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COMPARISON OF BIOCOMPATIBILITY OF ORGANIC POLYMERS MODIFIED IN VARIOUS TYPES OF NON-TEMPERATURE PLASMAS

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Abstract. Application and perspectives of plasma chemical rectors generating cold hybrid plasma for polymeric materials biocompatibility improvement are considered. Oxygen hybrid plasma was produced by joint action of a continuous or intermittent electron beam and a capacity coupled RF-gas discharge (13.56 MHz) on gaseous media at moderate pressures. Oxygen-containing functional groups were formed on the poly(ethylene terephthalate) surface, which increased its hydrophilicity. The plasma-treated polymers turned out to be noncytotoxic and biocompatible. Fibroblasts 72 h survival on hybrid plasma-modified poly(ethylene terephthalate) films was higher in comparison with control cells cultured on untreated polymers and substrates treated in RF-discharge only.

1. INTRODUCTION

For the effective use of polymers and plastics in biology and medicine, their preliminary modification and functionalization is often needed and therefore the development of new technologies for polymeric surfaces engineering is of great research and commercial importance.

Among the several techniques for the surface modification of polymeric materials, non-temperature plasmas are of the most frequently applied [see Sui et al. 2021; Zanini et al. 2020], since they offer a large number of advantages over conventional methods like mechanical abrasion, wet chemical cleaning, etching, etc. By the introduction of hydrophilic or hydrophobic groups the plasma-stimulated surface activation modifies the surface energy and the water wettability of polymers, affecting their adhesive interface bonding [see Fattah. 2019], binding of specific active molecules [see Soygun et al. 2020], antibacterial properties [see Ozge et al. 2014], and integration with living tissues [see Ozge et al. 2014; Rezaei et al. 2016].

The objective of the study was to compare the chemical composition and biocompatibility of the surface of poly(ethylene terephthalate) (PET) films treated in hybrid plasma, generated by joint action of a continuous or intermittent electron beam (EB) and RF-gas discharge on gaseous media at moderate pressures.

2. HYBRID PLASMA CHEMICAL REACTOR

PET films were modified in the hybrid plasma chemical reactor as it was described earlier in Vasiliev et al. 2019. All experiments were carried out using oxygen of the spectroscopic grade as a plasma gas at a pressure of P_m = 1.5 Torr and other parameters were as follows:

- the EB accelerating voltage, E_b = 30 kV;
- the EB current I_b = 1.5 mA
- the RF-frequency 13.56 MHz and the RF-power 10 W;
- gas flow rate 5 sccm (standard $cm^3 \times min^{-1}$);
- treatment time was 10 min.

Under these conditions, the material temperature did not exceed 40 ºC. The stability of the conditions was ensured by automatic control systems of the plasma chemical reactor.

The main hybrid reactor advantages are as follows:

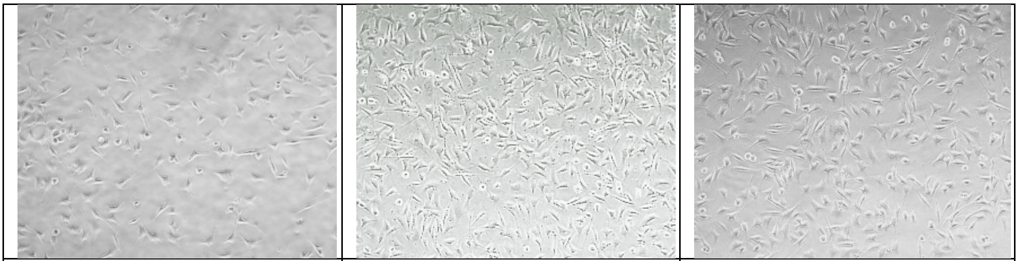
1. The reaction volume is uniform and doesn’t contract with the increase of the plasma generating gas pressure to values at which the RF-discharge is filamentary or does not glow at all;

2. Electron beam scanning can instantly control the reaction volume geometry, while active plasma particles concentrations can be controlled by the beam power independently, which allows to accurately localize the RF-discharge on the desirable polymer surface zone. On the other hand, the EB scanning, and the control of both the EB parameters and the plasma media characteristics prevent local overheating of the treated polymer. As a result, areas within which physical, chemical and functional properties change abruptly (structured patterns) or smoothly (gradient materials) can be formed on the surface. Experimental results that confirm these possibilities can be found in our papers [Vasiliev et al. 2019; Vasilieva et al. 2021].

3. EXPERIMENTAL RESULTS

The hybrid plasma treatment resulted in oxygen-containing polar hydroxyl, carbonyl, and carboxyl groups formation in the PET surface layers. Surface free energy increase and wettability enchantment up to 1.5-2 times in comparison with original PET were observed as well. The changes in the chemical composition of the polymeric surface together with the rise of its hydrophilic properties associated with the improvement of compatibility of the plasma-modified PET films with living cells and tissues.

The biological tests of plasma-treated PET samples were performed on BJ-5ta line of immortalized human fibroblasts cell culture, which is commonly used for assessment of the new materials cytotoxicity and biocompatibility.



a) b) c)

Figure 1: The optical microscopic images of the fibroblasts BJ-5ta after 48 h of their culturing on: a) – original PET; b) - PET treated in oxygen hybrid plasma; c) – blank culture sample.

In optical microscopic images, the fibroblasts spreading on the PET samples modified in oxygen hybrid plasma was observed (Figure 1) after 48 hours of their cultivation. The cells were exhibiting a flattened morphology that demonstrated good adherence to the polymeric surface. The normal cell morphology and proliferation patterns, which can also be seen in Figure 1 are similar to those of the negative control (blank culture), prove the noncytotoxic effect of the plasma-modified PET.

The MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] colorimetric assay did not also show any cytotoxic effect of PET modified in oxygen hybrid plasma. For instance, a tendency to a better cell growth was observed on hybrid plasma-modified samples after 72 h in comparison with the original PET films (the positive control) and PET substrates treated in RF-discharge only. This trend was confirmed by the colorimetric measurements of the individual values of fibroblast survival on single PET substrates (Figure 2): the optical densities of the supernatants obtained from cells incubated with hybrid plasma-modified PET samples were significantly increased with respect to the ones for the positive controls as well as for polymers after RF-discharge processing. Thus, the hybrid plasma and hybrid type plasma chemical reactors seem to be perspective for obtaining biocompatible polymers for tissue engineering and regenerative medicine.

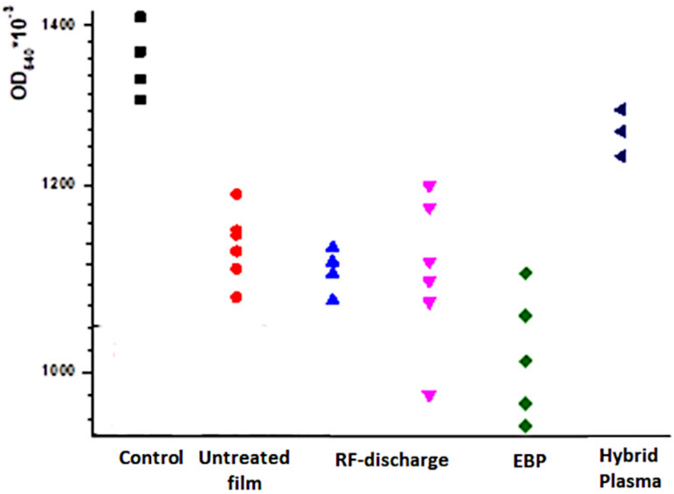


Figure 2: Individual values of the survival of BJ-5ta fibroblasts cultivated on PET films for 72 h in 24-well culture plates in comparison with the average survival value of control cells culture in the absence of PET films.
The average survival was assessed as the absorbance of biosamples measured at wavelength $\lambda = 540$ nm ($OD_{540} \times 10^{-3}$).

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