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Nitrogen plasma-based ion implantation of poly(tetrafluoroethylene): Effect of the main parameters on the surface properties

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ABSTRACT

The surface of poly(tetrafluoroethylene) (PTFE or Teflon) was treated by nitrogen plasma-based ion implantation. Accelerating voltages between 15 and 30 kV, fluences between 1×10^{17} and 3×10^{17} cm^{-2} and fluence rates between 3×10^{13} and 7×10^{13} cm^{-2} s^{-1} were applied. The effects of these main parameters were examined on the evolution of surface chemical composition, mean roughness, abrasive wear, wettability and surface electrical resistance. The aim was to obtain relationships, enabling to control the surface properties examined.

The F/C atomic ratio determined by XPS strongly decreased, correlating inversely with voltage. The mean surface roughness characterized by topography measurements, increased, correlating directly with fluence and inversely with voltage. The wear volume obtained by multipass scratch tests did not show clear relationship with the main process parameters, however, it increased upon treatment with the increase of surface roughness and O/C atomic ratio. The water contact angle increased at low voltages and high fluences, due to preferential increase of roughness, and decreased at high voltages and low fluences, owing to intense defluorination and incorporation of N and O. The electrical resistance of the PBII-treated surfaces decreased by several orders of magnitude, showing a significant inverse correlation with fluence. It continued to decrease for samples exposed to air, primarily after treatments performed with low fluences, due to post-treatment type oxidation.

1. Introduction

Poly(tetrafluoroethylene), PTFE, has a combination of advantageous properties including chemical resistance, thermal stability, high electrical resistivity and low friction coefficient. There has been an intense research activity associated with the surface modification of PTFE, to change some of its surface properties, for instance increase characteristics like adhesion to other materials, wettability or biocompatibility and decrease its wear. There are a limited number of studies, however, on the surface modification of PTFE by plasma-based ion implantation (PBII). As a versatile, relatively simple and cost-effective surface modification technique, alternative to traditional ion implantation, PBII offers a new possibility for surface modification of polymers, the potential of which has not been fully explored yet. In particular, PBII-treatment was applied to change the wettability of PTFE [1–3], improve its wear resistance [4] and activate its surface for enzyme attachment [5].

In a few recent publications we identified acceleration voltage, fluence and fluence rate to be the most important process parameters influencing the surface properties of PBII-treated polymers [6–10]. In this work, the effects of these parameters during PBII-treatment of PTFE in nitrogen were studied on the evolution of some important surface properties like chemical composition, mean roughness, abrasive wear, wettability and electrical resistance. The aim was to obtain relationships, which enable to control these properties. Furthermore, the post-treatment relaxation type behavior of the treated surfaces was also examined by measuring the surface electrical resistance as a function of time elapsed after treatment.

2. Materials and methods

2.1. Material applied and sample preparation

Commercial virgin grade PTFE manufactured by GAPI Group was used, from which disks of 9 mm diameter and 2 mm thickness were machined. The samples were polished with wet SiC papers (grit numbers P1200 and P4000) and then with wet felt sheet. Subsequently, they were rinsed in distilled water, then in 96% ethanol (puriss. grade, Reanal, Hungary) and dried in pure nitrogen flow.

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2.2. PBII-treatment

The PBII-treatment was performed in a home-assembled equipment. The base pressure in the stainless steel chamber was 4×10^{-4} Pa. A 27.13 MHz RF plasma generator was applied (Dressler, Germany). The basic parameters were as follows: high purity (99.995%) N_2 (Messer Ltd.), flow rate = 25 cm^3/min (STP), pressure = about 4×10^{-1} Pa, RF power = 150 W. The PBII-treatment of the samples was performed by a high voltage pulser (ANSTO, Australia). Accelerating voltages (U) between 15 and 30 kV, particle fluences (F) between 1×10^{17} and 3×10^{17} cm^{-2} and fluence rates (FR) between 3×10^{13} and 7×10^{13} cm^{-2} s^{-1} were varied. The pulse duration was 5 μs, the pulse frequency was varied between 42 and 140 Hz, to adjust the desired fluence rate. To limit the number of treatments and that of samples to be characterized, the approach of design of experiments was employed. A three-level fractional factorial design was used with three factors (U, F, FR) and nine treatment combinations, applying the Statistica 8.0 program (StatSoft, Inc.). The graphic representation of the experimental settings in the factorial space is shown in Fig. 1.

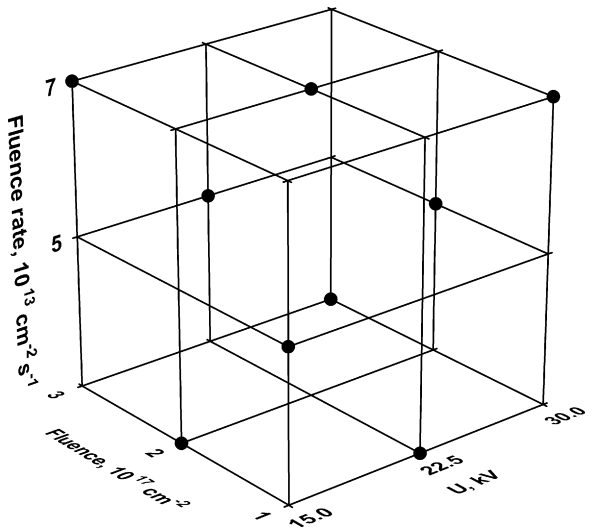

Fig. 1. Graphic representation of the experimental settings in the factorial space.

2.3. XPS analysis

XPS studies were done by a Kratos XSAM 800 spectrometer using Mg $K\alpha_{1,2}$ radiation and fixed analyzer transmission mode (80 and 40 eV pass energies for survey and detailed spectra, respectively). The spectra were referenced to the C 1s line (binding energy, BE = 285.0 eV) of the hydrocarbon type carbon. Data acquisition and processing were performed with the Kratos Vision 2 program. Quantification was done by the XPS MultiQuant program [11].

2.4. Characterization of topography and wear properties

Topography and wear properties were determined by a NanoTest 600 equipment (Micro Materials Ltd., UK). For multipass wear tests a sharp Rockwell type diamond head, 7 passes, 2 μm s^{-1} scanning velocity and 5 mN scratch load were used. The same sharp Rockwell head was used for topography tests, with 2 μm s^{-1} velocity and 0.02 mN load. The mean roughness values were determined on 20 μm portions of the topography curves.

2.5. Contact angle measurements

Contact angle measurements were done by the static sessile drop method at 23 °C, with double distilled water and diiodomethane (Sigma–Aldrich, Reagent Plus 99% grade), applying the SEE System apparatus (Advex Instruments, Czech Republic). A Hamilton syringe was used to inject 2 μl droplets. Each result of contact angle is an average of 5 measurements, performed always on previously non-wetted parts of the samples.

2.6. Determination of surface electrical resistance

Surface electrical resistance was measured at room temperature, considering the ASTM D257 standard test method for DC resistance, by a home-assembled equipment, based on a P-263 type power supply (Physik Instrumente, Germany) and a home-made digital picoampermeter.

3. Results and discussion

3.1. XPS results

The characteristics of the untreated sample were in agreement with those published in the literature. Thus, binding energies of the main C 1s and F 1s peaks found at 292.5 and 689.6 eV agreed well with the published values of 292.48 and 689.67 eV [12], respectively. The composition C 32.6 at%, F 66.0 at% and O 1.4 at% found corresponded closely to the theoretical values C 33.3 at% and F 66.7 at%. Upon N PBII-treatment, the relative intensity of the F 1s peak decreased, that of the C 1s peak increased and the N 1s peak appeared at about 399.5 eV testifying to incorporation of nitrogen. The amount of built-in N was between 4.6 and 12.6 at%. An increase of O-content could be also detected (up to 2.7–5.4 at%), apparently due to the post-treatment type oxidation. The F-content of the surface decreased to 46.1–24.3 at%, with a simultaneous increase of the C-content to 45.9–56.9 at%, resulting in a decrease of the F/C atomic ratio to values ranging between 1.0 and 0.43.

An advantage of the applied method of design of experiments is that the experimental results can be statistically analyzed. In particular, a useful dimensionless index called standardized effect can be estimated (including its linear L and quadratic Q components) for the factors U, F and FR. Their absolute values can be ranked in a Pareto-chart, and the ranking reflects the order of influence of a given factor on the property studied. Also, the significance level α can be computed, a comparison of which with a given effect allows judgment to be made about the statistical significance of the effect [13]. Fig. 2 depicts the Pareto-chart of the linear and quadratic components of the estimated standardized effects on the F/C atomic ratio of the factors U, F and FR. The dashed line corresponds to the

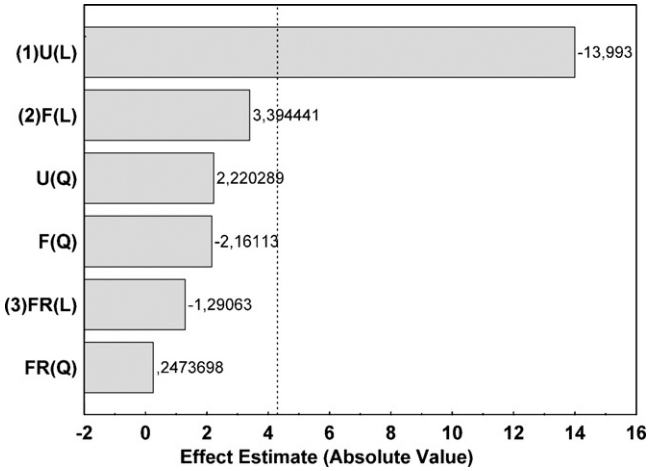

Fig. 2. Pareto-chart of standardized effects for the F/C atomic ratio.