Influence of ECR-RF plasma modification on surface and thermal properties of polyester copolymer

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In this paper we report a study on influence of radio-frequency (RF) plasma induced with electron cyclotron resonance (ECR) on multiblock copolymer containing butylene terephthalate hard segments (PBT) and butylene dilinoleate (BDLA) soft segments. The changes in thermal properties were studied by DSC. The changes in wettability of PBT-BDLA surfaces were studied by water contact angle (WCA). We found that ECR-RF plasma surface treatment for 60 s led to decrease of WCA, while prolonged exposure of plasma led to increase of WCA after N_2 and N_2O_2 treatment up to 70°–80°. The O_2 reduced the WCA to 50°–56°. IR measurements confirmed that the N_2O_2 plasma led to formation of polar groups. SEM investigations showed that plasma treatment led to minor surfaces changes. Collectively, plasma treatment, especially O_2, induced surface hydrophilicity what could be beneficial for increased cell adhesion in future biomedical applications of these materials.

Keywords: fatty acid, copolymers, water contact angle, differential scanning calorimetry, scanning electron microscopy.

INTRODUCTION

Plasma modification is used in many different technological processes for improving physical and/or chemical properties of material surface. Usually, plasma modification can be used for adhesion changes, improvement of hydrophilic or hydrophobic properties or immobilization of molecules on the material surface. Plasma deposition, plasma implantation or plasma polymerization are only few of many known plasma applications[1–5]. Plasma surface modification is well known and widely used, especially in bioengineering applications like improving of membrane separation or regeneration[6], avoiding biofouling[7], for proteins separation[8] or for tissue engineering[9–11].

Surface characteristics play a vital role in the functioning of different biomaterials since they are directly influencing biological response. The key physical properties of a biomaterial can be retained while only the outermost surface is modified to tailor the biointeractions. Hence, if surface modification is properly carried out, the mechanical properties and functionality of the device will be unaffected, but the tissue interface-related biocompatibility can be improved[12].

To follow this direction, we used plasma method for surface treatment of poly(aliphatic/aromatic-ester)s (PED). PED copolymers are composed of semicrystalline poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT) hard segments and amorphous fatty acid, e.g. dimerized linoleic acid (DLA) sequences as soft segment components. These materials have already shown excellent biocompatibility *in vitro* and *in vivo*[13–16]. PED copolymers are relatively hydrophobic materials due to the presence of long aliphatic fatty acid sequences in soft segments. Moreover, short sequences of butylene terephthalate (PBT) result in low surface free energy and also poor wettability. Such hydrophobic character of a polymer can be a limitation for tissue engineering applications because it can lead to a low initial cell seeding density, and slow cell growth due to insufficient adsorption of cell culture medium and

lack of specific cell-material interactions[17, 18]. Therefore, great challenge is hydrophilization of PED copolymer surface for advanced applications in tissue engineering. Hence, basic process parameters for successful surface modification and type of gas plasma for new material should be selected. It is already known, for example, that oxygen[19] and nitrogen[20] containing plasma has been shown to increase endothelial cell attachment.

In this paper, the type of gaseous plasma and treatment time are evaluated for plasma-PED material interactions, including surface wettability, surface morphology, and thermal properties.

MATERIAL

Multiblock poly(aliphatic/aromatic–ester)s containing hard segments of poly(butylene terephthalate) (PBT) and soft segments of butylene ester of dimerized fatty acid (BDLA) were prepared using dimethyl terephthalate (DMT, ZWCh "ELANA"), 1,4-butanediol (1,4-BD, BASF), magnesium titanate catalyst and dimerized fatty acid (dilinoleic acid, DLA – Croda, the Netherlands). Details about preparation of the materials can be found in[13]. Multiblock copolymer, here abbreviated as PBT-BDLA, containing 26 wt% hard segment and 74 wt% soft segments was prepared and used for plasma modification. Polymer, at such hard to soft segments content, is flexible and transparent material (tensile strength: 3,6 MPa, elongation at break: 770%[14, 15]. Chemical structure of PBT-BDLA copolymer is presented in Figure 1.
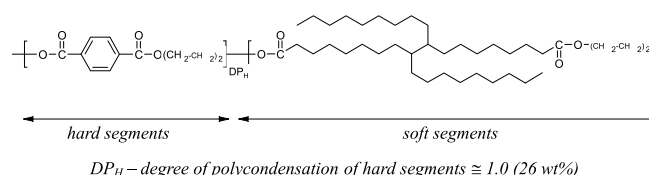

DP_H – degree of polycondensation of hard segments $\cong$ 1.0 (26 wt%)

Figure 1. Chemical structure of multiblock poly(butylene terephthalate-co-butylene dilinoleate)(PBT-BDLA)

Methods

Polymeric samples in form of thin foils (0.5 mm thick, the thickness typical for physical and mechanical testing) prepared by hot press melting between teflon plates at a temperature 10° higher than the melting point of a polymer were exposed to low–pressure plasma using PECVD apparatus (Roth&Rau, Germany). Used equipment allowed generation of radio-frequency (RF) plasma induced with electron cyclotron resonance (ECR).

All tests were performed at frequency of 13 MHz. The intensity of the RF – plasma was set to 300 W, bias values between 200–300 V and pressure in range of $1.74–2.32 \times 10^{-3}$ mbar.

Under these conditions, surface modification of copolymer was carried-out using different gas atmospheres as oxygen (O_2), nitrogen (N_2) and nitrogen/oxygen (70% N_2, 30% O_2, here abbreviated as N_2O_2). The gas flux was set to 60 cm^3/min. The treatment time varied between 60 and 180 seconds. Samples were cleaned with 70% ethanol and then vacuum dried at 40°C for 2 hours before plasma treatment.

Contact angle measurements were performed with Data Physics OCAH230 apparatus using sessile drop method.

Samples of the neat copolymer and after exposure to different plasma were characterized by Fourier transform attenuated total reflection infrared spectroscopy (ATR-FTIR). Spectra were obtained using the Bruker Vertex70 Fourier Transform Infrared Spectrometer scanning between 600 and 4000 cm^{-1}.

Differential scanning calorimetry (DSC) scans were performed with a TA Instruments (DSC Q100) apparatus. The samples were dried in vacuum at 70°C, and then kept in a desiccator. The process was carried out in a triple cycle: first heating, then cooling, and second heating in the temperature range from –120°C to 30°C higher than melting point of each copolymer. The rate of heating and cooling was 10°C min^{-1}. The glass transition temperature (T_g) was determined from the temperature diagrams as the mid point on the curve inflection.

Scanning electron microscope (SEM) JEOL JSM-840A was used to study surface topography before and after plasma treatment.

RESULTS AND DISCUSSION

It is already known that the plasma treatment affects only the utmost layer of the surface therefore it is not an easy task to observe surface chemical modification by FT IR analysis. However, in the case of heavy surface oxidation (loss of electrons) of polymers their infrared spectra may present some new characteristics. Figure 2 shows FTIR spectrum of the neat copolymer. Two characteristic peaks from carbonyl group C=O (a strong signal at 1740 cm^{-1}) and the signals at 1300 and 1099 cm^{-1} ascribed to stretching vibrations of the C-O bonds coupled with an aromatic ring can be detected thus confirming the formation of ethylene terephthalate units and the presence of hydroxyl-ended chains containing aliphatic/aromatic ester.

The comparison of FT-IR spectra for the neat sample (without plasma modification) and materials after plasma treatment showed any noticeable changes in chemical composition, independently of used gas atmosphere. The
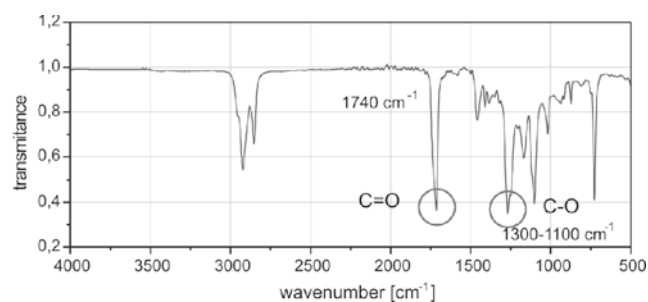

Figure 2. ATR FT-IR spectra of PBT-BDLA multiblock copolymer before plasma treatment

only exception was sample after N_2O_2 modification for 60 s (Figure 3) because of slightly broadened peak appearing at 3300 cm^{-1} which corresponds to an increase in the hydroxyl groups (–OH stretching at 3380 cm^{-1}) formed during plasma treatment. These changes can also be ascribed to secondary amine groups (N-H stretch at 3400 cm^{-1}). It is difficult, however, to determine the exact type of nitrogen functional groups, since there is a problem with strong overlapping of oxygen- and nitrogen- containing functionalities. Similar changes after nitrogen plasma treated of PET films were observed by Vesel et al.[19].
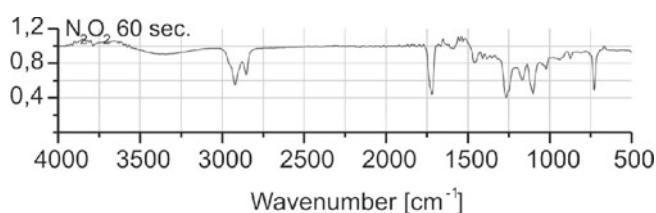

Figure 3. ATR FT-IR spectra of the PBT-BDLA material after N_2O_2 plasma treatment for 60 s

PBT-BDLA multiblock copolymer, which consists of high amount of soft segments (74 wt.%) is hydrophobic and therefore relatively high average dynamic contact angles versus water were found for this material, i.e. about 90° (Table 1).

Table 1. Water contact angle of PBT-DLA material after treatment with different gas plasma

Plasma/ time	60 s	90 s	120 s	180 s
	Water contact angle [°]			
Non-modified	90			
N_2O_2	45	66	69	71
O_2	50	51	53	56
N_2	60	58	70	84

Water contact angles (CA) are important macroscopic parameters characterizing surface wettability. Strong decrease of CA-values was observed for almost all kind of gas atmosphere and modification time. However, the lowest values of CA were found after 60 s treatment. With prolonged exposure time, the surface become again more hydrophobic as indicated by increasing water contact angle values, especially for N_2O_2 and N_2 atmosphere. Functional groups formed on the plasma-treated surface are not stable with time, as the surface tends to recover to its untreated state. Thus, the surface loses its hydrophilic character and becomes hydrophobic. The lowest values of water contact angle, and almost constant for the whole treatment time (180 s) were found for samples treated with O_2 (Fig. 4). It seems that oxygen plasma

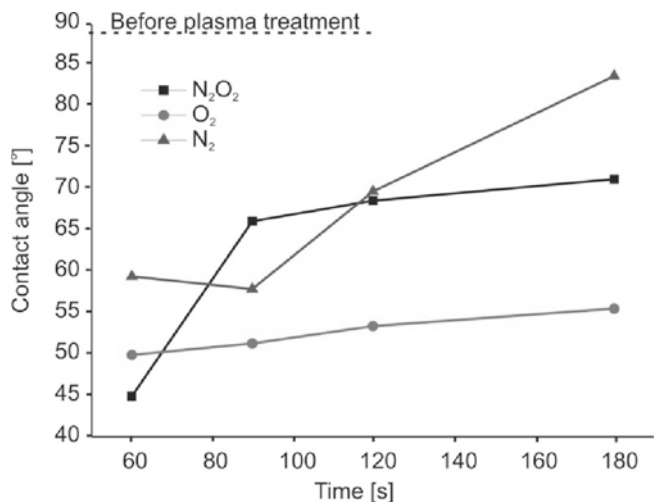imparts the best and the most stable hydrophilicity to PBT-BDLA surface.

Figure 4. Water contact angle changes *versus* treatment time

It should be mentioned that relatively stable increase of surface hydrophilicity after oxygen plasma modification as determined by the water contact angle measurements is due to a "saturation" of a surface with highly hydrophilic groups such as carbonyl or hydroxyl (–COOH, –OH)[6] rather than with more hydrophobic groups such as amide which are regarded as compounds with low water solubility. Therefore, polymer surface treatment

with N_2 and N_2O_2 shows increasing CA with increasing treatment time, especially for N_2O_2 where FT-IR spectra clearly indicated new bond formation (Fig. 3).

In case of oxygen plasma surface modification, the modification time was quite long and could be reduced down to 10–50 s. Similar conclusions are given by Cioffi et al.[21] They showed that modification time longer than 20 s at 50 W intensity do not have any influence on contact angle value and longer time of modification do not cause further reduction of contact angle.

The effect of the plasma treatment on the surface properties was studied also with SEM (Fig. 5). As can be seen from Figure 5a, reference material (the neat PBT-BDLA copolymer) shows flat surface with some impurities on it. Despite of these impurities, PBT-BDLA copolymer after N_2O_2 plasma shows slightly crimped surface. Polymer surface topography after O_2 (Fig. 5c) and N_2 (Fig. 5d) treatment shows rather flat and smooth surface (some cracks are visible on Figure 5c but these are probably from the Teflon mould used for film preparation). However, they can also come from local stresses induced by the plasma.

Table 2 summarizes the thermal properties of PBT-BDLA material. The glass transition temperature, T_g, of soft segments is relatively low (–51.1°C) and is shifted toward higher temperatures after plasma treatment (up to –33°C after N_2 and O_2 treatment). It is also interesting to notice that melting point ascribed to hard segments,
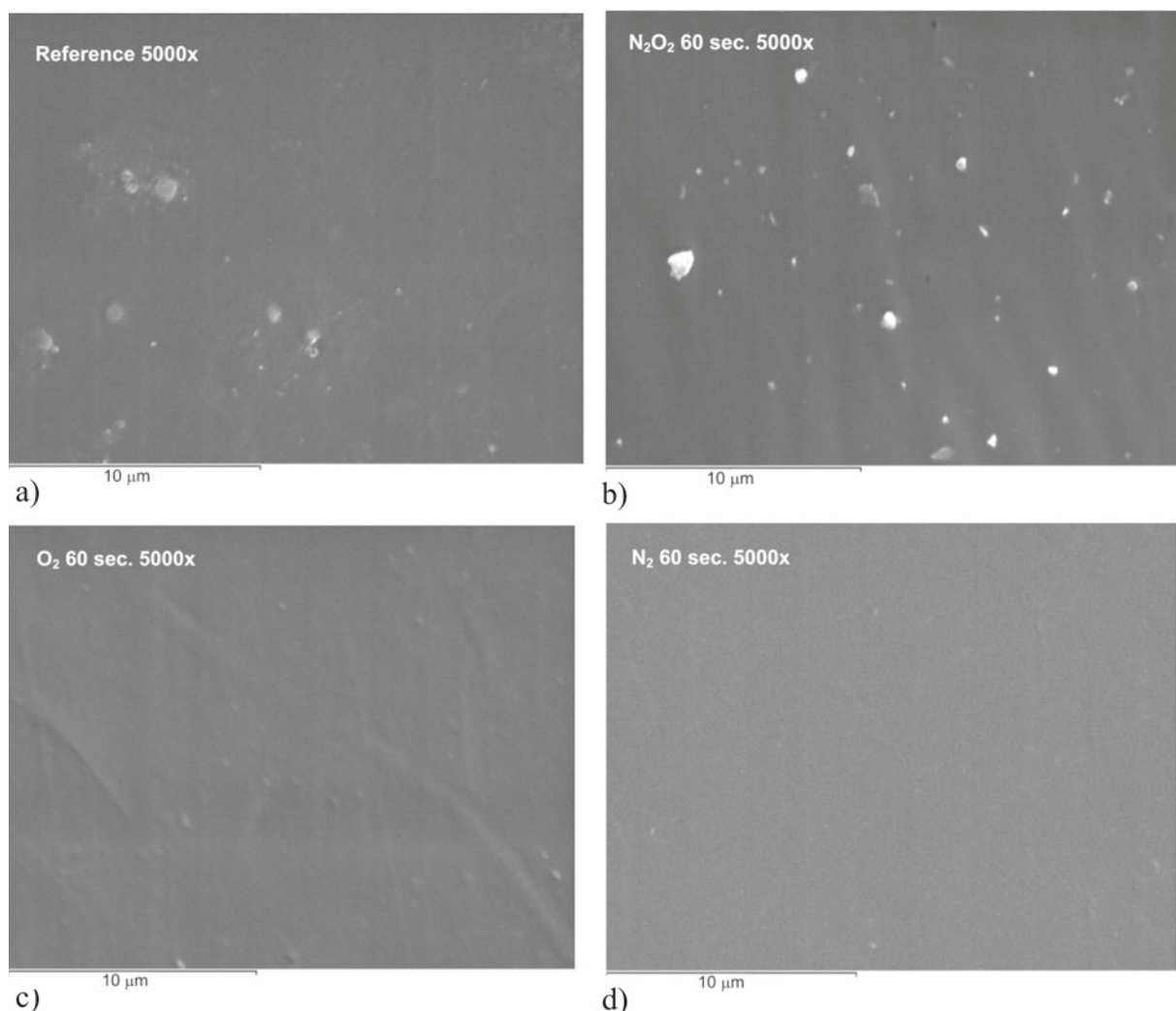

Figure 5. SEM pictures of non-modified material (a), after N_2O_2 (b), O_2 (c) and N_2 (d) plasma treatment for 60 s

T_m, is slightly increased for all materials from 117.9°C for the neat material up to 123.6°C after N_2O_2, 121.4°C after O_2 and 119.5°C after N_2 plasma treatment. These changes were observed after 60 s plasma exposure. However, after longer exposition time, namely 180 s, melting point decreases to almost initial (for not treated surface) value, with the exception of a material after O_2 treatment (increase of T_m to 126°C after 180 s exposure). Decrease of the difference between the glass transition temperature and melting temperature after plasma treatment is also indicating that microphase separation is also decreasing. It is worth to mention that PED copolymers have a microphase separated morphology similar to segmented poly(urethane-ester/ether/carbonate)s widely used in medical applications[22–23]. Microphase separated structure is an effect of thermodynamical incompatibility of soft and hard segments which results is microheterohenous structure stabilized by nanostructured rigid (crystalline) domains embedded in a soft (amorphous) matrix. While microphase separation decreases, longer hard (PBT) segments and more random structure is formed. Importantly, microheterogenous structure results in different hard and soft segments properties (hydrophilic and hydrophobic), which is case of segmented polyurethanes results in excellent blood compatibility due to regulation of protein absorption on material surface: albumin specifically adsorbs to hydrophilic domains (ester/ether/carbonate), while gamma-globulin adsorbs to hydrophobic (urethane) domains[24].

The analysis of crystallization temperature revealed a strong shift from 11.2°C for the untreated material up to 57.5°C for N_2O_2 plasma treated surface for 60 s. The crystallization enthalpy is also consequently decreased from 8.06 J/g up to 2.00 J/g. The observed changes indicated that for this particular exposure time and type of used plasma the bulk material properties were changed as already demonstrated by FT-IR spectra. It should also be noticed, that degree of crystallinity, w_c, calculated from the melting enthalpy of respective polymer divided by the melting enthalpy of 100% crystalline PBT (which is 140 J/g according[25]) decreases in all cases after plasma treatment (last column in Table 2).

CONCLUSIONS

In this paper, the results of low temperature plasma treatment of multiblock poly(aliphatic/aromatic–ester) copolymer composed of hard segments of butylene terephthalate and soft segments of butylene dilinoleate are presented. The surface of copolymer was modified using different types of gas plasma (O_2, N_2, N_2O_2) at different modification time. ATR-FTIR analysis showed no significant changes in chemical composition of the samples after plasma treatment with the only exception for N_2O_2 treatment for 60 s which led to polar groups formation. Plasma modification with different gas atmospheres is effective enough to change surface wettability. It allowed reducing contact angle from 90° down to 45°. We found that the surface energy (expressed by the water contact angle) achieved by N_2 and N_2O_2 plasma treatment was not stable. Only for O_2 plasma, a permanent changes on surface energy were observed. Plasma treatment also affected the microphase separation thus decreasing the difference between glass transition temperature of soft segments and meting temperature of hard segments. An investigated PBT-BDLA copolymer thus can be modified preferentially with oxygen plasma to obtain stable hydrophilization of polymer surface.

LITERATURE CITED

1. Huang, Y., Tian, X., Yang, S., Fu, R.K.Y. & Chu, P.K. (2007). Optical and mechanical properties of alumina films fabricated on Kapton polymer by plasma immersion ion implantation and deposition using different biases. *Appl. Surf. Sci.* 253, 9483–9488. DOI: 10.1016/j.apsusc.2007.06.011.
2. Singh, N.L., Qureshi, A., Rakshit, A.K., Mukherjee, S., Tripathi, A. & Avasthi, D.K. (2007). Surface modification of polymeric blends by nitrogen plasma immersion ion implantation. *Surf. Coat. Technol.*, 201, 8278–8281, DOI: 10.1016/j.surfcoat.2006.10.059.
3. Liu, X., Fu R.K.Y., Ding, Ch. & Chu, P.K. (2007). Hydrogen plasma surface activation of silicon for biomedical applications. *Biomolec. Engine.,* 24, 113–117. DOI: 10.1016/j.bioeng.2006.05.006.
4. Maitz, M.F., Poon, R.W.Y., Liu, X.Y., Pham, M.T., Chu, P.K. (2005). Bioactivity of titanium following sodium plasma immersion ion implantation and deposition. *Biomaterials* 26, 5465–5473. DOI: 10.1016/j.biomaterials.2005.02.006
5. Gancarz, I., Bryjak, J., Bryjak, M., Tylus, W. & Poźniak, G. (2006). Poly(phenylene oxide) films modified with allylamine plasma as a support for invertase immobilization. *Eur. Polym. J.* 42, 2430–2440. DOI: DOI:10.1016/j.eurpolymj.2006.07.008.
6. Wang, X., Tian, Y., Wang, Z. & Tao, Y. (2010). A novel hydrophilic modification of PTFE membranes using in situ deposited PANI. *J. Macromol. Sci. Phys.* 50, 172–178. DOI: 10.1080/00222341003648805.

Table 2. Temperature transitions from DSC measurements

Sample	ΔC_p [J/g°C]	T_g [°C]	T_m [°C]	ΔH_m [J/g]	T_c [°C]	ΔH_c [J/g]	w_c [%]
PBT-BDLA before plasma	0.6881	−51.1	117.9	10.29	11.2	8.06	7.1
N_2O_2 60 s	0.6912	−36.3	123.6	7.76	57.5	2.00	5.4
N_2O_2 180 s	0.4909	−44.4	118.0	6.15	30.8	8.79	4.3
O_2 60 s	0.4261	−37.9	121.4	8.35	33.5	9.34	5.8
O_2 180 s	0.2549	−33.4	126.5	7.71	43.9	9.31	5.3
N_2 60 s	0.5310	−34.9	119.6	8.38	30.9	10.6	5.8
N_2 180 s	0.2390	−33.0	116.5	8.94	45.0	11.5	6.2

T_g − glass transition temperature of soft segemnts; ΔC_p − change of heat capacity; T_m, T_c − melting and crystallization temperatures, respectively, of the hard segments; ΔH_m, ΔH_c – crystallization and melting enthalpy of the hard segments, respectively; W_c − mass content of crystallites in copolymer.

7. Vladkova, T. (2007). Surface engineering for non-toxic biofouling control (review). *J. Univ. Chem. Technol. Metall.* 42, 239–256.

8. Dung Tran, T., Mori, S. & Suzuki, M. (2007), Plasma modification of polyacrylonitrile ultrafiltration membrane, *Thin Solid Films,* 515, 4148–4152. DOI: 10.1016/j.tsf.2006.02.045.

9. Ryu, G.H., Won-Sun, Y., Hye-Won, R., Lee, I.S., Kim, J.K., Lee, G.H., Lee, D.H., Park, B.J., Lee, M.S., Park, J.C. (2005). Plasma surface modification of poly (D,L-lactic-co-glycolic acid) (65/35) film for tissue engineering. *Surface & Coatings Technology*, 193, 60–64. DOI: 10.1016/j.surfcoat.2004.07.062.

10. Han, D.K., Ahn, K.D., Ju, Y.M. & Ahn, S.. Preparation method of biodegradable porous polymer scaffolds having an improved cell compatibility for tissue engineering, US Patent 6861087, March 2005.

11. Aroca, A.S., Pradasa, M.M. & Gómez Ribelles, M.. (2007). Plasma induced polymerization of hydrophilic coatings onto macroporous hydrophobic scaffolds, *Polymer*. 48, 2071–2078. DOI: 10.1016/j.polymer.2007.02.017.

12. Stoffels, E., Kieft, I.E. & Sladek, R.E.J. (2003). Superficial treatment of mammalian cells using plasma needle. *J. Phys. D. Appl. Phys*. 36, 2908–2913. DOI: 10.1088/0022-3727/36/23/007.

13. El Fray, M. & Slonecki, J. (1996). Multiblock copolymers consisting of polyester and polyaliphatic blocks, *Die Angewandte Makromoleulare Chemie*, 234, 103–117. DOI: 10.1002/apmc.1996.052340110.

14. Prowans, P., El Fray, M. & Slonecki, J. (2002). Biocompatibility studies of new multiblock poly(ester-ester)s composed of poly(butylene terephthalate) and dimerized fatty acid. *Biomaterials* 23, 2973–2978, DOI: 10.1016/S0142-9612(02)00026-1.

15. El Fray, M., Bartkowiak, A., Prowans, P. & Slonecki, J. (2000). Physical and mechanical behaviour of electron-beam irradiated and ethylene oxide sterilized multiblock polyester. *J. Mater. Sci. Mater. Med.* 11, 757–762.

16. Renke-Gluszko, M. & El Fray, M. (2004). The effect of simulated body fluid on mechanical properties of multiblock poly(aliphatic/aromatic-ester) copolymers. *Biomaterials* 25, 5191–5198. DOI: 10.1016/j.biomaterials.2003.12.021.

17. Oh, S.H. & Lee, J.H. (2013). Hydrophilization of synthetic biodegradable polymer scaffolds for improved cell/tissue compatibility. *Biomed. Mater*. 8, 014101–014117. DOI: 10.1088/1748-6041/8/1/014101.

18. Lee, J.H., Kim, H.G., Khang, G.S., Lee, H.B. & Jhon, M.S. (1992). Characterization of wettability gradient surfaces prepared by corona discharge treatment. *J. Colloid. Interface. Sci.* 151, 563–570. DOI: 10.1016/0021-9797(92)90504-F.

19. Vesel, A., Junkar, I., Cvelbar, U., Kovac, J. & Mozetic, M. (2008), Surface modification of polyester by oxygen- and nitrogen-plasma treatment. *Surf. Inter. Anal.* 40, 1444–1453, DOI: 10.1002/sia.2923.

20. Siow, K.S., Britcher, L., Kumar, S. & Griesser, H.J., (2006), Plasma methods for the generation of chemically reactive surfaces for biomolecule immobilization and cell colonization – a review. *Plasma Process. Polym.* 3:392–418. DOI: 10.1002/ppap.200600021.

21. Cioffi, M.O.H., Voorwald, H.J.C. & Mota, R.P. (2003). Surface energy increase of oxygen-plasma-treated PET. *Mater. Character.* 50, 209–215, DOI: 10.1016/S1044-5803(03)00094-9.

22. Yang, M., Zhang, Z., Hahn, C., Laroche, G., King, M.W. & Guidoin, R. (1999). Totally implantable artificial hearts and left ventricular assist devices: selecting impermeable polycarbonate urethane to manufacture ventricles. *J. Biomed. Mater. Res. (Appl. Biomater)*. 48, 13–23, DOI: 10.1002/(SICI)1097-4636(1999)48:1<13::AID-JBM4>3.0.CO;2-4.

23. Xu, Y., Wu, X., Xie, X., Zhong, Y., Guidoin, R., Zhang, Z., Fu, Q. (2013). Synthesis of polycarbonate urethanes with functional poly(ethylene glycol) side chains intended for bioconjugates, *Polymer* 54, 5363–5373. DOI: 10.1016/j.polymer.2013.07.069.

24. Guidoin, R., Sigot, M., King, M. & Sigot-Luizar, M.F. (1992). Biocompatibility of the Vascugraft ®: evaluation of a novel polyester methane vascular substitute by an organotypic culture technique, *Biomaterials*. 13, 281–288. DOI: 10.1016/0142-9612(92)90051-O.

25. Camberlin, Y. & Pascault, J.P. (1984). Phase segregation kinetics in segmented linear polyurethanes: Relations between equilibrium time and chain mobility and between equilibrium degree of segregation and interaction parameter. *J. Polym. Sci. Polym. Phys.* 22, 1835–1844. DOI: 10.1002/pol.1984.180221011.