
VARIOUS TECHNOLOGICAL
PROCESSES

Structural-Phase State and Surface Properties of Composite Materials Based on Polylactide and Hydroxyapatite

V. A. Syusyukina*, Ye. Shapovalova, N. M. Korotchenko, and I. A. Kurzina

National Research Tomsk State University, pr. Lenina 36, Tomsk, 634050 Russia

*e-mail: vershinina_vlada@mail.ru

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Abstract—The phase composition and unit cell parameters were determined for composites based on polylactide and hydroxyapatite with the polylactide/hydroxyapatite weight ratios of 90/10, 80/20, 70/30, and 60/40. As the polylactide content of the composites is increased, they become less hydrophilic, and the surface energy σ_{S-G} increases from 29.13 to 74.35 mJ m⁻². The sample with the component weight ratio of 70/30 is characterized by the maximal roughness, and the Ca²⁺ and Mg²⁺ ions from simulated body fluid are actively adsorbed onto its surface, as proved by SEM examination of the composites.

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Biocompatible composite materials of wide spectrum are used as implants in modern medicine. The development of various medical biocomposites based on hydroxyapatite (HA) [1] and lactic acid polymers and oligomers [2] is a promising line of research at the junction of chemistry and biomedicine [3].

Composite materials allow useful properties of the components to be successfully combined to reach the required set of properties. The matrix in the material is a biocompatible polymer exhibiting high strength. Polylactide (PL) is the most promising in this respect. It undergoes biodegradation in a living body to form lactic acid, is biocompatible, and can positively influence the composite bioresorption rate. The composite material should contain hydroxyapatite as inorganic component ensuring affinity for the bone tissue. The choice of hydroxyapatite is governed by the fact that its chemical composition is similar to that of the mineral constituent of bones [4, 5]. A number of approaches to preparing composite materials based on PL and HA are described in the literature. Tormala et al. [6] considered the possibility of preparing a composite biomaterial based on HA and poly-L-lactide in the form of laminates. Their procedures involved simultaneous synthesis of the components.

Verheyen et al. [7] were able to prepare a biocompatible material by mixing HA with a PL solution before polymerization and obtained a highly porous sample. Shikinami and Okuno [8] described in detail a procedure for preparing a composite biomaterial by pressing a PL/HA mixture based on uncalcined and unsintered HA. The results obtained by Ignjatovic et al. [9, 10] are interesting for practice. They synthesized blocks of PL/HA composite biomaterial with highly crystalline HA component in two steps. The porosity of the composite, molecular mass, and amorphous/crystalline ratios in the composite can be appreciably changed by hot pressing at the melting point of the polymer. Furukawa et al. [11, 12] also suggested an approach to preparing ultra-high-strength PL/HA composite. However, the characteristics of the materials obtained using different methods widely vary. The influence of the composition on the properties of the composites is insufficiently understood. A procedure based on mixing the components in the solid state or in solution, followed by pressing, was suggested previously. This procedure is cost- and time-saving; it allows preparation of composite materials exhibiting the required set of properties, porosity, and bioresorption.

The influence of the composition and ratio of components on the functional properties of composites is a topical problem and is still poorly understood. The influence of the component ratio on the dissolution and bioresorption is also a topical problem. In this work, we studied composite materials prepared by mixing the components with subsequent pressing [13] and considered in detail the influence of the composition of the composites on the structure, phase composition, and bioresorption.

The study was aimed at preparing composite materials at varied PL/HA ratio and revealing the influence of the composition on the surface properties of the composites.

EXPERIMENTAL

To prepare the composite materials, we took PL and HA as starting components. The samples were prepared by mixing a solution of PL in chloroform ($c = 0.1 \text{ g mL}^{-1}$) with HA powder with continuous stirring at component weight ratios of 90/10, 80/20, 70/30, and 60/40. The obtained suspension was treated with ultrasound (40 kHz) for 20 min and then precipitated in a fivefold excess of ethanol. The fibers obtained were dried in an oven at 40°C until the solvent evaporated completely. The composites were subjected to mechanical grinding and then formed on a PGR-10 laboratory hydraulic press at a pressure of 200 bar [13]. To determine the wettability and roughness, the samples were prepared as pellets ($d = 2 \text{ cm}$, $m = 0.3 \text{ g}$).

The phase composition and structural parameters of the samples were studied with an XRD-6000 diffractometer using CuK_α radiation. The phase composition was analyzed using the PDF 4+ database and POWDERCELL 23 programs for full-profile analysis.

The contact angles of the samples with two liquids, water and glycerol, were determined using the Young–Dupré equation

$$\cos \theta = \frac{\sigma_{\text{S-G}} - \sigma_{\text{S-L}}}{\sigma_{\text{L-G}}}, \quad (1)$$

where $\sigma_{\text{S-G}}$ is the surface tension at the solid–gas interface, $\sigma_{\text{S-L}}$ is that at the liquid–solid interface, and $\sigma_{\text{L-G}}$ is that at the liquid–gas interface [14, 15].

The surface energy was calculated using DSA1 software with an EasyDrop installation (Krüss) using the Owens–Wendt equation

$$\sigma_{\text{S-L}} = \sigma_{\text{S-G}} + \sigma_{\text{L-G}} - 2(\sqrt{\sigma_{\text{S-G}}^{\text{D}} \sigma_{\text{L-G}}^{\text{D}}} + \sqrt{\sigma_{\text{S-G}}^{\text{P}} \sigma_{\text{L-G}}^{\text{P}}}), \quad (2)$$

where σ^{D} is the dispersion component, and σ^{P} , polar component of the surface energy.

By combining Eq. (2) with Eq. (1), we obtain the model of the Owens–Wendt–Rabel–Kaelble (OWRK) method (3), which is used for determining the components of the surface energy of solids:

$$\frac{\sigma_{\text{L-G}}(\cos \theta + 1)}{2\sqrt{\sigma_{\text{L-G}}^{\text{D}}}} = \frac{\sqrt{\sigma_{\text{L-G}}^{\text{P}}}}{\sqrt{\sigma_{\text{S-G}}^{\text{D}}}} \sqrt{\sigma_{\text{S-G}}^{\text{P}}} + \sqrt{\sigma_{\text{S-G}}^{\text{D}}}. \quad (3)$$

The sample roughness was measured with a Profilometr-296 device and was evaluated by the parameter R_a .

To evaluate the formation of the new calcium phosphate layer on the surface of the composite materials by the procedure suggested by Kokubo [16, 17], the samples were kept for 28 days at $T = 37^\circ\text{C}$ in simulated body fluid (SBF) identical in the mineral composition and concentration of ions to human blood plasma. The solution was renewed daily, and the total concentration of calcium and magnesium ions in it was measured by EDTA titration in the presence of Eriochrome Black T as indicator.

The surface morphology of the composites with the freshly formed calcium phosphate layer was examined by scanning electron microscopy after keeping the samples in the solution for 1, 2, 3, and 4 weeks. The electron micrographs were taken with a Hitachi TM-3000 device at an accelerating voltage of 15 kV under the conditions of sample charging elimination.

RESULTS AND DISCUSSION

We studied the phase composition of the composite, which is an important physicochemical characteristic of materials, because pressing involves additional mechanical action on the material and can lead to changes in its structural state. In the X-ray diffraction patterns, there are reflections characteristic of PL at 16.6865° ($I = 100$) and 19.1045° ($I = 16$) (card no.

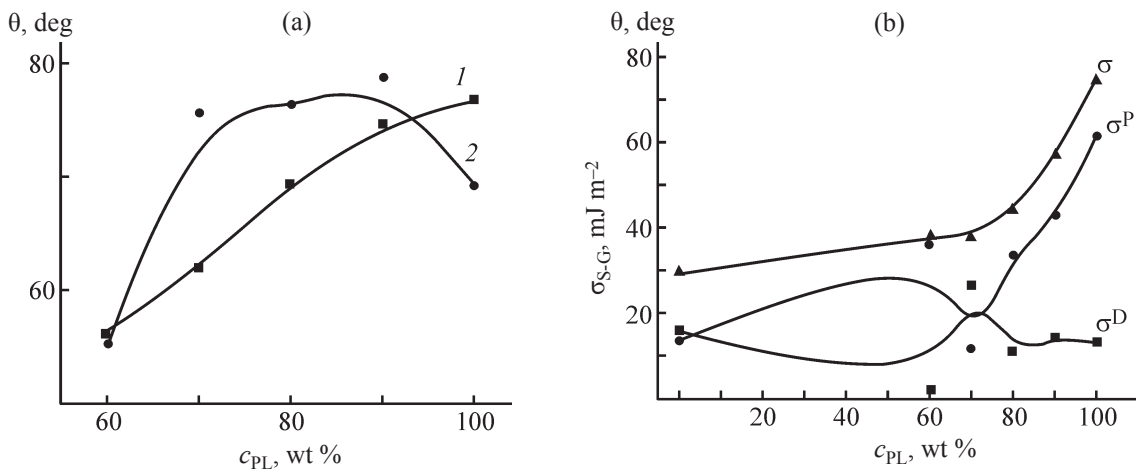


Fig. 1. Surface characteristics of poly lactide and composites based on it: (a) contact angles θ with (1) water and (2) glycerol; (b) surface energy σ_{S-G} : (σ) total, (σ^P) polar component, and (σ^D) dispersion component. (c_{PL}) PL content.

00-054-1917) [18] and of HA at 31.7600° ($I = 100$), 32.1800° ($I = 50.5$), and 25.860° ($I = 35.4$) (card no. 01-073-8418). The unit cell parameters correspond to hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. The diffraction patterns of the composites with different component ratios contain reflections characteristic of PL and HA. There are no new reflections and no shifts of diffraction lines, which indicates that the chemical composition and crystallographic identity of the initial components are preserved.

For poly lactide in the composites, the coherent scattering domain (CSD) size decreases by a factor of 2 relative to pure poly lactide (see table), suggesting formation of composites with elements of the HA structure coated with poly lactide. The crystalline domains of poly lactide in the composite material decrease. On the other hand, the CSD size for hydroxyapatite remains unchanged.

When using PL/HA composite materials as implants, the affinity of the composite for the biological medium is of prime importance. This affinity is determined by the surface energy and degree of wettability of the surface. Determination of the contact angles of the samples with water and glycerol showed that PL and composite materials are hydrophilic, whereas hydroxyapatite, which is highly porous, is superhydrophilic. The dependence of the contact angle with water on the gravimetric PL content is shown in Fig. 1a (curve 1). With an increase in the PL content in the composites, the contact angle increases, i.e., the material becomes less hydrophilic.

In wetting of the sample surface with glycerol, linear dependence of the contact angle on the PL content in the composites is not observed (Fig. 1a, curve 2). Hydroxyapatite absorbs glycerol at a high rate, and the composite with the PL/HA weight ratio of 60/40 is wetted with glycerol to the maximum extent compared to the other composite materials.

The composition dependence of the surface energy of the composites is plotted in Fig. 1b. As can be seen, with an increase in the poly lactide content the polar component of the surface energy increases, and the dispersion component simultaneously decreases. Samples containing 40 and 30 wt % hydroxyapatite deserve special discussion. At a low HA content, it is difficult to obtain a uniform system; this fact is confirmed by examination of the surface morphology. According to the SEM data, the composites can exhibit composition heterogeneity throughout the volume. There are domains containing predominantly HA or PL. When determining the contact angle, the result will strongly depend on the site where the drop is applied. In determination of the contact angle for the PL/HA 60/40 composite, the drop was applied to the site of predominant localization of HA, whereas for the PL/HA 70/30 composite the drop was applied to the site of PL localization.

It can be assumed that PL is characterized by the maximal surface energy. Therefore, deposition of HA and formation of HA-coated PL particles are possible on the sample surface under the conditions of sample preparation. The remaining fraction of hydroxyapatite,

Structural-phase characteristics of polylactide, composites, and hydroxyapatite

Sample	Phase		CSD size, nm		R_a , μm
	$(\text{C}_9\text{H}_{14}\text{O}_7)_n$	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	$(\text{C}_9\text{H}_{14}\text{O}_7)_n$	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	
PL	+	–	10	–	7.56 ± 0.50
PL/HA:					
90/10	+	+	4	9	2.65 ± 0.18
80/20	+	+	6	7	2.39 ± 0.20
70/30	+	+	6	4	4.21 ± 0.39
60/40	+	+	6	7	3.31 ± 0.15
HA	–	+	–	5	1.27 ± 0.10

not deposited on the PL surface, is precipitated from the solution, but a fraction of HA can remain in the system in the form of coarse agglomerates in the structure of the composite.

The adsorption of cells and interaction with the biological medium strongly depend on the surface energy of the composites. An increase in the surface energy can improve the biocompatibility of the material and allow its use as implants.

The surface energy depends not only on the chemical composition of the surface, but also on the surface roughness. We performed profilometric measurements (see table) and found that the PL roughness was $7.56 \pm 0.50 \mu\text{m}$. The porosity and surface roughness strongly depend on the sample preparation conditions, in particular, on pressing. The composites obtained are characterized by high roughness. The polymer material prepared by pressing PL particles exhibits the highest roughness, because polylactide particles are compacted worse than hydroxyapatite. The roughness R_a of hydroxyapatite is $1.27 \pm 0.10 \mu\text{m}$. Among composite materials, the composite with the PL/HA weight ratio of 70/30 exhibits the highest roughness: $R_a = 4.21 \pm 0.39 \mu\text{m}$. We performed the statistical processing of the roughness measurement results.

The roughness and surface energy are largely determined by the preparation conditions and ratio of the components. At high hydroxyapatite content (exceeding 30 and 40 wt %), under the conditions of formation of the composite, a part of HA remains in the solution and is not incorporated into the composite. A heterogeneous material with prevalence of polylactide on the surface is formed. At HA content of 30 wt %, the inorganic filler is

fully incorporated in the composite, and a system with uniform localization of the components is formed. In this case, the materials have high surface energy and sufficient roughness. Thus, the structural-phase state and surface properties of composite materials are very sensitive to the procedure of their preparation.

To evaluate the ability of the composite to form a new calcium phosphate layer on its surface, we performed an SBF study following the procedure described in [19]. Using the results of measuring the total concentration of Ca^{2+} and Mg^{2+} ions in the solution, we plotted the kinetic curves $\Delta c(\text{Ca}^{2+} \text{ and } \text{Mg}^{2+}) (\text{M}) - \tau (\text{days})$ of their accumulation on the substrate surfaces from SBF (Fig. 2). As can be seen, the rate of accumulation of Ca^{2+} and Mg^{2+} ions on the HA surface is characterized by the linear trend throughout the time of interaction with SBF. For the composites, the tendency to layer formation is different. The process is more complex and is characterized by the linear dependence only in the first 7 days. The PL/HA 70/30 sample is characterized by the maximal accumulation rate, whereas the layer on the PL/HA 80/20 composite is formed slowly.

The Ca^{2+} and Mg^{2+} ions are actively adsorbed from SBF onto the surface of pure HA and composite with the PL/HA weight ratio of 70/30 throughout the time of keeping the substrates in the solution. The rate of formation of the calcium phosphate layer on the surface of pure HA is higher than on the surface of the composites.

After keeping the samples in SBF, the calcium phosphate layer grows most actively on HA and on the PL/HA 70/30 composite. The SEM micrographs taken at 7-day intervals in the course of keeping the samples

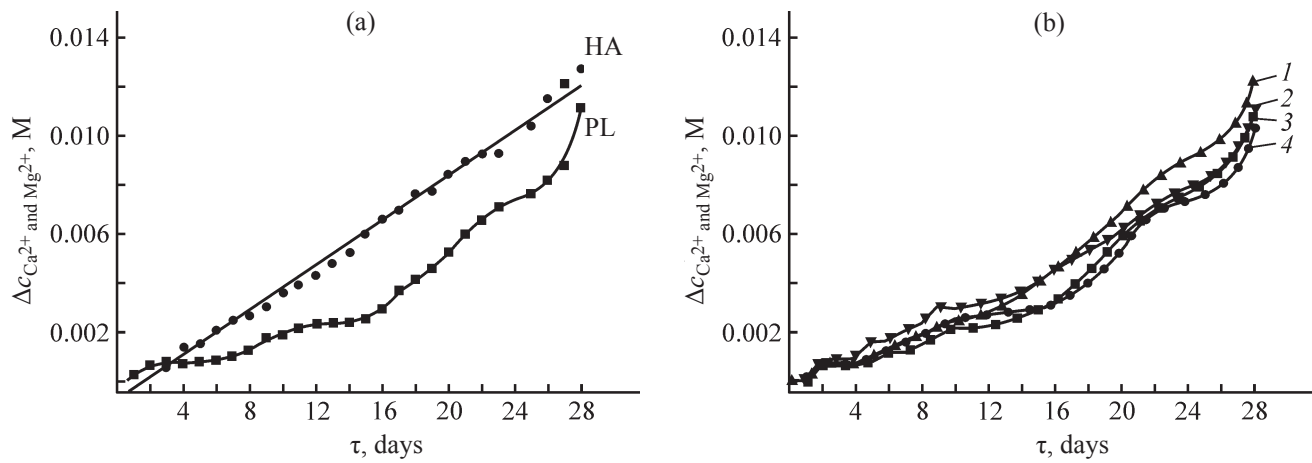


Fig. 2. Kinetic curves of adsorption of Ca^{2+} and Mg^{2+} ions from SBF (a) onto poly lactide (PL) and hydroxyapatite (HA) and (b) onto composites (1) PL/HA 70/30, (2) PL/HA 60/40, (3) PL/HA 90/10, and (4) PL/HA 80/20. (τ) Time.

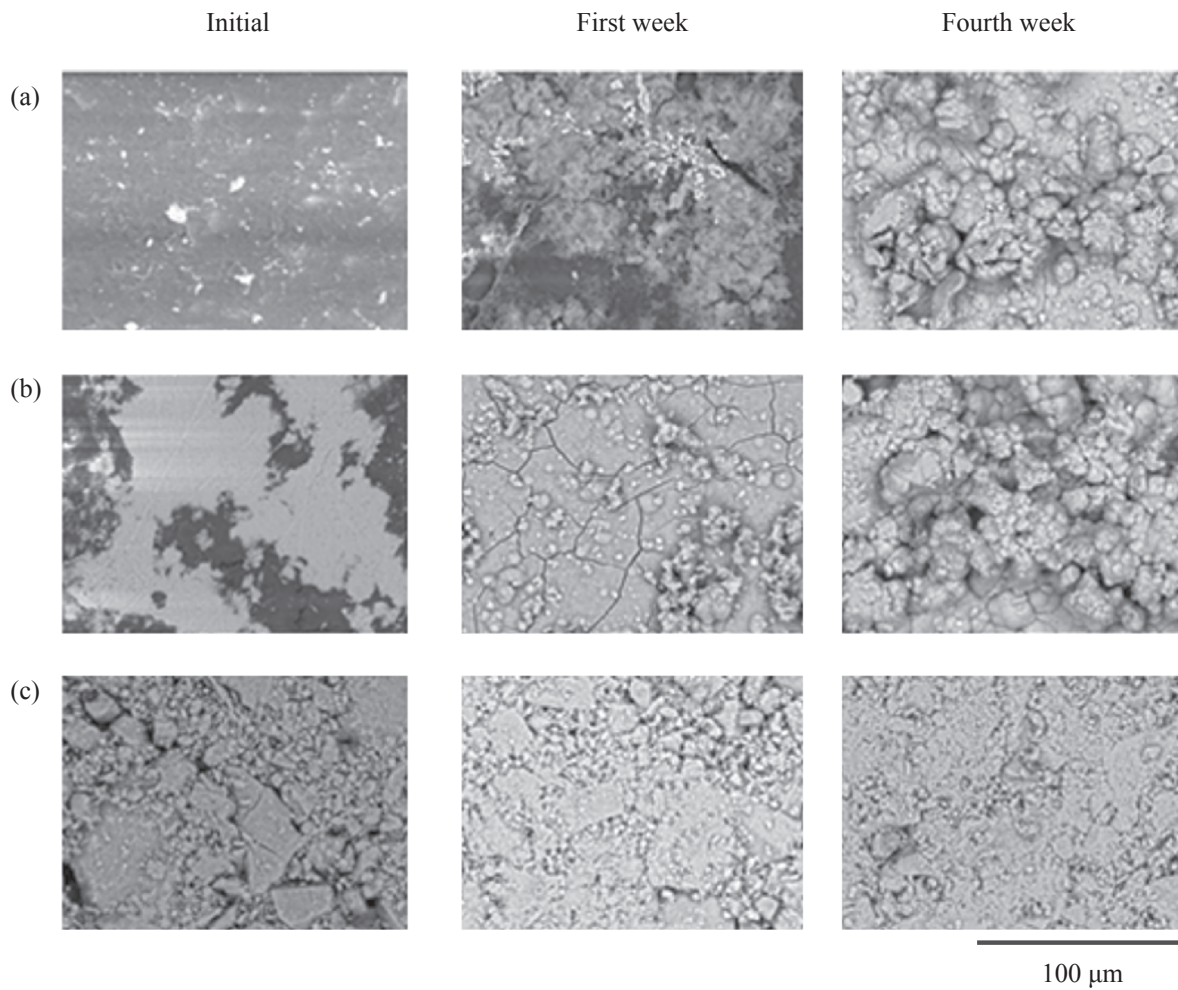


Fig. 3. Dynamics of the growth of the calcium phosphate layer on the surface of (a) poly lactide, (b) PL/HA 70/30 composite, and (c) hydroxyapatite over the course of 4 weeks. Magnification $\times 1000$.

in SBF (Fig. 3) clearly confirm the results of biomimetic studies and demonstrate the formation of calcium phosphate layers on composite substrates already after keeping them in SBF for 7 days.

The calcium phosphate layer on the substrate surface is formed by the mechanism suggested in [19–21]. The substrate surface bearing hydroxy groups attracts Ca^{2+} ions from the solution with their simultaneous adsorption on the surface and gradual change of the surface charge to partially positive. The process completes with the uptake of PO_4^{3-} ions. These consecutive-parallel processes lead to the formation of layers of poorly soluble calcium phosphates on the sample surface. Simultaneously with the formation of the calcium phosphate layer in the composites, PL dissolves with the formation of lactic acid. It should be noted that the PL hydrolysis rate increases with an increase in the HA content of the composite, i.e., HA present in the material favors acceleration of the PL hydrolysis.

CONCLUSIONS

(1) Composite materials were prepared by mixing a solution of polylactide in chloroform with hydroxyapatite powder at component weight ratios of 90/10, 80/20, 70/30, and 60/40. The physicochemical characteristics of the surface are very sensitive to the composition of the composites.

(2) For pure polylactide as component of composites, the CSD size decreases by a factor of 2, suggesting the formation of composites with polylactide-coated elements of hydroxyapatite structure, and is accompanied by a decrease in crystalline domains of polylactide. For hydroxyapatite, the main characteristics of crystallinity are preserved.

(3) All the samples obtained are hydrophilic ($\theta < 90^\circ$). With an increase in the polylactide content in the composite materials, the surface energy σ_{S-G} increases from 29.13 to 74.35 mJ m⁻².

(4) A study of the bioresorption of the materials shows that keeping the samples in SBF at 37°C for 28 days results in formation of a new calcium phosphate layer on the surface of the composites, which shows that the materials are capable of osteointegration.

(5) The polylactide/hydroxyapatite ratio of 70/30 is optimum for preparing materials with high functional

properties. The composite is characterized by the highest roughness ($R_a = 4.21 \pm 0.39 \mu\text{m}$); Ca^{2+} and Mg^{2+} ions are actively adsorbed from SBF onto its surface throughout the time of keeping the substrates in the solution.

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