Formation of biodegradable polymers as components of future composite materials on the basis of shape memory alloy of medical appointment

E O Nasakina, A S Baikin, K V Sergiyenko, M A Kaplan, S V Konushkin, A D Yakubov, A V Izvin, M A Sudarchikova, M A Sevost'yanov and A G Kolmakov

Baikov Institute of Metallurgy and Material Sciences, 49 Leninsky Avenue, Moscow, Russia

Email: nacakina@mail.ru

Abstract. The processes of formation of polymer polylactide or polyglycolideactide films for the subsequent creation of a layered composite with a biodegradable layer on the basis of a nickel-free shape memory alloy TiNbTaZr are studied. The structure of the samples was determined using an SEM. The correspondence of morphology of surfaces of and the substrate itself is noted. High adhesion of the polymer to the future basis of the developed composite material is supposed. The formed films is homogeneous and amorphous throughout the polymer volume. By varying the volume of solutions, it is possible to obtain films of a given thickness for any type of polymer, its molecular weight, and the solution concentration of the polymer in chloroform. Poly (glycolide-lactide) should be more plastic than polylactide.

1. Introduction
Medicine always appeals to other sciences in the search for new, more successful tools. Alloys with the shape memory effect (SME) and superelasticity are now one of the most interesting materials in the endoscopic implantology - when creating implants like Stent and Kawa-filter [1-12]. First, they have mechanical properties similar to the behavior of living tissues, which, when implant is installed and work in the body, provides less damage to the implant itself and the tissue damage. Secondly, the SME provides a "self- expansion" of the product, facilitating smaller dimensions of it in the delivery state, eliminating the need for additional means of their deployment and slowing down this process, which ultimately leads to a less traumatic effect of operations. But in addition to mechanical, there are still many characteristics of materials that are important in the production of these implants. And increasingly, multicomponent materials are being created now to improve and combine various functional properties. In particular, the creation of a composite material with a surface layer of a biodegradable biopolymer on the basis of an alloy with an SME will provide medical products with the possibility of local therapeutic effects through controlled release of drugs for a given time [13-15]. By correctly choosing a biodegradable polymer as a drug delivery system, it is possible to control the rate of release and concentration of the drug.

In this paper, we consider the formation of polymer components for layered composites on shape memory alloy substrates with biodegradable surface layers of polylactide and poly(glycolide-lactide).
2. Materials and methods
Polylactide / polyglycolide are soluble in most solvents, including chlorinated solvents. In the work, chloroform was chosen as the solvent. In comparison with other solvents, it exhibits a higher degree of dissolution of the polymers used, even at room temperature. It is assumed that in the process of obtaining polymer coatings, it will completely evaporate, leaving no negative biological effects in the final product.

By the method of casting from a polymer solution, it is possible to efficiently obtain bioresorbable layers, including with medicinal filler. By varying the polymer concentrations in the solvent, it is possible to control the film thickness, and hence the resorption time. The nature of the polymer and its molecular weight should also influence the film thickness and structure.

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.

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.

3. Results and discussion
The obtained samples were assigned ciphers intended for independent research in the future. The corresponding characteristics are listed in table 1. Figures 1-5 show SEM images of the surface and cross-sections of model coatings - polylactide and poly(glycolide-lactide) films.

| Cipher | Molecular weight, kDa | Concentration, g per 100 ml chloroform | Thickness, μm |
|--------|-----------------------|----------------------------------------|---------------|
| 1.1    | PLA                   | 45                                     | 1             | 0.042 |
| 1.2    | 5                     | 1                                      | 0.107         |
| 1.3    | 5                     | 1                                      | 0.339         |
| 2.1    | 90                    | 1                                      | 0.038         |
| 2.2    | 90                    | 3                                      | 0.125         |
| 2.3    | 90                    | 5                                      | 0.262         |
| 3.1    | 180                   | 1                                      | 0.039         |
| 3.2    | 180                   | 3                                      | 0.082         |
| 3.3    | 180                   | 5                                      | 0.152         |
| 4.1    | PLA                   | 45                                     | 1             | 0.066 |
| 4.2    | 5                     | 3                                      | 0.155         |
| 4.3    | 5                     | 1                                      | 0.224         |
| 5.1    | PGLA                  | 90                                     | 1             | 0.063 |
| 5.2    | 90                    | 3                                      | 0.148         |
| 5.3    | 90                    | 5                                      | 0.258         |
| 6.1    | 180                   | 1                                      | 0.032         |
| 6.2    | 180                   | 3                                      | 0.154         |
| 6.3    | 180                   | 5                                      | 0.252         |
Figure 1. SEM images of the samples surfaces a) 1.1, b) 3.1, c) 5.1, d) 4.1, e) 4.2
Figure 2. SEM image of the sample surface facing the substrate: a) 1.2, b) 2.1, c) 3.3

Obviously, the surface of polylactide and poly(glycolide-lactide) model films is a characteristic glassy surface without significant defects (figure 1). Neither the nature of the polymer (figure 1 a, d) nor its molecular mass (figure 1 a, b and c, d, respectively) nor the concentration in the solvent (figure 1 d, e) does not exert any significant influence.

An interesting observation is that in the case of analysis of the polymer film surface facing the substrate on which it was grown (figure 2), a clear correspondence of the morphology of these surfaces with a complete repetition of the initial relief is evident. The nature and amount of the polymer also do not affect the degree of repetition of morphology. Thus, an extremely high ability of polymers to fill the cavities of any roughness is observed, which should promote high adhesion of the polymer to the future basis of the developed composite material. This also leads to the assumption of high homogeneity and fluidity of the solution, which contributes to the best characteristics of the structure of the resulting film and the manufacturability of the process.

The thickness of the model films (figures 3-5, table 1) was 32 to 339 μm, depending on the type of polymer used, its molecular weight, and the concentration of the polymer solution in chloroform. There was no linear dependence. At the same time changing the volume of solutions it is possible to obtain films of the same thickness under any of these conditions.
Figure 3. SEM image of the cross section of the sample a) 1.1, b) 4.1, c) 1.2, d) 4.2, e) 1.3, f) 4.3
Figure 4. SEM image of the cross section of the sample a) 2.1, b) 5.1, c) 2.2, d) 5.2, e) 2.3, f) 5.3
Figure 5. SEM image of the cross section of the sample a) 3.1, b) 6.1, c) 3.2, d) 6.2, e) 3.3, f) 6.3

Uniformity of the composition without appreciable defects is also observed throughout the polymer volume. The formed films are amorphous. It was observed that, judging by the nature of the cross-
sections after cutting (figures 3-5), poly(glycolide-lactide) should exhibit greater plasticity than polylactide: the number of sharp marks from mechanical deformation practically reduces to zero.

4. Conclusions
1. Thin polymeric films of polylactide and polyglycidylidactide as the components for the subsequent formation of layered composites based on the shape memory alloy with drug filling were obtained and studied.
2. The surface of the polymer film facing the substrate on which it was grown reproduces completely the morphology of the surface of this substrate. Thus, an extremely high ability of polymers to fill the cavities of any roughness is observed, which should promote high adhesion of the polymer to the future basis of the developed composite material.
3. The formed films is homogeneous and amorphous throughout the polymer volume.
4. By varying the volume of solutions, it is possible to obtain films of a given thickness for any type of polymer, its molecular weight, and the solution concentration of the polymer in chloroform.
5. Poly (glycolide-lactide) should be more plastic than polylactide.

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