SURFACE PROPERTIES CHANGING OF BIODEGRADABLE POLYMERS BY THE RADIO FREQUENCY MAGNETRON SPUTTERING MODIFICATION

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Now biodegradable polymers, such as polylactic acid (PLLA) and polycaprolactone (PCL) are promising materials used in reconstructive surgery. These polymers are considered to be biologically safe and approved for clinical use by the US Food and Drug Administration [1]. All over the world biodegradable products for reconstructive medicine (screws, plates, pins and meshes) are becoming increasingly popular since they are gradually completely replaced by the patient's own tissues and excreted from the body with metabolic products. Biomaterial surface properties, such as wettability, surface free energy, play a decisive role for cells attachment and growth. The disadvantage of biodegradable polymers, limiting their use in reconstructive medicine, is their hydrophobicity. To make polymers hydrophilic surface they are often treated in gas discharge plasma. The method of radio frequency magnetron sputtering (RFMS) target of hydroxyapatite is one of the perspective methods for polymer surface treatment. RFMS method allows not only to increase the surface free energy, but also to create active centers such as compounds of calcium and phosphorus for cells growth and attachment into osteogenic direction. The paper purpose was to study the surface properties (wettability and surface free energy) of biodegradable polymers modified by RFMS.

Materials and methods

The effect of radio frequency discharge plasma was investigated on polymer films, obtained from 4% polymer material solution in dichloromethane (Panreac). Biodegradable polymers of Poli (L-lactide) PURASORB® PL 65 (Purac) and Policaprolactone PURASORB® PC 12 (Purac) were used. In order to prepare films, 12±1 grams of polymer solution were placed in specially prepared glass polished bottom basin. The basin was filled with distilled water for separating the formed film from the basin 24 hours after solvent removal and film formation. Then obtained film was placed in thermostat at 35 °C for 24 hours to remove residual moisture.

The polymer surface was modified with RFMS of hydroxyapatite solid target. The RFMS method is based on the sputtering of material in vacuum due to the target surface bombardment with the ionized working gas (usually argon) which is formed in the radio frequency discharge plasma when a magnetic field is applied. The equipment that allows forming thin calcium-phosphate coatings on different materials (metals, ceramics, and polymers) was developed in Tomsk Polytechnic University [2]. Radio frequency (RF) magnetron source supplied by RF generator with a maximum power of 2 kW and operating frequency of 13.56 MHz was placed in the vacuum chamber of the equipment. We used the following technological conditions: vacuum in the chamber was 5×10^{-5} Pa, working pressure of Ar 3×10^{-1} Pa, specific RF power of about 5 W/cm^2, RF power of 350 W and modification time of 30 sec, 1 min and 2.5 min.

Wettability of the modified polymer coatings was studied with the “Easy Drop” device (Krüss) with method of “sit” drop by measuring the contact angle of a liquid drop with volume of 3 ml placed onto the investigated surface. Measurements of the wetting boundary angle (the contact angle) were carried out one minute after placing the liquid on the surface. In order to avoid contamination of the surface and distortion of measurement results, measurements of the contact angle were carried out immediately after surface modification. Glycerin and water were used as the wetting liquids. The total surface energy, its polar and dispersion components were calculated with the Owens–Wendt–Rabel–Kaelble (OWRK) method [3].

Results and discussion

Tables 1 and 2 show investigated wetting angle and free surface energy values.

Table 1. Water and glycerol wetting angles of evaluated samples

Modification time, seconds	Wetting angle of water θ, degrees	Wetting angle of glycerol θ, degrees
PLLA		
0	87±12	84±6
30	46.1±0.7	45±5
60	33.6±1.8	42.2±1.8
150	41±3	56±13
PCL		
0	77±5	85±3
30	31.6±0.5	69±3
60	2±2	53.5±1.3
150	34.8±0.6	40±6

Plasma effects lead to the wetting angle reduction of the polymer material as by a polar (water) and a nonpolar (glycerol) liquid. However, more prolonged plasma exposure on the polymer leads to the wetting angle increasing (Fig. 1, 2). This possibly can be explained by the polymer structure destruction in the RF discharge plasma.

Free surface energy of polymer films increases (Table 2, Fig. 3, 4). The polar component makes the main contribution to the free surface energy. The polar component significantly increases due to the appearance on the polymer surface a large number of chemically active centers, such as the radicals formation, double bonds and cross-links, surface saturation by heavier ions – Ca and P. The reason for chemically active centers formation may be surface bombardment with argon ions and the polymer interaction with sputtering target atoms and ions. The polymer interaction with oxygen ions contained in the target material leads to the formation in polymer surface of C-O and O-C =O group.

Table 2. Free surface energy of the evaluated samples

Modification time, seconds	Free surface energy γ, mj/m^2	Dispersion component γ^d , mj/m^2	Polar component γ^p , mj/m^2
PLLA			
0	20±4	8.2±1.9	12±2
30	53±3	12.5±1.4	40.0±1.7
60	65.1±1.4	6.9±0.4	58.1±0.9
150	67±7	1.8±1.4	65±6
PCL			
0	33±2	0.8±0.3	32.1±1.7
30	119±2	4.0±0.4	115.4±1.5
60	113.2±1.5	0.43±0.09	112.8±1.4
150	63±3	9.2±1.3	53±2

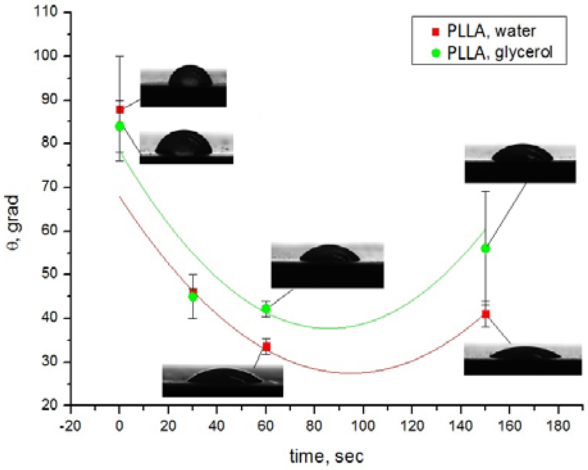

Fig. 1. Effect of modification duration on the PLLA samples wetting properties

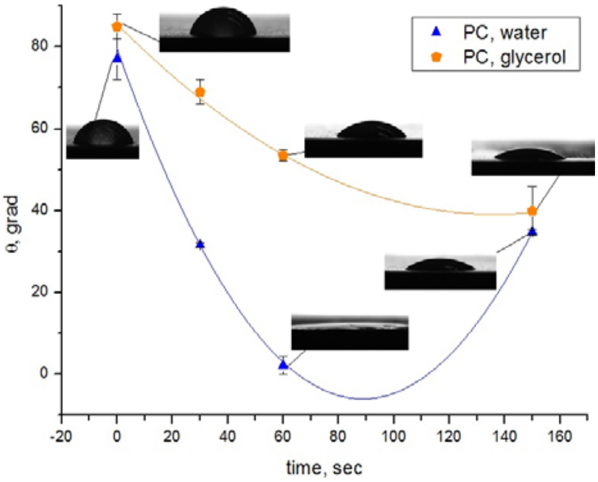

Fig. 2. Effect of modification duration on the PCL samples wetting properties

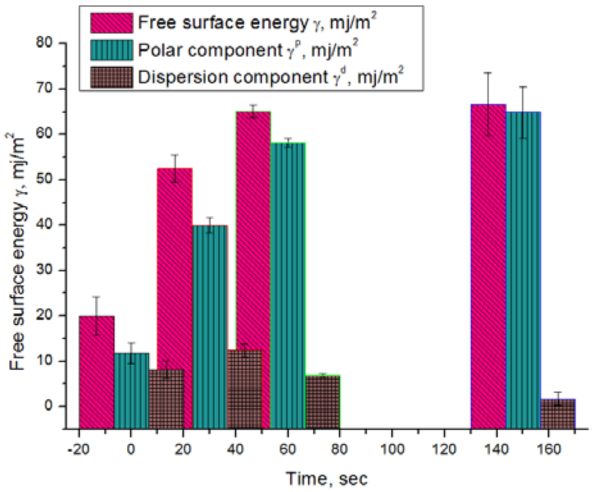

Fig. 3. Free surface energy (γ), polar (γ^p) and dispersion (γ^d) components of PLLA samples

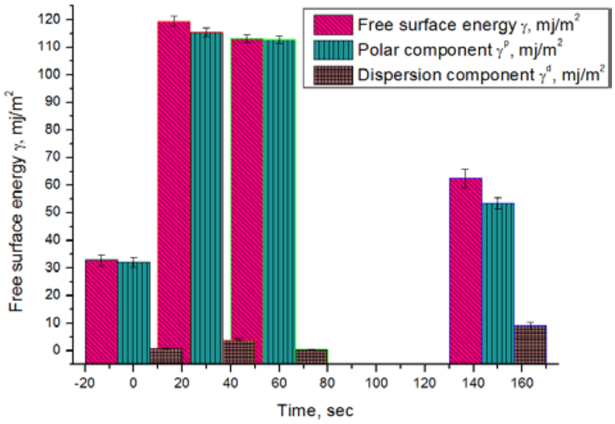

Fig. 4. Free surface energy (γ), polar (γ^p) and dispersion (γ^d) components of PCL samples

Conclusion

The paper investigated the modifying possibility of the biodegradable polymer materials surface (polylactic acid and polycaprolactone) in radio frequency discharge plasma, initiating hydroxyapatite solid target sputtering.

It was demonstrated that discharge plasma treatment adjusts the surface properties of biodegradable polymers – surface free energy and the wetting angle.

References

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