1s region resembles that of Mg/NH_3-treated PTFE, where the C1s spectrum was assigned to a mixture of products containing C=C, C-H, C-OH, C=O, COOH and CHF groups [4]. The larger intensity of CH_x peak in Mg-treated samples is understandable in terms of increased surface area of the carbonized samples.

The intensities of lines of C^α, C^β, F^α and Mg(KLL) do not show significant dependence on the take-off angle (between 5° to 70°). Consequently, the modified

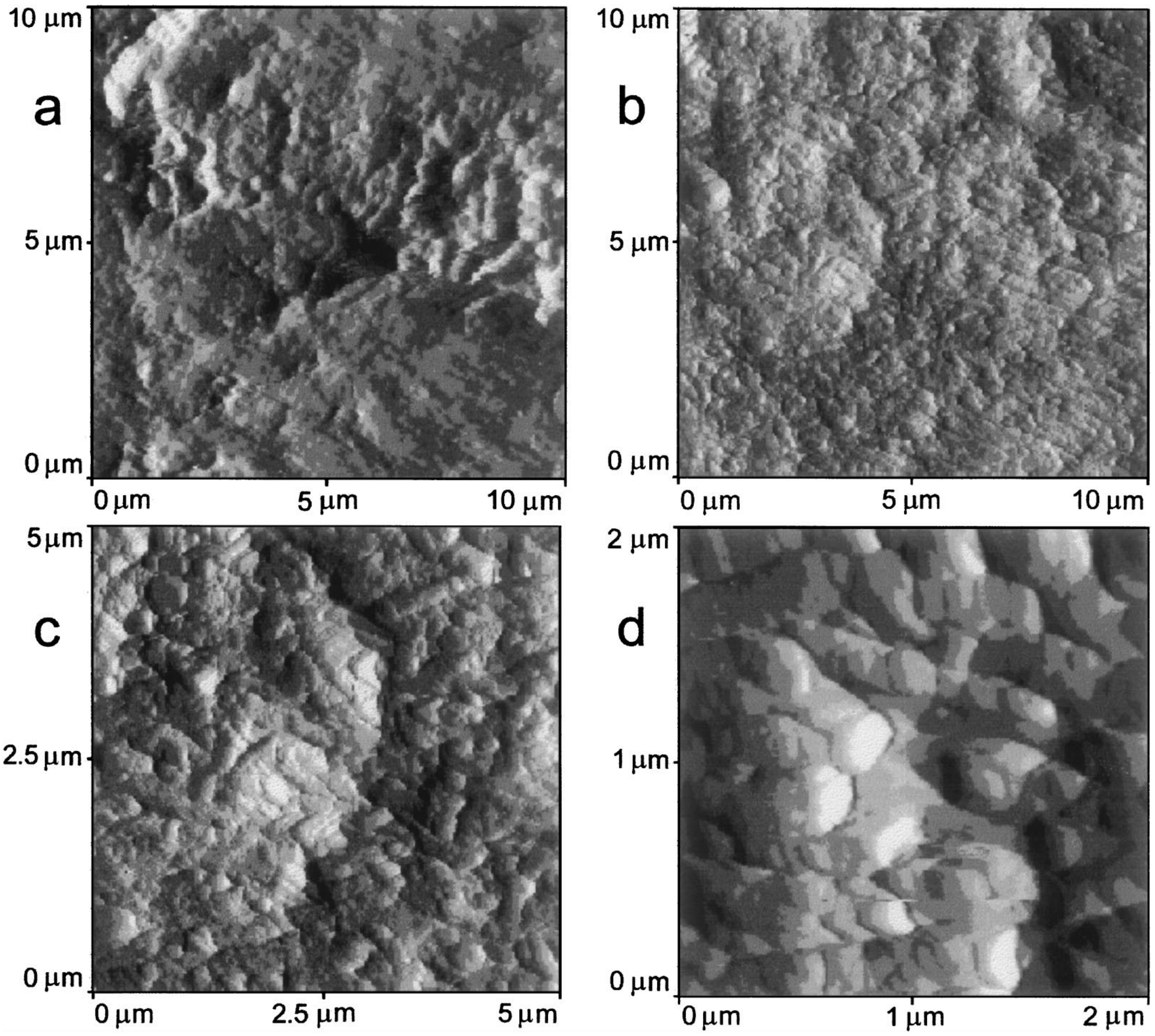


Figure 2 AFM patterns of PTFE foil before (a) and after (b–d) the treatment with Mg-amalgam for 96 hours at 25 °C.

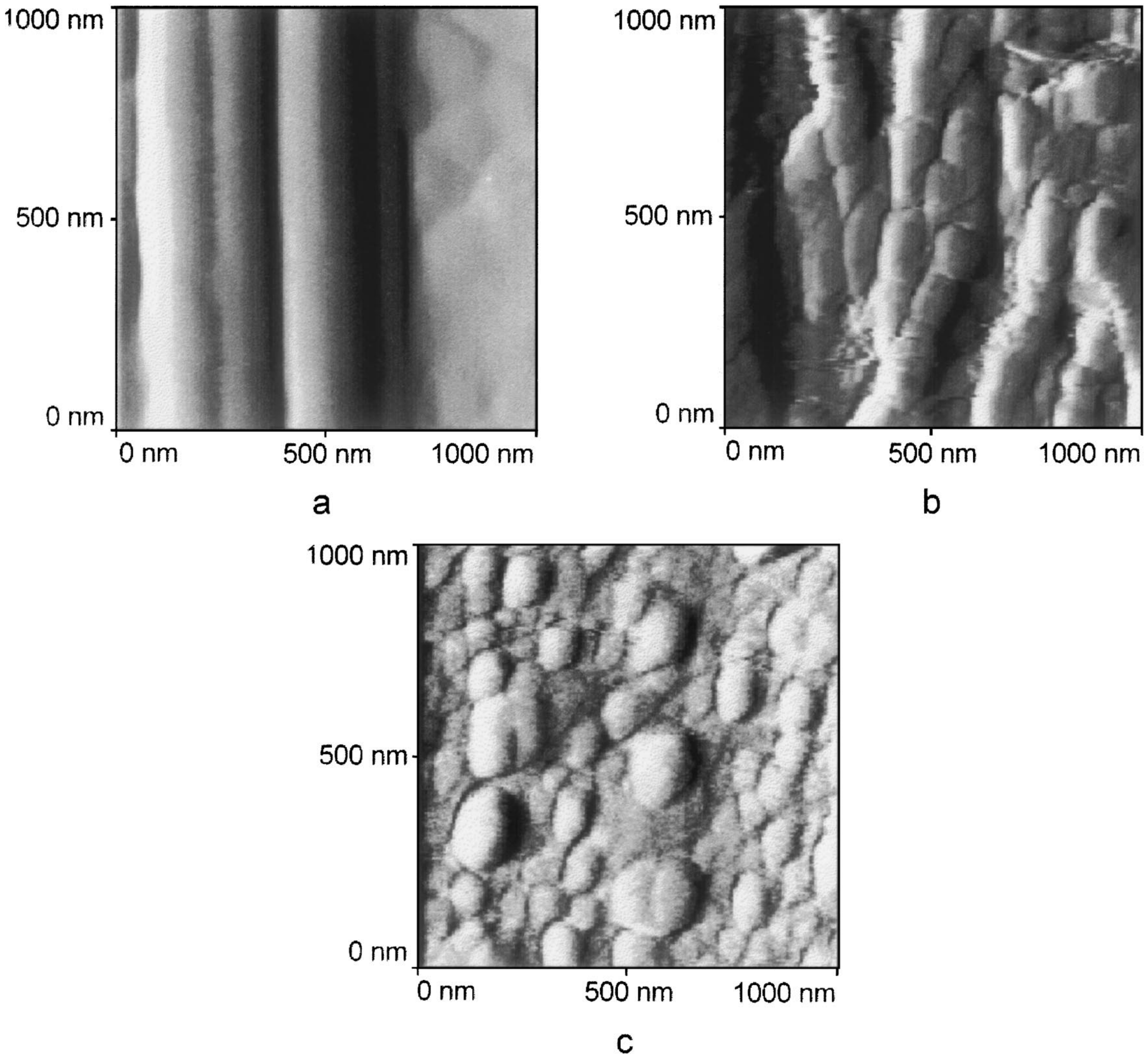


Figure 3 AFM patterns of oriented PTFE film before (a) and after (b and c) the treatment with Mg-amalgam for 1 hour at 25 °C (b and c refer to different typical places on the film).

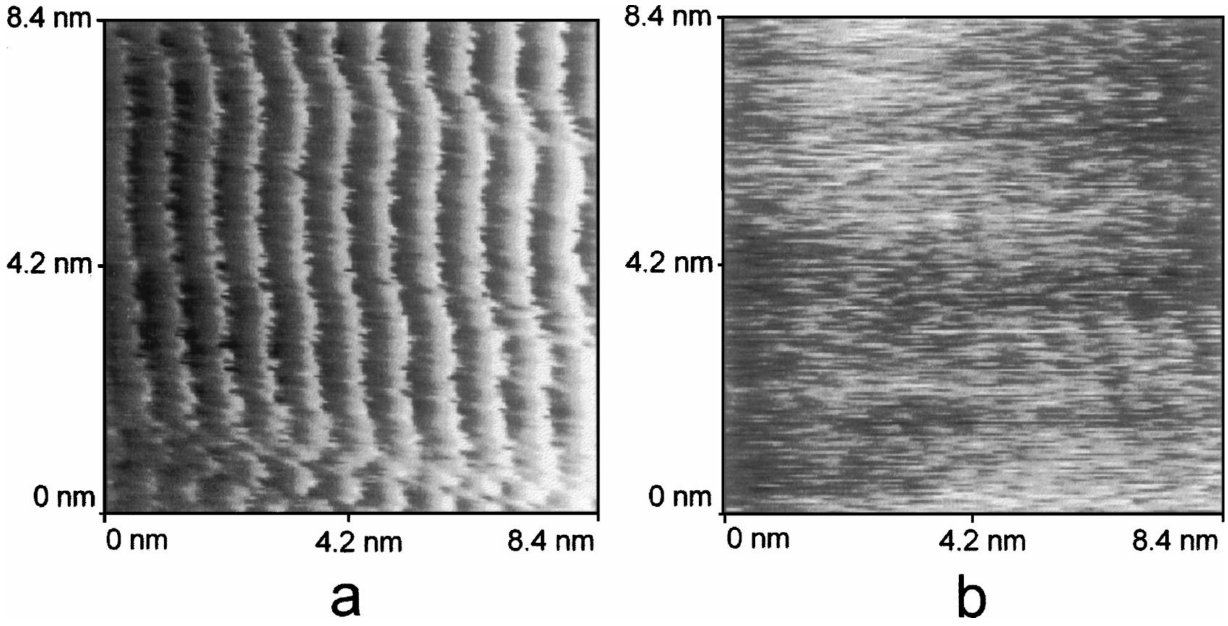


Figure 4 AFM patterns of flat areas of oriented PTFE film before (a) and after (b) the treatment with Mg-amalgam for 1 hour at 25 °C (cf. Fig. 3 for the same sample at lower resolution). Both images display raw data without any processing (e.g. by Fourier filtration).

layer, C-MgF_2 should be thicker than the sampling depth of XPS (which varies with the cosine of the take-off angle). This allows to estimate that the layer thickness is larger than ca. 15 nm [4].*

3.3. Atomic force microscopy

Fig. 2 displays AFM patterns of pure PTFE foil (Goodfellow) and that after the treatment with Mg amalgam. The increase of surface roughness as a result of the Mg treatment is apparent, although the starting PTFE foil is also far from being flat at the same magnification scale. The observed effects are similar to those reported for Mg/NH_3 treatment of PTFE [4]. In this case, scanning electron microscopy demonstrated surface inhomogeneities, which were, however, detected in larger scale of about 10–80 μm.

The morphological changes are more clearly visualized on highly-oriented PTFE films (Fig. 3). The starting films contain linear parallel ribs in the direction of dragging. The ribs (typically tens of nm in height) are separated by relatively flat areas (Fig. 3a). Upon Mg treatment, the ribs become more pronounced, but their orientation is partly perturbed (Fig. 3b). The originally flat areas show characteristic spherical grains of diameter of about 20 to 200 nm and the height of about 20 nm (Fig. 3c). Their appearance demonstrates the volume increase caused by "Mg insertion" during defluorination. The spherical morphology may indicate a nucleation-type reaction. It is initiated in single separated points, from which the reaction spreads radially in all directions.

Fig. 4 displays the high-resolution AFM picture of the starting oriented PTFE film (Fig. 4a) and that after modification with Mg-amalgam (Fig. 4b). The oriented molecules are detected at the flat areas of the virgin film (Fig. 4a). (After image filtration employing 1D-FFT, even the expected helix of fluorine atoms around the carbon chain is clearly visible (cf. Ref. [13])). However, the perfect molecular-level ordering of PTFE macromolecules (Fig. 4a) is damaged in the Mg-modified material (Fig. 4b). The same was observed also if the PTFE films were modified by Li amalgam [13]. Only very rarely, there were detected some signs of molecular-level orientation on the Mg-treated surface; these features seem to be visible (although not too clearly) on Fig. 4b. We cannot exclude that these areas may still correspond to the residual PTFE, which was not affected by the Mg amalgam. (Note that XPS confirms the presence of C and F atoms, whose binding energies are not much different from those of PTFE (Section 3.2)). A secondary effect, which may also change the molecular-level morphology, is the surface oxidation in air (cf. Section 3.2). The oxidative breakdown cannot be avoided in the used AFM set up, where the measurements are carried out on ambient atmosphere.

4. Conclusions

The defluorination with Mg amalgam was studied, for the first time, both on ordinary PTFE foils and on highly ordered PTFE film made by friction deposition. Similar to Mg/NH_3 solutions [4], Mg-amalgam reacts with PTFE (foil or oriented film) only in a thin surface layer. Consequently, the PTFE foil remains white even after hundreds of hours of contact with Mg-amalgam at 150 °C. These findings are in contrast to the known reactivity of amalgams of alkali metals (Li, Na, K) which cause always: (i) a stoichimetrically quantitative defluorination, and (ii) the layer propagation into the bulk polymer is well-defined as long as one of the active substances is consumed [1]. The striking difference in reactivity of alkali metals and Mg can hardly be interpreted in terms of the reaction thermodynamics since the Mg amalgam has even more negative redox potential than Na or K amalgams. The found differences are tentatively interpreted, in terms of the electrochemical model of amalgam carbonization [1]. The blocking effect is presumably caused by hindered transport of charge (electrons or Mg^{2+} cations) through the modified layer. However, the physical reason for such a poor ionic conductivity of the Mg-modified layer remains unknown.

The surface layer, prepared by the action of PTFE and Mg-amalgam, contains MgF_2 in a mixture with complicated, air-sensitive, carbonaceous product. XPS indicates that the modified layer involves also a large number of residual C-F bonds. The modified carbonaceous layer is oxidized in air, which is reflected by a characteristic C1s spectrum of surface oxides. The composition and properties of modified surface again resemble those of Mg/NM_3 surface [4].

Significant structural changes on both macroscopic and molecular levels were observed by AFM in the film after the action of Mg-amalgam. The Mg-modification generally promotes higher surface roughness. Since the commercial PTFE foil is also relatively rough at comparable magnification, these effects are better apparent on highly oriented PTFE films made by friction deposition. The surface relief is characterized by spherical grains, which probably originate from nucleation-type Mg insertion. The molecular-level ordering of PTFE films is strongly perturbed by the action of Mg-amalgam. The Mg-modified surface is almost fully reconstructed; it contains only a small proportion of organized linear molecules.

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* Preliminary depth-profile studies employing Rutherford Backscattering Spectrosopy have shown that the thickness of the Mg-containing layer is typically about 50 nm. (We are grateful to Dr. Patrick Bertrand, Catholic University, Louvain, for providing us with the RBS data).

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