

# Experimental investigation of plasma-immersion ion implantation treatment for biocompatible polyurethane implants production

R I Iziumov, AY Beliaev<sup>1</sup>, I V Kondyurina<sup>2</sup>, I N Shardakov<sup>1</sup>, A V Kondyurin<sup>3</sup>, M M Bilek<sup>3</sup> and D R McKenzie<sup>3</sup>

<sup>1</sup>Institute of Continuous Media Mechanics UB RAS, Perm, Russia

<sup>2</sup>School of Medicine, University of Sydney, Sydney, Australia

<sup>3</sup>School of Physics, University of Sydney, Sydney, Australia

E-mail: [izumov@icmm.ru](mailto:izumov@icmm.ru)

**Abstract.** Modification of the surface layer of polyurethane with plasma-immersion ion implantation (PIII) and studying its physical and chemical changes have been discussed in this paper. The goal of the research was to obtain carbonized layer allowing creating biocompatible polyurethane implants. The experiments of PIII treatment in various modes were performed. The investigation of the modified surface characteristics was carried out by observing the kinetics of free surface energy for two weeks after treatment. The regularities between treatment time and the level of free surface energy were detected. The explanation of high energy level was given through the appearance of free radicals in the surface layer of material. The confirmation of the chemical activation of the polyurethane surface after PIII treatment was obtained.

## 1. Introduction

The necessity of restoring or substitution the damaged human tissues by artificial device produced using different polymers or metal alloys, has determined the development of a separate section of modern medicine – the implantology.

The main purpose of such type of surgery is to restore lost characteristics and properties of tissue or, if possible, its improvement. The most important requirements to the characteristics of the implantable material are biocompatibility, mechanical properties (strength, elasticity or hardness, coefficient of friction, durability), chemical properties (corrosion resistance, the absence of toxic emissions), the weight and the economic aspect [1]. Nowadays many research groups are carried out investigations aimed at studying the possibility of applying polymer materials in medicine (food grade polypropylene (Anulon-92) [2], polystyrene [3], polymethylpentene [4, 5], polyethylene [6, 7], polyethylene terephthalate (PET) [8], thermo-plastic polyurethane (Elastollan® 1180A50) [9], polyhydroxybutyrate (PHB), poly-L-lactic acid (PLLA) [10, 11], polytetrafluoroethylene (PTFE) [12], biodegradable polymer [13]). Polymeric materials are becoming more popular due to the fact that it satisfies almost all specified requirements [14-16]. Its surface may provide immobilization of biologically active molecules and living cells, however, this quality requires significant improvements [17,18]. Rational way to solve this problem is to develop a technique of treatment the outer layer, modifying it so that it becomes a safe, friendly, biocompatible capsule for the body and the inner part of the implant would have the rest of the required parameters.



Among a number of ways to modify the surface (chemical exposure, temperature processing, the corona discharge, ultraviolet irradiation [19, 20]), one of the most promising areas of research is also the use of plasma-immersion ion implantation (PIII). With this technology, it is possible to create on the material surface the layer having the property of biocompatibility; moreover the process itself is clean and leaves no traces on the surface of by-products. Also, comparing with other conventional techniques, PIII advantage consists in the ability to precisely control the surface modification, regardless of its geometry [21].

In numerous papers related to the study the possibilities of PIII technology, it is shown that the structure and surface chemical properties of the treated polymer are dependent on the gas from which the plasma is generated, and the time and intensity of treatment. It is considered the application of the following gases and its mixtures: helium [22], nitrogen [8], oxygen, argon and argon + oxygen mixture [23]. There is often the interest to analyse the influence of the experimental parameters within some range (the pressure of the plasma, gas flow, power, time of treatment). In our experiments we performed the treatment in the nitrogen plasma with ion energy of 20keV. Treatment time was varied from 80 to 800 seconds that corresponds to  $5 \cdot 10^{14} - 10^{16}$  ions/cm<sup>2</sup>.

To analyse the effect of ion-plasma treatment on the surface of the material it is often used a combination of several methods of experimental studies such as optical microscopy [3], atomic force microscopy (AFM) [2, 4], scanning electron microscopy (SEM) [2, 3], x-ray photoelectron spectroscopy (XPS) [3, 4], infrared spectroscopy (FTIR) [2], the study of the surface energy by measuring the contact angle [2, 4], tensile test [2], thermal analysis (Differential Scanning Calorimetry TA) [2], spectrophotometry [2], Rutherford backscattering spectroscopy (RBS) [4], electrokinetic analysis [4], goniometry [4], ablation of PMP surface layers determined by gravimetry [4]. For biocompatibility study experiments with mouse embryonic fibroblasts [2, 6], human osteosarcoma cells [3] and human blood (haemolytic potential, thrombogenicity) [2, 8] are performed. In our work, we have applied the analysis of the kinetics of the surface energy, including its polar and dispersive components, as a function of the past time after treatment; in addition we plan to take advantage of XPS and infrared spectroscopy.

The above studies have shown that, depending on the purpose, in one case, ion-plasma treatment can dramatically increase the number of adhered cells or bioactive molecules as well as positively affect the uniform distribution of cells on the surface of the material and their viability. In another case, decrease of platelet adhesion is confirmed that causes the improvement of the blood compatibility.

## 2. Materials and methods

### 2.1. PIII treatment of PU samples

For the treatment on PIII device we used the samples of size  $1 \times 2$  cm<sup>2</sup>. Experimental investigations include set of PIII-treatments of polyurethane samples for 40, 80, 400 and 800 s (corresponding to an ion fluency of  $5 \cdot 10^{14}$ ,  $10^{15}$ ,  $5 \cdot 10^{15}$ ,  $10^{16}$  ions/cm<sup>2</sup>). The source of ions was inductively coupled radio-frequency nitrogen plasma powered at 13.56 MHz. The nitrogen gas used for PIII was 99.99% pure. The plasma power was 100W with reverse power of 12W when matched. The plasma density during treatment was monitored by a Langmuir probe with rf-block from Hiden Analytical Ltd. The base pressure was  $10^{-6}$ Torr ( $\sim 10^{-4}$  Pa); the pressure of nitrogen during implantation was  $2 \cdot 10^{-3}$ Torr ( $\sim 4.4 \cdot 10^{-2}$  Pa).

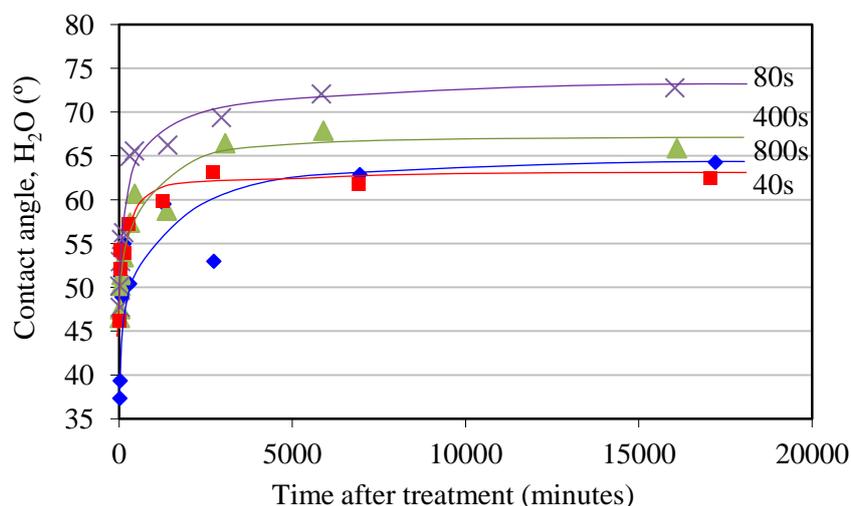
The samples were treated in plasma chamber by ion beam, which was extracted from plasma by the application of high voltage (20kV) at a frequency of 50Hz with duration of pulses of 20 $\mu$ s. The polyurethane samples were placed on a holder with a mesh. The mesh was electrically connected to the holder and held in front of the sample on the distance of 5 cm.

### 2.2. Contact angles and surface free energy

The contact angles of two liquids (de-ionized water and diiodomethane) on the surface of PU were measured by contact angle analyzer Kruss DS10 based on the sessile drop technique. For calculating the surface free energy and its polar and dispersive components the Rabel model with regression method was used. There was a set of 11 measurements of 5 drops of each liquid per sample. After ion-plasma treatment the kinetics was being monitored during 2 weeks (20, 30, 40 minutes, 1, 2, 5, 7, 23 hours, 2, 4, 11 days after treatment).

### 3. Results

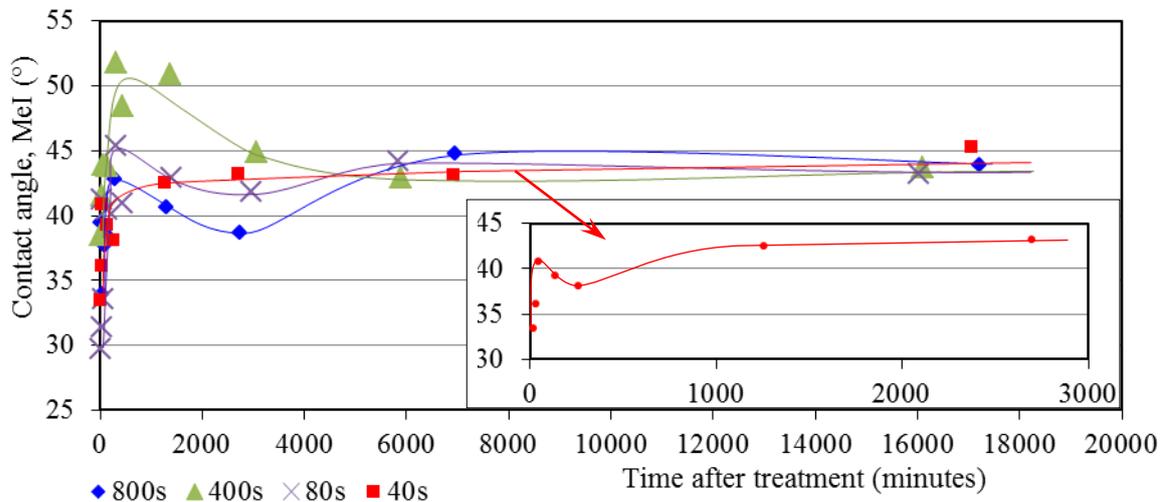
The first contact angle measurement was carried out immediately after extracting the sample from the PIII device, which process included injection of air into a vacuum chamber and took 20 minutes. The obtained data showed an inverse dependence between the values of contact angles of water and treatment time. The contact angle for the sample treated for 40 seconds was equal to  $48 \pm 2^\circ$ , for 80 seconds:  $47 \pm 1.5^\circ$ , for 400 seconds:  $45 \pm 0.9^\circ$ , for 800 seconds:  $38 \pm 0.4^\circ$ . After 2 weeks the contact angle has increased and reached a stable value. For the sample treated for 40 seconds, the contact angle became equal to  $63 \pm 2.3^\circ$ , for 80 seconds:  $73 \pm 1.7^\circ$ , for 400 seconds:  $66 \pm 1.3^\circ$ , for 800 seconds:  $64 \pm 1.4^\circ$  (figure 1).



**Figure 1.** Kinetics of water contact angle after treatment samples in 4 modes of PIII

In this case, the correlation between the treatment time and the contact angle remained only for three treatment modes (80, 400, 800 seconds). The sample treated over the shorter time of 40 seconds, has showed the lowest value of the contact angle, standing out from the overall trend.

Kinetics of diiodomethane contact angle was significantly different from water and it was nonmonotonic. Although as in the case of water the treatment also decreased the contact angle but to a lesser degree. The correlation between the angle and the plasma treatment time is not observed, and after two weeks after treatment the contact angle has reached the level of  $44 \pm 0.5^\circ$  for all the samples, regardless of treatment time (figure2).



**Figure 2.** Kinetics of diiodomethane contact angle after PIII treatment during two weeks

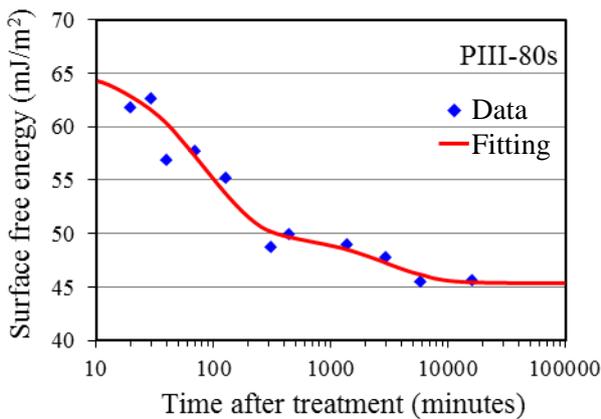
The dependence between the total free energy and the treatment time has the correlation similar to the dependence of water contact angle. After 2 weeks for 3 PIII modes there was a direct dependence between the treatment time and energy value: the sample treated for 80 seconds had 45.5 mJ/m<sup>2</sup>, for 400 seconds: 48 mJ/m<sup>2</sup>, for 800 seconds: 49.5 mJ/m<sup>2</sup>. But the treatment during 40 seconds gave the highest value: 50.5 mJ/m<sup>2</sup>.

Analysis of the experimental data was carried out by approximation (figure3) using a function (equation (1)) represented as a sum of two exponential functions:

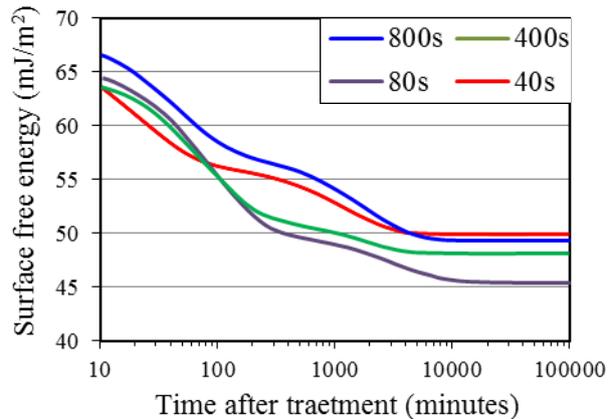
$$f(t) = a_0 + a_1 \exp(-t / k_1) + a_2 \exp(-t / k_2) \quad (1)$$

where  $f$  is a total free energy;  $t$  is time after PIII treatment;  $k_1$  and  $k_2$  are the rate constants of the two characteristic stages;  $a_0$ ,  $a_1$  and  $a_2$  are the constants to be defined.

The effectiveness of such method of approximation was demonstrated in [24], in which the observed phenomenon is qualitatively similar.



**Figure 3.** Example of data and its fitting



**Figure 4.** Kinetics of total surface free energy

Analysis of the kinetics of the surface free energy (figure4) revealed that after PIII treatment of PU two characteristic relaxation processes appeared, the first of which was predominant over the second one, but faded rapidly, after which only the second process occurred. This is confirmed by the fact that the characteristic time for the first process ( $k_1$ ) although has a large spread (from 24.3 to 45 min) but

comparing to the second one ( $k_2$  varies from 1258.5 to 3177.8 min) has significantly (by two orders of magnitude) smaller value (Table 1).

**Table 1.** The constants of fitting function and its values in limiting cases for total surface free energy

Time of treatment, s	$f(0)$ , mJ/m <sup>2</sup>	$f(\infty)$ , mJ/m <sup>2</sup>	$k_1$ , min	$k_2$ , min
40	67±1.1	50±0.7	24.3±5.3	1258.5±438.3
80	65.5±0.9	45.5±0.5	89.9±14.3	3177.8±1805.9
400	65±0.5	48±0.2	80.5±9.6	1638.6±841.7
800	66±1.2	49.5±0.5	45±10.8	1789.9±815.2

Extrapolation of the data allows determining the value of free energy at the time immediately after treatment,  $f(0)$  (Table 1). This value is essentially independent of the treatment time and equals 66±1 mJ/m<sup>2</sup>. Similar way we determined the level, which energy reached at the expiration of arbitrarily large period of time,  $f(\infty)$ . It is equal to 50.5, 45.5, 48, 49.5 mJ/m<sup>2</sup>, respectively for 40, 80, 400, 800 seconds of treatment.

The qualitative behavior of the total energy is caused by polar component, because a dispersive component remains during two weeks practically constant. Its value was inside the range of 40±5 mJ/m<sup>2</sup> and had no dependence on the treatment time.

Polar component after 2 weeks decreased significantly (by 35-55%). Moreover, there was a direct correlation between the reduction of energy and the PIII mode: for the sample treated for 40 seconds, reduction was 35% (from 20 to 13 mJ/m<sup>2</sup>) for 80 and 400 seconds: 53% (8 to 17 mJ/m<sup>2</sup> and from 21 to 10 mJ/m<sup>2</sup>, respectively) for 800 seconds: 55% (from 26 to 12 mJ/m<sup>2</sup>).

After 2 weeks remaining values of polar components were 3, 8, 10, 12 mJ/m<sup>2</sup>, respectively for 40, 80, 400, 800 sec. Thus, we can trace the situation similar to total free energy, where the 40 seconds treatment is out from the overall trend (Table 2).

**Table 2.** The constants of fitting function and its values in limiting cases for polar component of the surface free energy

Time of treatment, s	$f^p(0)$ , mJ/m <sup>2</sup>	$f^p(\infty)$ , mJ/m <sup>2</sup>	$k_1^p$ , min	$k_2^p$ , min
40	24±0.4	13±1.1	20±4.8	767±388.1
80	20.5±0.3	7.5±0.5	107±21.2	3121±1265.3
400	23±0.8	10±0.7	42.9±16.8	2224±574.5
800	28±0.5	12±1.3	43.8±16.9	5494.2±4559.4

#### 4. Conclusion

In this work the investigation of polyurethane modification to create chemically active surface layer in material was performed. By monitoring the kinetics of surface free energy and its polar and the dispersive components it was established that treatment of the material leads to significant and irreversible changes in the surface layer. It results in a sharp increase of the surface energy after PIII treatment and preserving its sufficiently high, in comparison with untreated PU, level that reflects significant chemical changes on the surface of polymers. At the same time, such a considerable increase of energy (up to a level of about 67 mJ/m<sup>2</sup>) and behavior of its polar and dispersive components can be attributed to only the appearance of free radicals in the material, which in turn makes it possible to add, using existing techniques, to polyurethane the property of biocompatibility. Using a level  $f(\infty)$ , which is reached by energy after a sufficiently long period of time, as a criterion of selecting a treatment mode, we can make the assumption that among all variants of treatment the briefest one (40s) may be the most preferable for us by the fact that stored energy and, therefore, the concentration of free radicals onto the surface has the highest level among all the considered variants.

At this stage of research it can be claimed that the application of PIII technology has enabled to activate surface layer of polyurethane that offers the prospect of further modification of the surface to the level of biocompatibility.

## 5. Acknowledgements

The work was supported by the Russian Foundation for Basic Research (grant 13-01-96009\_r\_ural\_a and grant 14-08-96003\_r\_ural\_a) and the Ministry of Education of Perm Region under agreement (S-26/632).

## 6. References

- [1] Gomathi N, Sureshkumar A and Neogi S 2008 *Curr. Sci.* **94** 1478–1486.
- [2] Gomathi N, Rajasekar R, Babu R, Mishra D and Neogi S 2012 *Mat. Sci. and Eng. C* **32** (7) 1767
- [3] Recek N, Mozetič M, Jaganjac M, Milkovič L, Žarković N and Vesel A 2013 *Vacuum* **98** 116
- [4] Slepíčka P, Trostová S, Slepíčková Kasálková N, Kolská Z, Malinský P, Macková A, Bačáková L and Švorčík V 2012 *Polymer Degradation and Stability* **97** 1075
- [5] Michaljaničová I, Slepíčka P, Slepíčková Kasálková N, Sajdl P and Švorčík V 2014 *Vacuum* **107** 184
- [6] Rimpelová S, Slepíčková Kasálková N, Slepíčka P, Lemerová H, Švorčík V and Ruml T 2013 *Mat. Sci. and Eng. C* **33** 1116
- [7] Kondyurin A, Naseri P, Fisher K, McKenzie D R and Bilek M M 2009 *Polymer Degradation and Stability* **94** 638
- [8] Junkar I 2013 *Vacuum* **98** 111
- [9] Alves P, Cardoso R, Correia T R, Antunes B P, Correia I J and Ferreira P 2014 *Colloids and Surfaces B* **113** 25
- [10] Slepíčková Kasálková N, Slepíčka P, Bačáková L, Sajdl P and Švorčík V 2013 *Nuclear Instruments and Methods in Physics Research Section B* **307** 642
- [11] Slepíčka P, Trostová S, Slepíčková Kasálková N, Kolská Z, Sajdl P and Švorčík V 2012 *Plasma Processes Polym.* **9** 197
- [12] Rezníková A, Kolská Z, Hnatowicz V, Stopka P and Švorčík V 2011 *Nucl. Instr. Meth. B* **269** 83
- [13] Morent R, De Geyer N, Desmet T, Dubruel P and Leys C 2011 *Plasma Processes Polym.* **8** 171
- [14] Silva E A and Mooney D J 2004 *Current Topics in Developmental Biology* **64** 181
- [15] Shin H, Jo S and Mikos A G 2003 *Biomaterials* **24** 4353
- [16] Ma Z, Kotaki M, Yong T, He W and Ramakrishna S 2005 *Biomaterials* **26** 2527
- [17] Küttel O M, Martinu L, Poitras D, Klemberg-Sapieha J E and Wertheimer M R 1992 *Materials Science and Engineering B – Advance* 321
- [18] Aflori M, Drobotă M, Timpu D and Barboiu V 2008 *Journal of Optoelectronics and Advanced Materials* **2** 291
- [19] Behnisch J, Hollander A and Zimmermann H 1993 *Surf. Coat. Technol.* **59** 356
- [20] Mirabedini S M, Rahimi H, Hamedifar S and Mohseni M 2004 *Int. J. Adhes.* **24** 163
- [21] Boenig H V 1882 *Plasma Science and Technology*, Cornell University Press, Ithaca, New York
- [22] Aflori M, Drobotă M, Dimitriu D, Stoica I, Simionescu B and Harabagiu V 2013 *Mat. Sci. and Eng. B* **178** 1303
- [23] Chen Y, Gao Q, Wan H, Yi J, Wei Y and Liu P 2013 *Applied Surface Science* **265** 452
- [24] Kosobrodova E, Kondyurin A, McKenzie D R and Bilek M M M 2013 *Nuclear Instruments and Methods in Physics Research B* **304** 57