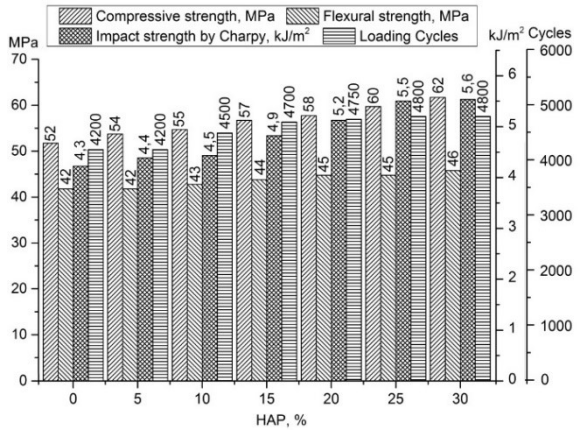


**Fig. 1.** *The mechanical properties of the studied samples with respect to the pure PLA*

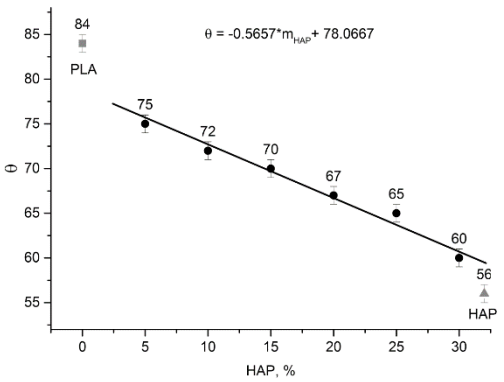


**Fig. 2.** *The limiting contact angle for the composites wetted by an isotonic solution*

position.

Figure 2 presents the wetting angle θ for the studied composites as a function of HAP content $m_{HAP}$, with pure PLA material (84±1°) and HAP based ceramics (56±1°) marked as reference points. The wettability of pure PLA by physiologic fluids is very low with the limiting angles reported in literature lying in the range of 84°–95° [2].

### Conclusions

In this work, the composite biocompatible material based on PLA and HAP was developed, fabricated and analyzed. The synthesis of the initial composite powder and its processing into the filament suitable for the additive manufacturing was described in details. The optimized extrusion and printing parameters were also evaluated and discussed for a range of composites with the mass fraction of HAP varying from 5 % to 30 %. Overall, the obtained data indicated that combining HAP with PLA within a single material ensured the synergy of the physical, chemical and mechanical properties of both initial components. Thus after the successful clinical trials, the composite and fabrication approach described in this work could be implemented in the regenerative medicine for the production of implants with any arbitrary shapes.

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# THE METHOD OF NMR FOR INVESTIGATION OF LIQUID-LIQUID EQUILIBRIUM IN ETHANOL – FORMIC ACID – ETHYL FORMATE – WATER SYSTEM

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Development of coupled processes (these processes combine phase transition and chemical reaction) for chemical technology requires detailed information on structure and features of phase diagrams of reacting systems since phase transition that takes place during synthesis can complicate and fundamentally change realization of technological process. For example, to organize industrial synthesis of esters, it is necessary to take into account location of the heterogeneity region on phase diagram (its presence is explained by the limited mutual solubility of ester and water), since kinetics of syn-

thesis can change significantly when the chemical reaction takes place in the area of splitting of reacting mixture due to the difference in the properties of aqueous and organic coexisting phases. In this regard, for industrial technologies of synthesis, initial concentrations of reagents are chosen in such a way to avoid undesirable phase transformations and to carry out synthesis in a homogeneous solution. The object of investigation was ethanol – formic acid – ethyl formate – water system with reaction of ethyl formate synthesis at 25 °C and 35 °C. Ethyl formate is an industrially important ester used, for example, in the production of paints and varnishes and polymer materials, in pharmaceutical and food industries. To study the area of splitting of solution (i.e. liquid-liquid equilibrium, LLE), the method of nuclear magnetic resonance (NMR) was used. This method for determining of compositions of equilibrium liquid phases is a new, unconventional method for systems under study and for set task. Experimental investigation of LLE in ethanol – formic acid – ethyl formate – water system and in its ternary subsystems ethanol – ethyl formate – water and formic acid – ethyl formate – water, the experimental technique presented in a paper [1] was modified. Sample preparation was carried out in the following way: initial ternary and quaternary mixtures of known overall composition belonging to the heterogeneous area were prepared in vials (5 ml) by gravimetric method and then sealed vials were placed in a liquid thermostat. After reaching phase equilibrium (about 5 min), samples were taken from both phases into new vials (2 ml) and then auxiliary substances were added into vials: ethyl formate (standard substance), deuterated chloroform (solvent, about 90 % of sample volume) and methanol (it was added only into the samples of aqueous phase to homogenize the mixture of partially soluble water and chloroform). Finally, samples were taken from both vials (2 ml) into NMR tubes and compositions of liquid phases were studied by 1H NMR spectroscopy using 500 MHz Buker AVANCE III NMR spectrometer, equipped with a BBI probe head with inner coil for 1H nuclei. The spectra were acquired with an acquisition time of 3 s, a relaxation delay of 1 s, and a pulse with 30° flip angle; 16 scans were accumulated. The processing of the acquired spectra was carried out using Bruker TopSpin software. The uncertainty of determination of peaks' areas is estimated to be 3 %. The peaks in NMR spectrum could be assigned to particular sets of chemically equivalent nuclei. The peak area is directly proportional to the number of nuclei in the corresponding set. If the components of a solution under study and assignment of peaks are known, then it is possible to calculate molar fractions from the values of peaks' areas. About 50 experimental point were obtained for each temperature. After processing the spectra and determining the compositions of coexisting phases, the data were visualized using Origin 9.5 software, 3D solubility surface (a set of tie-lines connecting the points of composition of coexisting phases) was presented in concentration tetrahedron. Such presentation allow estimate exactly form, size and position of the surface (i. e. heterogeneous area) of system under study at 25 °C and 35 °C: the surface is located inside the concentration tetrahedron, it passes near the edge «ethyl formate – water» (this edge corresponds to the binary subsystem with limited solubility), the surface is ended with two triangular faces corresponding to the ternary subsystems "ethanol – ethyl formate –water" and "formic acid – ethyl formate – water", it occupies relatively small part of the concentration tetrahedron (total concentration of acid and alcohol on the surface does not exceed 0.25 mole fraction). The results of investigation contribute to development of the fundamental thermodynamic theory and the thermodynamics of multicomponent liquid-phase systems with chemical interaction; they complete the picture of phase behavior of the systems with reaction of ester synthesis; the results can also be used, for example, to develop new and optimize existing industrial processes of ester synthesis with the aim of increase of their environmental friendliness, energy efficiency and resource saving.

The study was carried out using the funds of grant of Russian Science Foundation (project № 17-73-10127).

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