Studying of the polymeric surface layer biodegradation of composite material of medical appointment

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Abstract. The processes of biodegradation in phosphate buffer with pH 7.4 of polymer polylactide or polyglycidactide films for the subsequent creation of a layered composite with a biodegradable layer on the basis of a nickel-free shape memory alloy TiNbTaZr were studied. The structure of the samples was determined by SEM. In the case of polylactide, uniformly inhibited biodegradation is observed, the parameters of which almost do not depend on the molecular mass. Biodegradation of polyglycidactide passes in two stages and significantly exceeds the parameters of lactide dissolution. Polylactide after 60 days of immersion in phosphate buffer loses its transparency, and glycolidactide disintegrates into separate tiny fragments.

1. Introduction

A good example of materials biomechanically compatible with the living body is titanium shape memory alloys (SMA), showing similarity to living tissues [1-13]. The most common of these is titanium nickelide, but the composition of this material largely includes toxic nickel that can affect surrounding tissues directly from the surface of the implant or be released into aggressive physiological environments as a result of corrosion, which simultaneously leads to product destruction and body damage [14-16].

As an alternative while creating medical implants a material with high corrosion resistance and biocompatibility, exhibiting a similar level of superelasticity and shaping, should act. Non-nickel alloys, which also contain titanium as the basic element and such metals as tantalum, niobium, zirconium, etc., are the most close and interesting at this moment. These materials are actively developed and studied.

At the same time, it is of interest to work on the formation of functional composite materials on the basis of SMA, in particular with surface polymeric layers - stable as a all-over casing for hollow reticular minimally invasive implants, preventing the germination of tissues, and biodegrading for the local delivery of necessary medicinal substances for a given period of time [17-19].

The purpose of this work was to study the laws of biodegradation of the polymer surface of layered composite materials with a base of TiNbTaZr in neutral media modeling the physiological.

2. Materials and methods
Poly-D,L-lactide (PLA) and Poly-glycolide-D,L-lactide (PGLA, molar ratio 30/70) of molecular weights of 45, 90 and 180 kDa were used as starting materials of the biodegradable surface layers of future biocompatible composites. Chloroform was used as the solvent.

To create model films, we prepared hitches of polymers weighing 10 g (± 0.01 g) per 200 ml of chloroform. The solution was heated to 80 °C and stirred until homogeneous for 1 hour. The resulting solution was kept for another 5 minutes at 80 °C and pour into glass pallets. Drying was carried out for 2 days in air at 37 °C in a thermostat. At the end of the drying, the resulting films were removed.

Before the tests, the samples were carefully dried from chloroform tracks and weighed. Biodegradation tests were carried out in phosphate buffer with a pH of 7.4, samples were maintained for a certain time, taken out, dried and weighed. The loss of mass was determined.

Morphology and layered elemental composition (including the use of transverse sections) of the surface of the materials before and after the tests were examined with a scanning electron microscope (SEM) of TESCAN VEGA II SBU, equipped with an attachment for the energy dispersive analysis of INCA Energy.

3. Results and discussion

Figure 1 shows an example of the cross-sectional structure of a polymer film. Uniformity of the composition without appreciable defects is observed throughout the polymer volume. The formed films are amorphous. Neither the nature of the polymer nor its molecular mass does not exert any significant influence.

The patterns of changes in the polymers biodegradation over time are shown in figures 2-3.

With increasing molecular weight of polylactide (45, 90 and 180 kDa), the rate of biodegradation increases insignificantly (figure 2). So for 60 days for a polylactide with a molecular mass of 45 kDa, the weight loss is 7.3%, for 90 kDa - 9%, and for 180 kDa - 9.4%. A gradual decrease in the rate of biodegradation at any molecular mass with a similar dependence on time is noted. Taking into account the value of the mass loss of polymer films to the used volume of the model solution, saturation of the solution as a cause of this behavior is shallow. It is of interest to examine the molecular structure change of the polymer during biodegradation.

In the case of poly(glycolide-lactide) with a ratio of 30/70, the situation is different (figure 3). With a short degradation time the initial site of biodegradation curve similar to polylactide is observed. However, with an increase in molecular weight (45, 90 and 180 kDa) it is reduced. So for poly (glycolide-lactide) with a molecular weight of 45 kDa, it is 21 days, for 90 kDa - 7 days, and for 180 kDa - 3 days. Then there is a sharp increase in the rate of biodegradation, which reaches about 80% of the polymer breakdown, and then goes to the plateau. Thus, biodegradation of poly (glycolide-lactide) occurs in 2 stages. Presumably at the first stage, water is sorbed through amorphous sections and hydrolysis, and in the second stage, the crystallites decay under the action of sorbed water and
phosphates [19]. And even at the initial stage the dissolution rate is 2-3 times higher than in pure polylactide, which can be explained only by the introduction of a glycolide into the structure.

Figure 2. The dependence of biodegradation on the holding time of polylactide samples by molecular weight: a) 45 kDa, b) 90 kDa, c) 180 kDa.
Figure 3. The dependence of biodegradation on the holding time of poly(glycolide-lactide) samples by molecular weight: a) 45 kDa, b) 90 kDa, c) 180 kDa.
Films based on polylactide, regardless of the molecular weight, on day 60 lost transparency, acquiring a white color (figure 4, a, c). Films based on poly (glycolide-lactide), having the same transparency at the initial period of biodegradation (figure 4b), lost their integrity by day 60, settling on the filter in the form of fine sediment.

**Figure 4.** State of polymer films with molecular weight 180 kDa after immersion in buffer solution: a) polylactide for 1 day, b) poly(glycolide-lactide) for 1 day, c) polylactide for 60 days.

### 4. Conclusions

Thin polylactide and polyglycolyldactide films as the components for the subsequent formation of layered composites based on the shape memory alloy with drug filling were obtained and studied.

In the case of polylactide, uniformly inhibited biodegradation is observed, the parameters of which almost do not depend on the molecular mass. Biodegradation of polyglycolyldactide passes in two stages and significantly exceeds the parameters of lactide dissolution. Polylactide after 60 days of immersion in phosphate buffer loses its transparency, and glycolyldactide disintegrates into separate tiny fragments.

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