

**SURFACE MODIFICATION OF TECHNICAL ENGINEERING
POLYMERS BY PARTICLE BEAM TECHNIQS
AND SURFACE CHARACTERISATION**

THESIS
KLÁRA KERESZTURI

EÖTVÖS LORÁND UNIVERSITY
FACULTY OF SCIENCE
CHEMISTRY DOCTORAL SCHOOL

HEAD OF CHEMISTRY DOCTORAL SCHOOL
DR. GYÖRGY INZELT

ANALYTICAL CHEMISTRY, COLLOID- AND
ENVIRONMENTAL CHEMISTRY, ELECTROCHEMISTRY

HEAD OF DOCTORAL PROGRAM
DR. GYULA ZÁRAY

SUPERVISOR
DR. ANDRÁS TÓTH
CANDIDATE OF CHEMICAL SCIENCES

HUNGARIAN ACADEMY OF SCIENCES
CHEMICAL RESEARCH CENTER
INSTITUTE OF MATERIALS AND ENVIRONMENTAL CHEMISTRY

2010

1. Introduction, antecedents

The claims are higher and higher to produce polymers and polymer-based tools with special properties (for example prosthesis, catheters, implants, biological active materials, intelligent polymers and monitored drug-delivery systems).

In order to apply polymers and plastics in some special applications it is often necessary to modify a few nano- or micrometer thick layer of the surface, while the favourable array properties do not change. The aims can be the improvement of wettability (with different kind of liquids), paintability, biocompatibility and bioactivity, functionalization of the surfaces, production of hard and wear resistant layers, development of protecting or water-repellent materials, etc.

Different kind of physical surface modification processes (for example UV- and gamma-ray or electron beam, glow discharge and atmospheric plasma techniques); physical and chemical vapour deposition and different kind of particle beam techniques are current beside the traditional liquid and gas phase chemical techniques applied to modify and improve the surface properties. There is intensive research activity to study the modified polymer surfaces and to explore structure – property type relationships.

Surface modification of the polymers by particle beams (atom and ion beams) is an evolving, (either theoretically or practically) perspectivistic, multidisciplinary area.

The main speciality of this treatments, that the energy, transmitted to the polymer-matrix, can be orders of magnitude higher, compared to the traditional ionizing radiation (e.g. γ -vagy electron-radiation). Changes of the chemical composition and structure, generated in the surface layer, cause simultaneously significant changes in such polymer properties like mechanical, electrical and optical parameters, solubility, wettability, biocompatibility, etc.

The fast atom-source can be applied under atom beam treatments and different type of ion implantations can be applied as ion beam techniques to modify the surfaces. The fast atom source was originally developed as a new ionizing technique of the mass spectrometry in the 1980's. Later it was applied to deposit diamond like carbon (DLC) layers, nitrate stainless steel. This technique was applied in our institute (Hungarian Academy of Sciences, Chemical Research Center, Institute of Materials and Environmental Chemistry) to increase the component selectivity of organosilicon gas separation membranes and the wear resistance of ultra-high molecular weight polyethylene.

The ion implantation techniques are often applied processes in the surface modification. Energy of the implanters is usually medium or high (a few hundred keV–MeV), which can be used to modify polymer surfaces. One of the biggest disadvantages of the

method is that implantation of the tools can be uniform only with moving and rotating the irregular shape objects because of the guided beam.

The plasma immersion ion implantation was particularly developed in the 1980's to modify the surface of large irregular shape metal objects. Applicability of the technique to modify polymer surfaces was earlier studied. The details of the studies can be found in one of our publications [K5] and in the dissertation. A typical example is decrease of surface electrical resistance of the polyimide, alteration of wettability of poly(tetrafluoro-ethylene) applied metal implantation, deposition of TiN-layer onto polycarbonate substrate, deposition of DLC-layer onto polyethylene surface, etc. In our institute the plasma immersion ion implantation of ultra-high molecular weight polyethylene was an important theme of a particular examination. Under these experiments the wear resistance of the polymer was raised substantially. The experimental results are applied by the Protetím Kft. in Hódmezővásárhely (Hungary) to produce enlarged life-time hip joint prostheses.

It is relevant circumstance that up to now the scientific researches in the theme dealt with studying effects of decisively high energy ions (above 50-100 keV). Furthermore it is important to mention that the specific parameters of the evolving surfaces (composition, structure, modified depth, generated physical and chemical changes) especially depend on the treatment conditions (like the substantial nature of the target and the bombarding particles, energy of particles, fluence, fluence rate, etc.) and the dominant energy transfer mechanism (electron stopping or nuclear stopping) due to the interaction. Determination of the processing parameters – structure – performance type relationships is inadequate. The reason why these are not adequate is putatively not only the fact that too many experiments are necessary because of the too many variables but the complex characterisation of the generated structure and performance changes claims numerous experiments, too.

The polymers, served as substantial system of the examinations, are not only cheaper expletives in the different kind of applications of the traditional structural materials but these provide facilities for new technical engineering applications and wind themselves into the most demanding scopes. Application of these polymers extends fast, especially in the developed countries, particularly in the machine, vehicle, instrument, electrical power and electronics industry, etc.

Development of such surface properties, which are not (or just in a small compass) typical originally of the solid materials, can open up new application facilities.

2. Aims

At the beginning of my experimental work the aim was set to study interactions of some practically important technical engineering polymers (poly(tetrafluoro-ethylene) (PTFE), poly(ethylene-terephthalate) (PET), polyamide-6 (PA), bisphenol-A-polycarbonate (PC)) and particle beams (atom and ion beams).

I was looking for answers to the following questions:

- What kind of *composition* and *chemical structure changes* take to place in the surface layer of the studied polymers under treatment by different kind of particle beams?
- What kind of changes occur under treatment by different kind of particle beams in such properties of the studied polymers like *wettability* and *surface free energy*?
- How does the *surface electrical resistance* change under treatment by particle beams?
- What kind of *mechanical* (hardness, Young modulus) and *tribological* (wear resistance) changes take to place in the surface layer of the studied polymers under treatment by different kind of particle beams?
- How do the *composition*, the *structural*, *mechanical*, *tribological*, *energetical* and *electrical properties* of the polymer surface *depend on the particle energy, fluence* and *fluence rate*?
- Is it possible to find '*processing parameter – structure – performance*' type relationships?

3. Experimental part

3.1. Materials, sample preparation

The substantial systems of the examinations were the following commercial virgin grade polymers: poly(tetrafluoro-ethylene), poly(ethylene-terephthalate), polyamide-6 and bisphenol-A-polycarbonate. The samples were treated after polishing, cleaning with ethanol in ultrasonic bath and drying in pure nitrogen gas flow.

3.2. Applied surface modification techniques

The treatments of polymers have been done by low energy (1 keV) fast atom-source (fast atom bombardment, FAB), and low and medium energy (maximum 40 keV) plasma immersion ion implantation (PIII).

The polymer surfaces were treated at the beginning by FAB 114 type saddle field cold cathode fast atom-source in pure hydrogen, helium and nitrogen gas. These treatments particularly intended to get to know the effects of the treatment gases on the polymer surfaces. The particles were accelerated by 1 kV accelerating voltage. On the grounds of the treatment time, reckoning with current of the secuder electrons, the numbers of the particles, falling into the surface layer, (fluence) was $1 \times 10^{17} \text{ cm}^{-2}$.

On the grounds of the FAB-treatments further samples were treated in plasma immersion ion implanter in nitrogen plasma. The acceleration voltage changed in the range of 15 – 30 kV, the fluence rate changed between $3 \times 10^{13} - 7 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ and the fluence varied in the interval of $1 \times 10^{17} - 3 \times 10^{17} \text{ cm}^{-2}$ after systematic experimental plan.

3.3. Applied surface investigation methods

X-ray photoelectron spectroscopy (XPS) was applied to determine the chemical composition and chemical structure of the untreated and treated polymer surfaces. The XPS spectra were referenced to the C 1s line (binding energy, BE = 285.0 eV) of the hydrocarbon type carbon.

Raman microspectroscopy was applied to determine the real thickness of the polymers treated by FAB-technic.

Static sessile drop method was applied to study the wettability of the polymer surfaces. Distilled water and diiodomethane were the test liquid during the measurements. Captures were recorded about the drops sitting on the polymer surfaces by a digital camera. Geometrical data of the drops were determined by studying the captures. Contact angles were determined on the grounds of the geometrical data.

Surface free energy and polar and dispersive component of the surface free energy were determined by Owens-Wendt calculation from contact angle data.

Comparative surface electrical resistance measurements have been done between the untreated and treated samples.

Indentations were applied on the samples. Characteristic hardness (H) and Young modulus (E) of the polymers were calculated on the grounds of the Oliver-Pharr theory.

Abrasive wear resistance was studied by multipass wear tests. Volume loss (V) values were calculated in view of the geometrical parameters of the applied indenter and the degree of the irrevocable deformations.

Adhesive tribological properties were determined by pin-on-disc method. Tests were done under dry and water-lubricated conditions at very low and high Pv (load – rotation velocity) factors.

4. New scientific results (thesis)

4.1. Thesis of surface treatment experiments by fast atom-source

1. The chemical and physical properties of the PTFE surface changed significantly under FAB-treatment applied H₂, He- and N₂ gases [K2]:
 - a) formation of fluorinated amorphous carbon like surface layer can be observed, thickness of the layers exceeded the penetration depth (calculated by SRIM-program) of particles;
 - b) average surface roughness increased; the smallest nuclear mass of the bombarding particle, the higher degree rise of the average surface roughness can be determined under FAB-treatment applied H₂, He és N₂ gases;
 - c) the reactive hydrogen and nitrogen FAB treatments increased the wear resistance of the surface layer;
 - d) water contact angles decreased on the FAB-treated surfaces, increased hydrophilic nature of the polymers remained durable.

4.2. Thesis of surface treatment experiments by plasma immersion ion implantation

2. Significant changes can be observed in the *chemical composition* and *chemical structure* of the surface layers after N-PIII treatments of PTFE, PET, PA and PC [K1, K4, K5]:
 - a) N-incorporation can be observed into the surface layer in the case of every polymer;
 - b) F-content decreased, C- and O-content increased, in agreement with these data the fluorinated degree of the C-atoms decreased in the case of the PTFE;
 - c) O/C ratio of the PET surfaces decreased, the ester groups degraded and partially changed into urethane groups;
 - d) C-content of the PA and PC decreased significantly, original amide and carbonate groups degraded and new groups appeared, so in the case of PA formation of imine, protonated amine and urethane groups, while in the case of PC formation of imine, tertiary amine and amide groups can be determined.
3. Changing processing parameters affect *contact angles* and so *hydrophobic* and *hydrophilic properties* of the surfaces, formed under treatment, which are new from the point of view of chemical composition and structure. [K1, K4, K5]:
 - a) water contact angle, under modification of PTFE surface, increased by increasing average roughness but the contact angles and hydrophobic nature decreased with

- increasing acceleration voltage and fluence rate, which can be explained by high degree N-incorporation and post-oxidation, which compensate over the effect caused by roughness;
- b) water contact angles, measured on the PA and PC surfaces, decreased, hydrophilic nature and surface free energy became stronger, which can be explained by N-incorporation and post-oxidation; the higher acceleration voltage and fluence, the stronger hydrophilic nature.
4. **Surface electrical resistance** decreased more orders of magnitude under and after N-PIII treatment. The higher acceleration voltage and fluence rate, the higher degree of decrease of surface electrical resistance. [K1, K4, K5]
5. **Wear resistance against abrasion** change under N-PIII treatment of polymers [K1, K4, K5]:
- a) wear resistance of PTFE decreased parallel with increasing O/C ratio and average surface roughness;
- b) wear resistance of PET can either decrease or increase in the studied range but operating parameter settings can be found (high acceleration voltage and high fluence), which increase substantially the wear resistance;
- c) wear resistance of PA and PC increase clearly, volume loss of PA may as well decrease to 10%, and this value can decrease to 60% in the case of PC. The higher acceleration voltage and fluence, the less volume loss.
6. It was determined, that ***H/E ratio*** of N-PIII treated PET, PA and PC are relevant to wear resistance against abrasion [K1, K5]:
- a) volume loss decreased with increase of *H/E* ratio of the PET sample;
- b) PC polymer has a characteristic *V – H/E* relationship with minimum. In the case of PA increase of *H/E* ratio can involve improving wear resistance in the interval under $H/E \approx 0.11$, while above this value volume loss increases with increase of *H/E* ratio.
7. In the case of the N-PIII treated PET it was determined, that adhesive component of the friction, combining low load with low rotation velocity, can decrease, while the value of the component increases with combining high load and high rotation velocity because of appearing sliding friction between the pin and the disc. [K3]
8. **Substantial relationships** were determined **among the different kind of parameters** under N-PIII treatment (based on a three-level fractional factorial design) of PTFE, PET, PA and PC, and after complex (surface chemical, electrical, energetical, nanomechanical and tribological,) examination of the samples [K1, K4, K5]:

a) **composition – performance type relationship** was determined in the case of PA, as the N-incorporation in little quantities decreases strongly the resistant of the surface against abrasive wear but this effect failing rapidly by incorporation of nitrogen in big quantities;

b) **chemical structure – performance type relationship** was determined in the case of the PC, as incorporation of the nitrogen in big quantities into tertiary amine type groups, evidently because of cross-linking, gradually improve resistance of the surface against abrasive wear.

It is not appropriate to increase extremely the N-content neither in the case of the PC. Because it leads to increase of N-concentration in the imine groups, which is disadvantageous from the point of view of the wear resistance;

c) **process parameter – structure – performance type relationship** was determined in the case of the PC, as N-concentration, which correlates with abrasive wear resistance, increases in the tertiary amine groups by increasing fluence and fluence rate.

5. Application of the results

On the evidence of experiments, performed with the colleagues, and the results involved in the publications and in the dissertation a patent was submitted to improve mechanical and tribological properties of oxygen and/or halogen heteroatom-containing thermoplastic technical engineering polymers. [SZ1]

The exposed information and relationships can have more common importance, as the generated chemical changes of the surface cause substantial changes in the topographical, mechanical, tribological, energetical and electrical properties. Some possible applications are mentioned below:

Increasing surface free energy of PTFE and the new information, concerning relaxation processes after treatment, can be useful to produce *vessel prosthesis*.

Strengthening hydrophobic nature can be utilized to develop *self-cleaning surfaces*.

The results concerning to decrease microabrasive wear, determined under treatment of PET by particle beams, can be applied in machine industry.

Informations, concerning to decrease of microabrasive wear, can be useful indirect to increase gas barrier capacity of PET bottles, as increase of the wear resistance can be explained by cross-linking and the gas barrier capacity of PET bottles can be assigned by cross-linking, too. Increase gas barrier capacity of the PET bottles is important in the point of view of foodpackaging.

The results, which are connected with extensive increase of microabrasive wear resistance of the PA, can be applied by so kind of area of the engineering industry,

where stresses are not too strong, but it is necessary to keep the array properties besides improvement of tribological properties of the tools.

Wear resistance of the PC, increased by particle beams, can be important to produce special optical lenses and glasses with high wear resistance.

Extensive increase of polymer surface electrical conductivity generated by particle beams can give point of reference to develop such polymer-based electronical tools like diodes, field-effect electronical instruments and tools, etc.

6. Publication list

6.1. Publications related to thesis

K1. K. Kereszturi, A. Tóth, M. Mohai, I. Bertóti, *Surface chemical and nanomechanical alterations in plasma immersion ion implanted PET*, Surf. Interface Anal. 40 (2008) 664-667.

K2. K. Kereszturi, A. Szabó, A. Tóth, G. Marosi, J. Szépvölgyi, *Surface modification of poly(tetrafluoroethylene) by saddle field fast atom beam source*, Surf. Coat. Technol. 202 (2008) 6034-6037.

K3. G. Kalácska, L. Zsidai, K. Kereszturi, M. Mohai, A. Tóth, *Sliding tribological properties of untreated and PIII-treated PETP*, Appl. Surf. Sci. 255 (2009) 5847-5850.

K4. K. Kereszturi, A. Tóth, M. Mohai, I. Bertóti, J. Szépvölgyi, *Nitrogen plasma-based ion implantation of poly(tetrafluoroethylene): Effect of the main parameters on the surface properties*, Appl. Surf. Sci. 256 (2010) 6385-6389.

K5. A. Tóth, K. Kereszturi, M. Mohai, I. Bertóti, *Plasma based ion implantation of engineering polymers*, Surf. Coat. Technol. 204 (2010) 2898-2908.

6.2. Miscellaneous publications

K6. K. Kereszturi, I. Szalai, *Briggs – Rauscher Reaction with 1,4 Cyclohexanedione Substrate*, Zeitschrift für physikalische Chemie 220 (2006) 1071-1083.

K7. K. Kereszturi, I. Szalai, *Dynamics of bromate oscillators with 1,4-cyclohexanedione in a continuously fed stirred tank reactor*, Chem. Phys. Lett. 428 (2006) 288-292.

K8. I. Bertóti, M. Mohai, K. Kereszturi, A. Tóth, E. Kálmán, *Carbon based Si- and Cr-containing thin films: Chemical and nanomechanical properties*, Solid State Sciences 11 (2009) 1788-1792.

K9. A. Tóth, **K. Kereszturi**, M. Mohai, I. Bertóti, J. Szépvölgyi, *Műanyagok plazma-alapú felületkezelése*, Műanyag- és Gumiipari Évkönyv 8 (2010) 38-45.

6.3. Presentations

E1. **K.Kereszturi**, A. Tóth, M. Mohai, I. Bertóti: *Surface modification of poly(ethylene-terephthalate) by plasma immersion ion implantation*, X. Doctoral School, Mátraháza, Hungary, May 9, 2007. (hungarian)

E2. **K. Kereszturi**, A. Tóth, M. Mohai, I. Bertóti: *Surface chemical and nanomechanical alterations in plasma immersion ion implanted PET*, Autumn School on Materials Science and Electron Microscopy 2007, Berlin, Germany, October 8-11, 2007. (english)

E3. **K. Kereszturi**, A. Tóth: *Surface modification of technical engineering polymers by fast aton-source*, HAS CRC IMEC Seminar, Budapest, Hungary, November 13, 2007. (hungarian)

E4. **K. Kereszturi**, A. Tóth, M. Mohai, I. Bertóti: *Surface modification of solide surfaces*, ELTE, Report of PhD students, Budapest, Hungary, November 17, 2007. (hungarian)

E5. **K. Kereszturi**, A. Szabó, A. Tóth, G. Marosi, J. Szépvölgyi: *Surface modification of poly(tetrafluoroethylene) by saddle field fast atom beam source*, Eight annual MML European User meeting, Madrid, Spain, October 15, 2008. (english)

E6. **K. Kereszturi**, A. Tóth, M. Mohai, J. Szépvölgyi: *Deposition of chromium-layer onto untreated and FAB-treated teflon by RF-magnetron sputtering*, VIII. Day of Materials Science for PhD students, Veszprém, Hungary, November 27, 2008. (hungarian)

E7. **K. Kereszturi**, A. Szabó, A.Tóth, Gy. Marosi, J. Szépvölgyi: *Surface modification of poly(tetrafluoro-ethylene) by saddle field fast atom-source*, Science Days of the Chemical Research Center of the Hungarian Academy of Sciences, Budapest, Hungary, December 5, 2008. (hungarian)

E8. **K. Kereszturi**: *Surface modification of technical engineering polymers by particle beams*, HAS Meeting of Comittee of Surface Chemistry and Nanostructures, presentation of the PhD thesis, Budapest, Hungary, June 19, 2009. (hungarian)

E9. **A. Tóth, K. Kereszturi**, M. Mohai, I. Bertóti: *Plasma-Based Ion Implantation of Engineering Polymers*, 10th international Workshop on Plasma-Based Ion Implantation & Deposition, São José dos Campos, São Paulo, Brazil, September 7-11, 2009.

E10. K. Kereszturi, A. Tóth, M. Mohai, I. Bertóti: *Surface modification of polyamide-6 by plasma immersion ion implantation*, VII. Hungarian Conference On Materials Science, Balatonkenese, Hungary, October 11-13, 2009. (hungarian)

E11. K. Kereszturi, A.Tóth, M. Mohai, I. Bertóti: *Surface modification of polycarbonate by plasma immersion ion implantation*, IX. Day of Materials Science for PhD students, Veszprém, Hungary, November 12, 2009. (hungarian)

E12. K. Kereszturi, A.Tóth, M. Mohai, I. Bertóti: *Plasma immersion ion implantation of common technical engineering polymers*, Science Days of the Chemical Research Center of the Hungarian Academy of Sciences, Budapest, Hungary, November 26, 2009. (hungarian)

E13. K. Kereszturi: *Surface modification of solid surfaces by particle beam techniques and surface characterisation*, HAS CRC IMEC Seminar, presentation of the PhD thesis, Budapest, Hungary, June 17, 2010. (hungarian)

6.4. Posters

P1. K. Kereszturi, A. Tóth, M. Mohai, I. Bertóti: *Surface chemical and nanomechanical alterations in plasma immersion ion implanted PET*, 12th European Conference on Applications of Surface and Interface Analysis, Brussels, Belgium, September 9 – 14, 2007.

P2. I. Bertóti, M. Mohai, A. Tóth, K. Kereszturi: *Si- and Cr-containing carbon based thin films: Chemical and nanomechanical properties*, 12th European Conference on Applications of Surface and Interface Analysis, Brussels, Belgium, September 9-14, 2007.

P3. K. Kereszturi, A. Tóth, M. Mohai, I. Bertóti: *Surface characterisation of PTFE, modified by designed experiments of nitrogen plasma immersion ion implantation*, 13th European Conference on Applications of Surface and Interface Analysis, Antalya, Turkey, October 18-23, 2009.

6.5. Patent

SZ1. A. Tóth, K. Kereszturi, M. Mohai, I. Bertóti, J. Szépvölgyi, G. Kalácska: *Process to improve mechanical and tribological properties of oxygen and/or halogen heteroatom-containing thermoplastic technical engineering polymers*, PCT/HU2008/00012, February 5, 2008.

Hungarian patent announcement P 07 00129, February 6, 2007.