

Studying of the Polylactide or Polyglycolidactide Surface Layer Biodegradation in Neutral Media for the Subsequent Layered Composite Creation

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Abstract: The processes of biodegradation in phosphate buffer with pH 7.4 and 0.9 wt.% NaCl of polymer polylactide or polyglycolidactide 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 and an optical microscope. For polylactide films the rate of biodegradation did not depend on the mass of the film. A gradual decrease in the rate of biodegradation at any mass with a similar dependence on time is noted. With an increase in the mass of films based on poly(glycolide-lactide) the rate of biodegradation increased. And even at the initial stage the dissolution rate is 2-3 times higher than in pure polylactide. On day 180, complete dissolution of the polyglycolidelactide was observed (even a precipitate was not observed) and completely entire polylactide films, however, lost their transparency, was noted.

Keywords: polylactide, polyglycolidactide, biodegradation, biocompatible material, medical appointment

1. Introduction

A good example of biomechanically compatible materials is titanium shape memory alloys (SMA), showing similarity to living tissues [1-13]. The most common of these is nitinol, 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 for medical implants creating a material with high corrosion resistance and biocompatibility, exhibiting a similar level of superelasticity and shaping, must be selected. 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 especially 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 films for future 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 2, 6 and 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 and 0.9 wt.% NaCl solution. 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, and an optical microscope.

3. Results and discussion

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 concentration in the solvent does not exert any significant influence. The greater the concentration of the polymer (the weight of the sample in the same volume of solvent and so the formed film mass) was, the thicker the formed film was. The surface area was maintained the same.

The patterns of changes in the polymers biodegradation over time are shown in figures 1-2.

For polylactide films the rate of biodegradation did not depend on the mass of the film (figure 1). The degree of biodegradation for these films on day 60 was 8-9%. A gradual decrease in the rate of biodegradation at any 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.

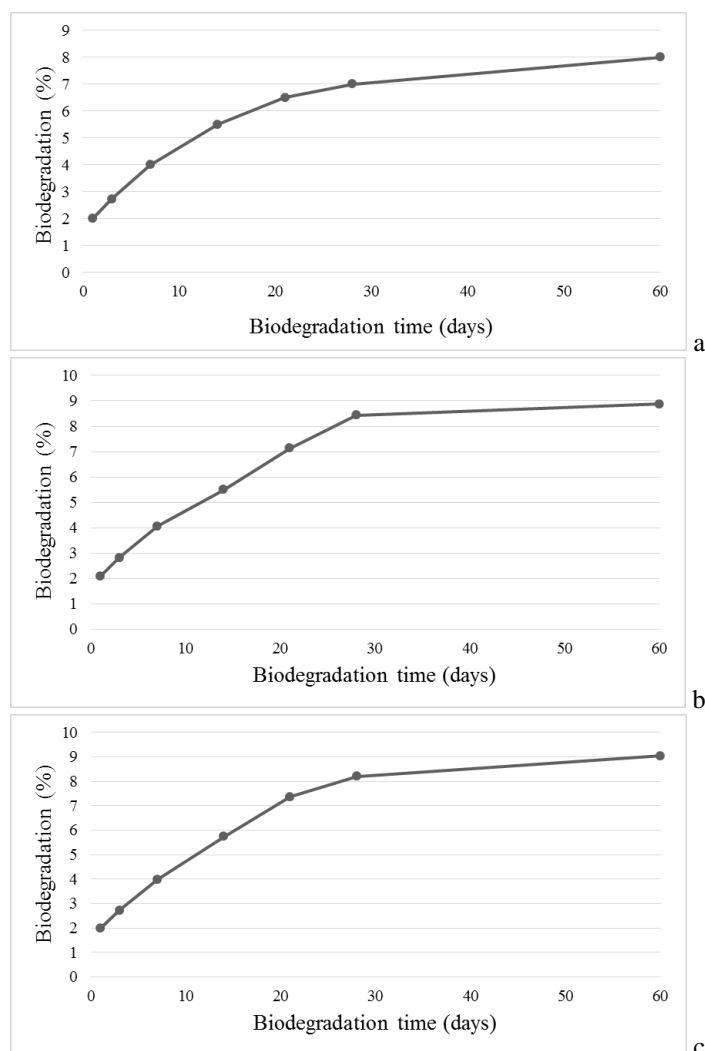


Figure 1. The dependence of biodegradation on the holding time of poly(lactide) samples with 90 kDa molecular weight and different concentration per 100 ml of solvent: a) 1 g, b) 3 g, c) 5 g.

With an increase in the mass of films based on poly(glycolide-lactide) (figure 2), the rate of biodegradation increased. For samples of films prepared from poly (glycolide-lactide) with a molecular weight of 90 kDa with a

mass of 10 g, the degree of biodegradation at day 30 reached 80%. And for 2 g - on day 60 it reached only 37%. Such a change in the rate of biodegradation presumably is due to the fact that the process of hydrolysis of poly (glycolide-lactide) proceeds throughout the whole volume of the polymer [19]. The increase in the weight of the polymer in the manufacture of films led to an increase in the thickness of the resulting film and, correspondingly, to an increase in its volume, accelerating the biodegradation process. 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. In general, inhibition of the biodegradation process can also be observed, which may be explained by the heterogeneous structure of the polymer, which is formed both in the form of amorphous sections and crystallites [19]. And the dissolution parameters depend on their mutual distribution over the volume of the film.

Films based on polylactide on day 60 lost transparency, acquiring a white color (figure 3, a-f). But it can be noted that the smallest loss of transparency is observed for the thickest film (figure 3 f). Films based on poly (glycolide-lactide), having the same transparency at the initial period of biodegradation (figure 3, g-l), lost their integrity by day 60, settling on the filter in the form of fine sediment, and lost transparency, also acquiring a white color already on the seventh day.

The same patterns were observed in the case of sodium chloride solution. On day 180, complete dissolution of the polyglycolidelactide was observed (even a precipitate was not observed) and completely entire polylactide films was noted.

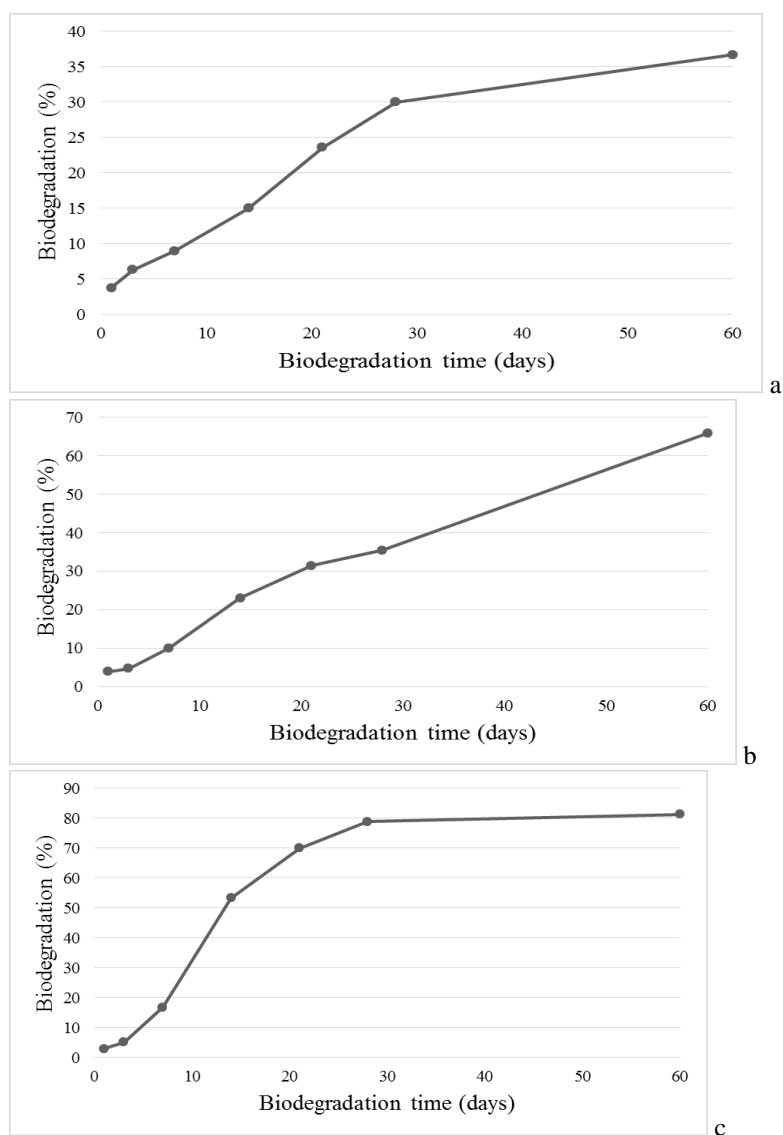


Figure 2. The dependence of biodegradation on the holding time of poly(glycolide-lactide) samples with 90 kDa molecular weight and different concentration per 100 ml of solvent: a) 1 g, b) 3 g, c) 5 g.

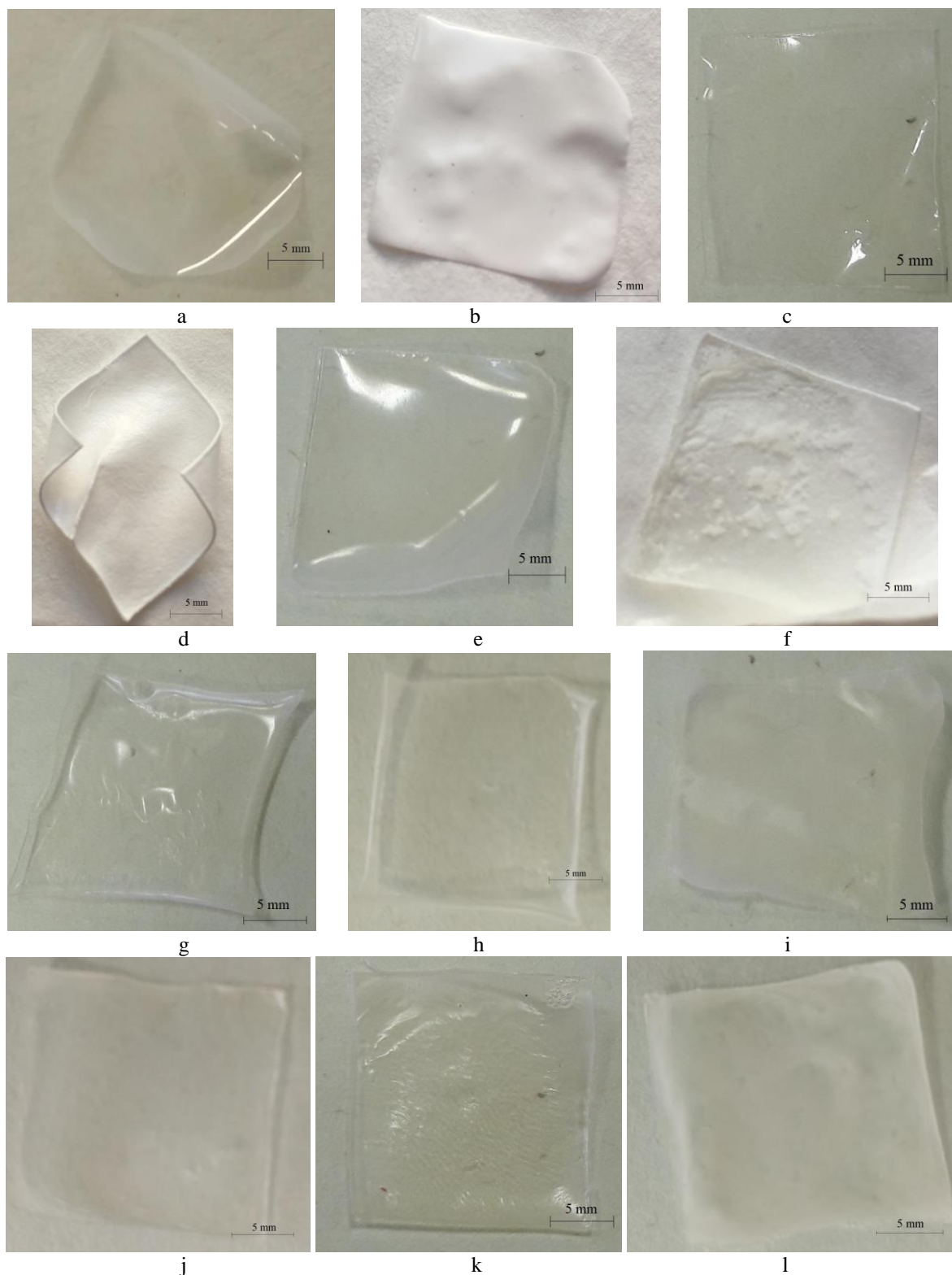


Figure 3. State of polymer films with molecular weight 90 kDa after immersion in phosphate buffer solution: a) polylactide, 1 g per 100 ml of solvent, for 1 day, b) polylactide, 1 g per 100 ml of solvent, for 60 day, c) polylactide, 3 g per 100 ml of solvent, for 1 day, d) polylactide, 3 g per 100 ml of solvent, for 60 day, e) polylactide, 5 g per 100 ml of solvent, for 1 day, f) polylactide, 5 g per 100 ml of solvent, for 60 day, g) poly(glycolide-lactide), 1 g per 100 ml of solvent, for 1 day, h) poly(glycolide-lactide), 1 g per 100 ml of solvent, for 7 day, i) poly(glycolide-lactide), 3 g per 100 ml of solvent, for 1 day, j) poly(glycolide-lactide), 3 g per 100 ml of solvent, for 7 day, k) poly(glycolide-lactide), 5 g per 100 ml of solvent, for 1 day, l) poly(glycolide-lactide), 5 g per 100 ml of solvent, for 7 day.

4. Conclusions

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

For polylactide films the rate of biodegradation did not depend on the mass of the film. A gradual decrease in the rate of biodegradation at any mass with a similar dependence on time is noted. With an increase in the mass of films based on poly(glycolide-lactide) the rate of biodegradation increased. And even at the initial stage the dissolution rate is 2-3 times higher than in pure polylactide. On day 180, complete dissolution of the polyglycolidelactide was observed (even a precipitate was not observed) and completely entire polylactide films, however, lost their transparency, was noted.

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