

Effect of the surface modification of HAp nanoparticles by oleic acid on the properties of HDPE nanocomposites containing thereof

Viktor Tokarev¹, Denis Kalin¹, Maxim Chobit¹, Maria Tokareva²

1. Department of Organic Chemistry, Lviv Polytechnic National University, UKRAINE, Lviv, 12 S. Bandery Street, E-mail: viktor.s.tokarev@lpnu.ua

2. Department of Civil Safety, Lviv Polytechnic National University, UKRAINE, Lviv, 12 S. Bandery Street,

Abstract – This research is devoted to obtaining of HAp-filled nanocomposites with enhanced performans. The goal has been achieved by using HAp nanoparticles modified by oleic acid. This results in an essential increase in the mechanical properties of the obtained nanocomposites as compared to HDPE nanocomposites containing unmodified HAp.

Keywords – Nanocomposite, Hydroxyapatite (HAp), High-Density Polyethylene (HDPE), Surface Modification, Oleic Acid.

Introduction

Important challenges caused by the concern for improving the quality and longevity of people's lives require the development of new functional materials that can be implanted in the human body and replace or facilitate repairing damaged organs. In particular, there is a great demand for materials that replace bone tissue because of, on the one hand, the ageing of the world's populations, and on the other hand, high level of domestic and industrial injuries. In armed conflicts, this need increases significantly. Especially because of the war, there is currently a great need for materials that replace bone tissue. In cases of bone fractures, orthopaedic dentistry and plastic surgery often find it necessary to create temporary or permanent prostheses. Medical applications of xenografts can cause viral infections, while the use of autografts is limited.

It is common practice in orthopaedics now to widely use metal implants such as cobalt-chromium alloys, stainless steel, and titanium alloys for limb injuries. Due to the excessive strength compared to human bone, such implants can cause pathological bone resorption [1], osteopenia, osteoporosis, or even rejected by the body due to insufficient biocompatibility [2]. Therefore, currently orthopaedics is trying to move from metal implants and xenografts/autografts to bioceramic composites possessing high biocompatibility and characterized by a strength corresponding to human bone.

One of the promising ways to obtain such materials is the creation of polymer composite materials filled with mineral nanoparticles, especially hydroxyapatite (HAp) [3,4]. HAp is a natural material that is a component of human bone [5]; natural bones of mammals and humans contain 70% or more of minerals, primarily HAp. Incorporation of HAp as a filler into polymers improves their biocompatibility [6,7]; but, on the other hand, it brings about a deterioration in physico-mechanical properties of the obtained composites [8, 9]. As shown in [5], poor strength of composites is the result of a large difference between the surface energies of the HAp particles and the polymer matrix, i.e. their incompatibility. Many diverse techniques have been developed and used to improve the interfacial compatibility between HAp fillers and polymer matrix; mostly, this is achieved by applying various methods of modifying the filler surface, which are reviewed in [10, 11]. The type of surface modifier applied is highly dependent on the nature of the matrix polymer, which can be conventional synthetic polymers (polyethylene, polypropylene, epoxy resins, etc.), natural polymers (collagen, starch, chitin, chitosan, etc.), synthetic biocompatible and biodegradable polymers (e.g. polylactic acid, hydroxyalkanoate, polyamide, polyglycolic acid);

each of them has its own advantages, disadvantages, and suitable uses [12]. The two last types of polymers are usually characterized by inferior physico-mechanical properties. Moreover, their biodegradation *in vivo* leads to a further deterioration of their performance. Polymers of the first type are quite strong materials, while they have low or no biocompatibility, but it can be improved by adding HAp fillers [6]. However, to achieve sufficient physico-mechanical properties of composites based on these type polymers, the polar surface of HAp filler should be modified for its better compatibility with polymer matrix.

Here we present the results obtained in the study of applying oleic acid as a surface modifier for HAp nanoparticles aimed at obtaining the polymer nanocomposites with improved performance.

Experimental techniques

Materials

Calcium nitrate $\text{Ca}(\text{NO}_3)_2$ and diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ were used as the precursors for the synthesis of hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ nanoparticles (**HAp NPs**).

Oleic acid (**OA**) was used as a surface modifier of HAp NPs.

Ethyl acetate (**EA**), used as a solvent, was distilled and dried over CaCl_2 before the use.

All reagents were of reagent grade quality supplied by Sigma-Aldrich Co.

A commercial high-density polyethylene of grade **HDPE** 21008-075 (GOST 16338-85) was applied as a matrix polymer for obtaining the nanocomposites. HDPE of this grade is approved for application in medical accessories and devices, as well as in the food industry.

Synthesis of hydroxyapatite nanoparticles

HAp NPs were synthesized by a precipitation reaction occurring when two aqueous solutions of precursors salts CaNO_3 and $(\text{NH}_4)_2\text{HPO}_4$ were mixed in accordance with method described elsewhere [13]. Briefly the procedure was as follows. Initially aqueous solutions of precursors salts both with the concentration of 5 wt.% were prepared separately in the amounts corresponding to the molar ratio $\text{Ca/P} = 1.67$. The first solution containing Ca^{2+} ions was thermostated at 70°C and vigorously stirred with a magnetic stirrer (700 rpm). The solution of $(\text{NH}_4)_2\text{HPO}_4$ was then added dropwise to the first solution for 4 hours. Because the phosphate solution is slightly alkaline ($\text{pH} \sim 8$), an NH_4OH solution was used to maintain the pH of the reaction mixture to a value of 11. Afterwards the reaction mixture was allowed to mature for 20 hours under continuous stirring (500 rpm) while maintaining the temperature of 70°C . After synthesis, the mixture was filtered and washed three times with distilled water. Afterwards the precipitate was dried at 80°C to constant weight. The resulting powder of nano HAp was characterized by X-ray diffraction (**XRD**), Fourier transform infrared spectroscopy (**FTIR**) and Scanning Electron Microscopy (**SEM**).

Surface modification of HAp

Modification of HAp was performed as follows. 0.05-0.25 g of the surface modifier OA, that corresponded to 1-5 wt.% relatively to the amount of HAp, was dissolved in 10 ml of EA. 5 g of HAp was added to this solution and stirred with a magnetic stirrer (500 rpm) for 2 hours at ambient temperature. The precipitate of the modified HAp was separated by decantation, rinsed with a fresh portion of EA, decanted again, and dried at 60°C to a constant weight. The resulting powder was characterized similarly to the previous sample.

Obtaining of nanocomposite HDPE/HAp

HDPE/HAp nanocomposites were prepared according to the following procedure. A mixture of 1.6 g of HDPE and 0.4g of HAp (pure or modified) was mixed and finely ground in a mortar. The resulting fine powder was then press-molded at high temperature into specimens for further examination. To prevent sticking of nanocomposites to the surface of press-mold, its working

surface was covered with a polyethylene terephthalate thin film, afterwards the press-mold was filled with the HDPE/HAp mixture. The press-mold was kept under load (27 kPa) for 1 hour, then thermostated at 180 °C for 4 hours, and finally placed again under load (27 kPa) for 1 hour. As a result, the standard type -II dumbbell-shaped specimens of nanocomposites for testing the tensile properties and the impact strength were obtained. These specimens were also used for measurement of the surface hardness of nanocomposites.

Characterization of HA and HDPE-HA nanocomposites

X-ray diffraction studies of the structure of HAp samples were performed exploiting an automated diffractometer DRON-3. Cu K α radiation (wavelength 0.154 nm) from a Cu X-ray tube, run at 20 mA and 40 kV, was used. X-ray diffractograms of the samples were recorded in the 2 θ range from 10 to 60 ° at a scanning speed of 1 °/min.

Fourier transform infrared spectra of HAp nanoparticles before and after surface modification with OA, as well as the samples of pure HDPE and HDPE/HAp nanocomposites, were recorded using a Cary 630 FTIR instrument in the range of 4000-650 cm⁻¹ at resolution of 2 cm⁻¹ and averaged after 32 scans.

Scanning electron microscopy was used to observe and prove the effect of deagglomeration of HAp nanoparticles caused by the OA modifier, and to study the morphology of the fracture surface of nanocomposites. Scanning electron microscopes Selmi REM-106I were used for this purpose.

Thermomechanical studies of nanocomposites were carried out on a TIRA Vicat tester FVW R7/90. For testing, a specimen of the tested material was placed on a horizontal stand and pressed on top with a steel needle, having a flat end with an area of 1 mm², loaded with a weight of 5.0 kg (49 N), that corresponds the pressure of 49 Pa. A specimen was heated at the rate of 50 K/h. As the temperature raised, the needle under load gradually dipped into the specimen because of its softening, the deviation of the needle from the initial position was recorded every 1 minute using a clock-type indicator.

Evaluation of mechanical performance of nanocomposites

Tensile testing was performed in accordance with ISO 527 1:2019 standard exploiting a Universal Testing Machines Tira Test 2000 at room temperature with the crosshead speed 10 mm/min. At least five the type II dumbbell-shaped specimens of each nanocomposite were tested. The averaged values of tensile strength and maximum elongation at break were reported in the results, the deviation did not exceed 7% in all trials.

Impact strength was determined on a TIRA Charpy pendulum impact tester in accordance with ISO 8256:2004 standard. The mean values obtained for at least five specimens of each nanocomposite were reported.

The surface hardness of the obtained nanocomposites was determined on a König Pendulum Hardness Tester M-3 according to ISO 1522:2022 standard. The surface hardness was calculated using the formula (1):

$$T = \tau_p / \tau_g \text{ (relative units)} \quad (1)$$

where τ_p is the oscillation time of the pendulum on the nanocomposite surface, sec; τ_g is the oscillation time of the pendulum on a glass plate, sec.

The oscillation time was measured in three parallel experiments. If the difference in the results did not exceed 2 sec, these results were averaged. If the difference exceeded 2 sec, two more tests were performed; and the results were averaged omitting maximum and minimum values.

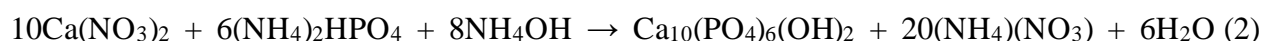
Results and discussion

Obtaining of nanocomposites filled with the surface-modified HAp, supposed to be used as materials for manufacture of artificial bones, is a two-step process.

The first step includes obtaining and a surface-modification of nano-HAp. In our case, OA has been used as a modifier. OA has an amphiphilic structure with highly polar and reactive carboxyl group and lipophilic tail. The presence of carboxyl group in molecule of OA provides its interaction with the superficial hydroxylic (base) groups of HAp, i.e. provides chemisorption of OA. The chemisorption of OA provides bonding with the HAp surface of the OA lipophilic tails, which should promote better affinity of the filler nanoparticles towards the polymer matrix, and in turn lead to improvements of the nanocomposite performance.

Obtaining of the final nanocomposite is the second stage. Nanocomposites have been obtained on the base of thermoplastic polymer (HDPE) by fusing the mixes of powdered polymer with nano-HAp. For comparison both unmodified and surface-modified HAp nanoparticles have been used as fillers to reveal the effect of the surface modifier OA on performance of the final nanocomposites.

The pure hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ nanoparticles have been synthesized in aqueous solution as described above via the interaction of two precursors salts, namely CaNO_3 and $(\text{NH}_4)_2\text{HPO}_4$, in accordance with following reaction:



Freshly synthesized HAp nanoparticles have been subjected to surface modification with OA as a surface modifier to improve a compatibility of hydrophilic highly polar HAp nanoparticles towards the non-polar polymer matrix (polyethylene). The procedure used is described above. It was supposed that the surface modification ought to be realized via the interaction of the carboxylic group of OA with the superficial base centers of HAp according to the presented scheme (Fig. 1):

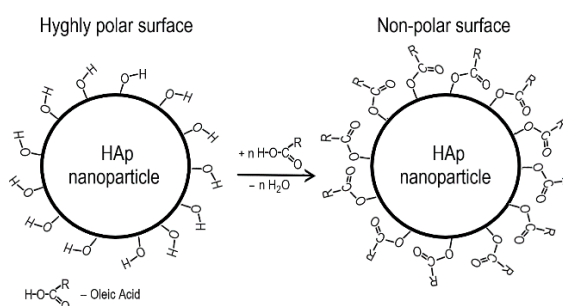


Fig. 1. Schematic representation of OA chemisorption at the surface of HAp nanoparticles.

In our view, well consisting with other authors [14], turning of a highly polar surface of HAp nanoparticles into a non-polar one should cardinaly enhance its affinity towards the polyethylene matrix, thus improving the wettability and compatibility of HAp nanoparticles as well as their dispensability in the polymer matrix. Finally, this should lead to an improvement in the mechanical performance of the obtained nanocomposites as compared with nanocomposites obtained using unmodified HAp nanoparticles, which was the main target of this study.

The choice of OA as a surface modifier, among other fat acids, is explained by the fact that the OA molecule occupies the largest surface area (at the interface compared to that of other fat acids with the same number of Carbon atoms in the carbon tail [15]). This effect is explained by the 'unique molecular shape' of OA, which has a kink at the middle of its molecule, unlike its analogues, e.g. elaidic and stearic acids (Fig. 2).

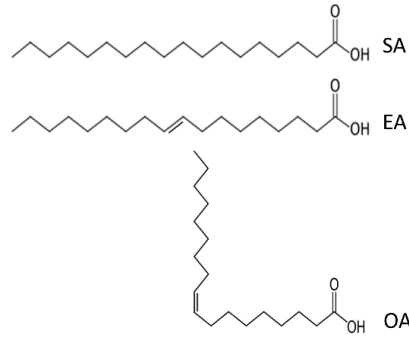


Fig. 2. Structure of stearic (SA), elaidic (EA) and oleic (OA) acids.

Understandable Comprehensible, the larger area occupied by the one modifier molecules the lower surface concentration of this modifier required to completely cover the modified surface; i.e. one needs lower amount for modification of the nanoparticle's surface turning it from hydrophylity to oleophylity. Thus OA has preferences in this sense compared with other its analogues. Additionally, OA is quite cheap and easy available reagents.

To reveal effect of OA chemisorption on the properties of HAp nanoparticles, a comparative investigation was carried out by X-ray diffractometry, FTIR spectroscopy and SEM of HAp samples, both as synthesized and after surface-modification.

1. Characterization of HAp nanoparticles

The results of X-ray diffraction analysis of the synthesized HAp sample are shown in Fig. 3.

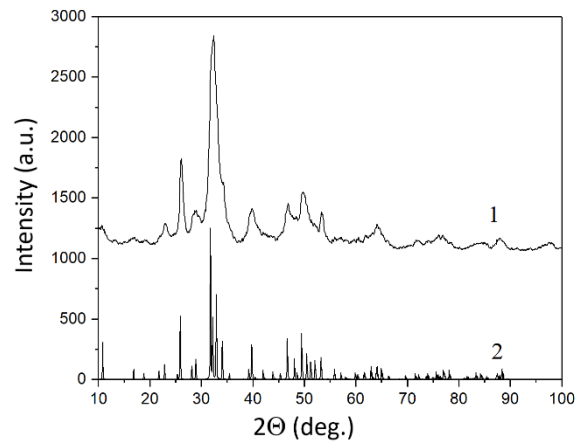


Fig. 3. XRD patterns of the synthesized HAp samples (1) and standard HAp (JCPDS file number 9-0432) given for reference (2).

It clearly indicates that the obtained sample is composed by pure hydroxyapatite with the hexagonal structure, since all its diffraction peaks correspond to the peaks of the reference XRD pattern (JCPDS file number 9-0432) of standard HAp [16]; there are no any other peaks in XRD pattern of synthesized HAp. However, there is a difference between these two XRD patterns, one can note appreciable broadening of all peaks in the previous XRD pattern, which can be explained by nanosize of the synthesized HAp nanoparticles [17]. Moreover, the relationship between the crystallite size and full-width at half-maximum of the XRD peak allows to estimate an average particle size (L) using Debye-Scherrer equation 3 [18]:

$$L = \frac{0.9 \cdot \lambda}{\beta \cdot \cos\theta} \quad (3)$$

where λ is the wavelength of X-ray (0.154 nm), β is the full width at half maximum (FWHM), θ is the angle of diffraction and L is the crystallite size.

The average sizes of HAp crystallites, calculated using equation 3 and data obtained for several diffraction peaks in Fig. 3, are summarized in Table. 1, which shows that the synthesized nanocrystals of hydroxyapatite have a rather elongated shape with dimensions of about 9×18 nm.

Table. 1

Crystallographic data of the obtained HAp

2θ (degree)	d (Å)	$I_{\text{int.}}$ (a. u.)	(hkl)	B (degree)	b (degree)	β (degree)	L (nm)
26.12	3.4110	603	(002)	0.693	0.138	0.555	18.0
31.83	2.8110	849	(211)	0.740	0.154	0.586	15.4
32.33	2.7686	746	(112)	0.730	0.158	0.572	17.2
32.89	2.7231	1555	(300)	1.431	0.159	1.272	9.4
34.27	2.6169	262	(202)	0.821	0.159	0.662	13.9

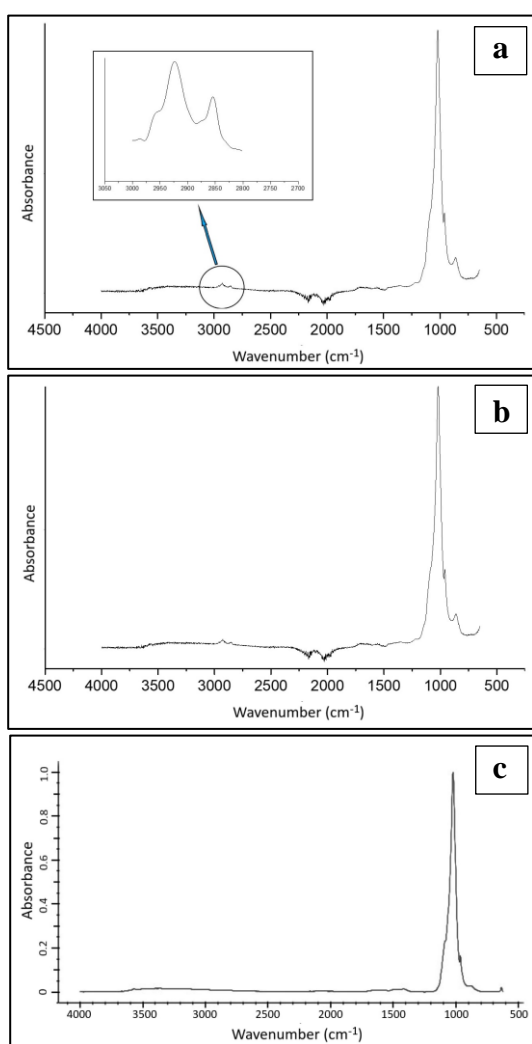


Fig. 4. FTIR spectra of HAp: a) HAp nanoparticles modified with 2% OA; b) pure HAp nanoparticles as synthesized; c) reference Spectrum of HAp Wiley ID SIAL_ATR-IR_011624 SpectraBase

<https://spectrabase.com/spectrum/G6i44b42hBS>

To confirm the chemisorption of OA at the surface of HAp, FTIR spectra have been recorded for samples of unmodified and surface modified HAp powders. Fig. 4 shows the FTIR spectra of HAp nanoparticles prior and after surface modification with 2% OA; the FTIR spectrum ID G6i44b42hBS for HAp (Fig. 4, c), taken from SpectraBase [19], is also given there for reference.

It is clearly seen that the FTIR spectrum (Fig. 4, b) of the pure HAp nanoparticles synthesized corresponds well to the reference spectrum (Fig. 4, c). The peaks in the range of $800-1200 \text{ cm}^{-1}$ are present in both spectra. Particularly, the peaks around 1020 cm^{-1} to 1090 cm^{-1} correlate with asymmetrical P-O bonds stretching vibrations [20].

Compared to the previous spectra, new peaks appear in the FTIR spectrum of the surface-modified HAp nanoparticles (Fig. 4, a) in the range of $2800-3000 \text{ cm}^{-1}$, which can be especially well recognized in the inset to this figure. Indeed, absorption bands at 2926 cm^{-1} and 2853 cm^{-1} correspond to asymmetric stretching $\nu_{\text{as}}(\text{CH}_2)$ and symmetric stretching $\nu_{\text{s}}(\text{CH}_2)$ of methylene groups, respectively. Obviously, these groups belong to carbon chain of oleic acid, thus confirming the presence of its molecules at the surface of modified HAp nanoparticles, i.e. successful modification.

Dynamic light scattering (DLS) was applied for an analysis of particle size distribution of the HAp powder prior and after surface modification with 2% OA (Fig. 5).

As can be seen from results shown in Fig. 5, the unmodified HAp particles have an average size of 254 nm and are characterized by a unimodal size distribution with a rather narrow polydispersity, polydispersity index value = 0.09. Appreciably large average size of HAp particles determined by DLS analysis, compared with that estimated when using XRD data, can be explained by high tendency of HA nanoparticles to agglomerate.

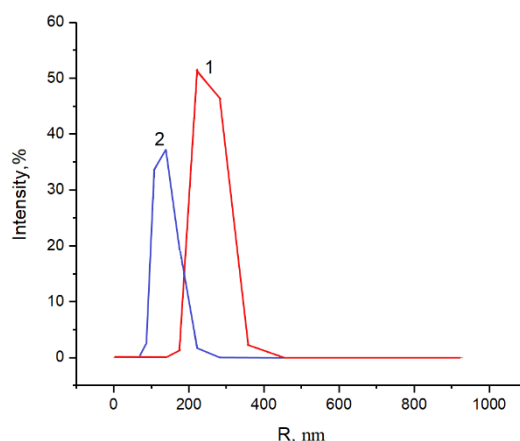


Fig. 5. Particle size distribution of the HA powder: (1) - unmodified HAp, HAp modified with 2 wt.% OA (2).

The surface modification of HAp nanoparticles with 2% OA brings about their partial deagglomeration, which is reflected in dropping down an average size up to 135 nm, the polydispersity remains unimodal, although it becomes somewhat larger, after surface modification polydispersity index value = 0.25. A deagglomeration under the OA modification is reflected in an increase in the specific surface area of HAp nanoparticles. The specific surface area, determined by the standard N₂ adsorption technique, increases from 180 m²/g for unmodified HAp up to 290 m²/g after its modification with 2% OA.

An agglomeration of HAp nanoparticles is also confirmed by SEM. Images of unmodified and surface modified HAp powders are shown in Fig. 6.

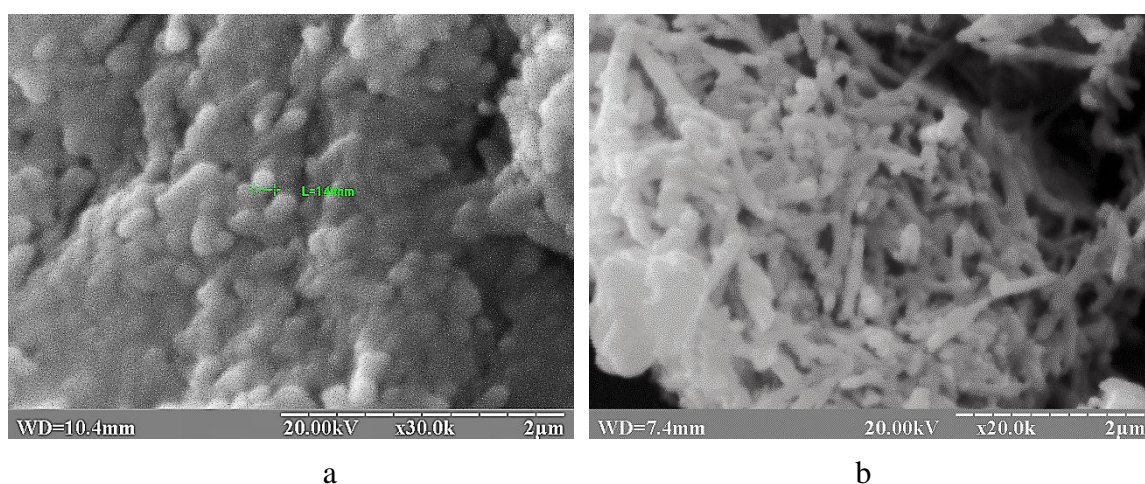


Fig. 6. SEM image of HAp powder (a), modified with 2 wt.% OA (b)

Comparing the left and right images, the effect of partial deagglomeration caused by chemisorption of OA at the surface of HAp nanoparticles is clearly seen. In the second case, the particles are not so densely packed as in the case of unmodified HAp. Probably, this phenomenon

can be explained by diminishing the hydrogen bonds after surface modification caused by the substitution of hydroxyl groups at the surface of HAp particles with salt bonds, as shown in Fig. 2.

Obtaining the final nanocomposite is the second stage. Nanocomposites have been obtained on the base of thermoplastic polymer (HDPE) by fusing polymer granules with filler. A modified HAp was used as a filler.

To confirm that the HAp modification is effective in improving the physical and mechanical properties of the nanocomposites, they were compared with nanocomposites filled with unmodified HAp. which was OK. A sample with unmodified HAp was also obtained to compare the effect of the modifier on the properties of the final nanocomposite.

2. Characterization of HDPE/HAp nanocomposites

The HDPE-based nanocomposites have been obtained using both unmodified and surface-modified HAp nanoparticles for the comparison.

The following formulation of nanocomposites were used: 80 wt.% of HDPE and 20 wt.% of HAp. There was no sense to obtain nanocomposites with a HAp content of more than 20% because of their very high brittleness. Both unmodified and modified HAp nanoparticles were used as fillers to reveal the effect of the surface modifier OA on performance of the final nanocomposites. In the case of modified HAp filler, the amount of OA was varied: nano-HAp modified with 1, 2 and 5 wt.% (relatively to the taken HAp amount) were obtained and composed with HDPE.

The procedure of obtaining the specimens of nanocomposites is described in Experimental techniques.

Figure 7 shows the FTIR spectra of pure HDPE and nanocomposite of HDPE with HAp modified with 2 wt.% of OA.

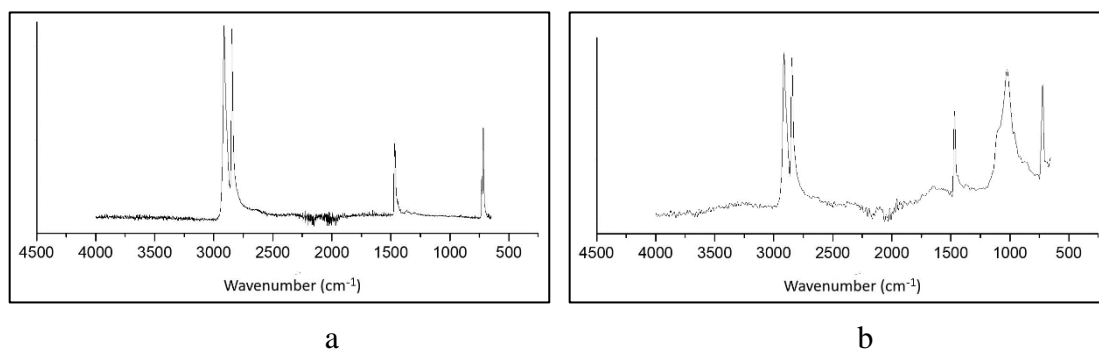


Fig. 7. FTIR spectra of pure HDPE (a) and nanocomposite of HDPE with nano-HAp modified with 2 wt.% OA (b)

The following characteristic absorption peaks are observed on the FTIR spectrum of pure HDPE: 2913 cm^{-1} and 2846 cm^{-1} correspond to asymmetric stretching and symmetric stretching of methylene groups $-\text{CH}_2-$, respectively; 1471 cm^{-1} the bending of the HDPE structure; 1364 cm^{-1} corresponds to $-\text{CH}_3$ symmetric deformation; 717 cm^{-1} corresponds to rocking deformation [21].

In the FTIR spectrum of nanocomposite of HDPE with the surface-modified nano-HAp, besides the aforementioned peaks, new very strong absorption peaks are observed in the region of $800\text{--}1200\text{ cm}^{-1}$, especially at 1020 cm^{-1} , which are obviously attributed to HAp nanoparticles (compare with Fig. 4). Thus, the FTIR spectra gives strong evidence for formation of nanocomposites.

Studies of the thermomechanical properties of HDPE nanocomposites with unmodified and modified HAp nanoparticles (Fig. 8) do not show difference in their Vicat softening temperature. The reason of such behaviour can be explained by the fact that the Vicat softening temperature is determined predominately by properties attributed to the polymer matrix which is a continuous

phase. A notable increase in the softening temperature can be observed only in the case of strong bonding the matrix polymer to the filler; but this is not our case. However, less deformation of the specimen under load after its softening in the case of nanocomposites with surface-modified HAp nanoparticles evidences about a stronger interaction of the matrix polymer with the OA-modified surface of HAp nanoparticles that with the bare surface of unmodified HAp.

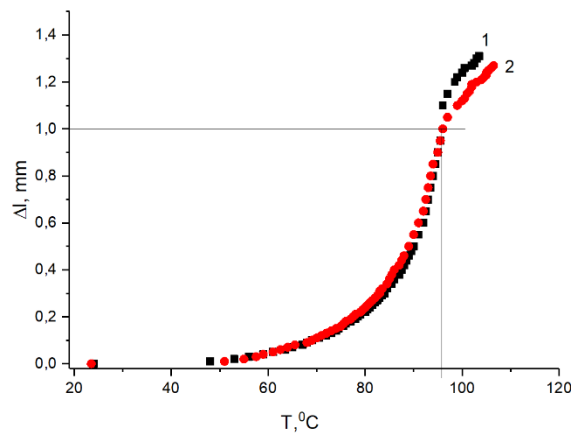


Fig. 8. Thermomechanical properties of HDPE nanocomposites with: unmodified HAp (1); HAp modified with 2 wt.% OA (2).

The comparative investigation of the physico-mechanical properties of HDPE/HAp nanocomposites has been performed.

The results of the tensile strength and impact strength testing of nanocomposites are shown in Table 2. One can notes a significant increase in both the tensile strength and impact strength of nanocomposites caused by application of 2 wt. % of OA for a surface modification of HAp nanoparticles. Indeed, the tensile strength of nanocomposites with 2%-modified HAp increases by 66% and the impact strength increases by 10% (Table 2, line 4) as compared to those of nanocomposites with unmodified HAp (Table 2, line 2). It worth be noticed, that at the same time, when the content of OA was increased to 5 wt. %, the properties of the nanocomposite obtained sharply deteriorated, its fragility sharply increases, so it was not possible to obtain specimens for testing. Thus, 2 wt. % of modifier is seamed to be an optimum amount.

Table. 2

Tensile strength and impact strength for the resulting nanocomposites

#	Ratio of HDPE/HAp (%)	Content of modifier (%)	Elongation at break (%)	Tensile strength (MPa)	Tensile strength gain (%)	Impact strength (kJ/m ²)	Impact strength gain (%)
1	100/0	–	85,25	27,6	–	35,0	–
2	80/20	0	1.42	17,1	–	28,4	–
3	80/20	1	1.71	22,4	+30	29,3	+3,0
4	80/20	2	1.78	28,6	+66	31,5	+10

Fig. 9 shows the fracture surface of the HDPE/HAp nanocomposite, in which the size of the HAp agglomerates is in the same range as for HAp in powder (Fig. 10). Additionally, to reveal HAp nanoparticles, the samples of HDPE/HAp nanocomposites were subjected to concentrated nitric acid for 15 minutes at 60°C. Under these conditions the entire HAp was washed away, while the polyethylene matrix remains with the fingerprints appeared after removing HAp nanoparticles (Fig. 10). These SEM images confirm the presence of nanoscale HAp in the nanocomposite. Comparing the SEM images in Fig. 10, the conclusion can drown that in the case of the surface-modified HAp its agglomerates are smaller and distributed more evenly throughout the polymer

matrix (the cavities remained are much smaller and well distributed) as compared with nanocomposite containing unmodified HAP.

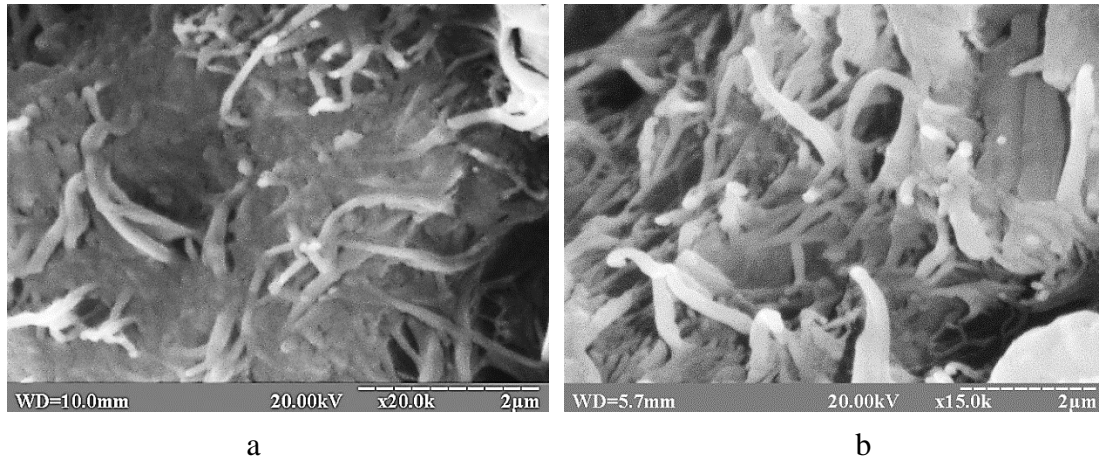


Fig. 9. SEM images of the fracture surface of HDPE nanocomposites with: unmodified HAP (a); HAP modified with 2 wt.% OA (b)

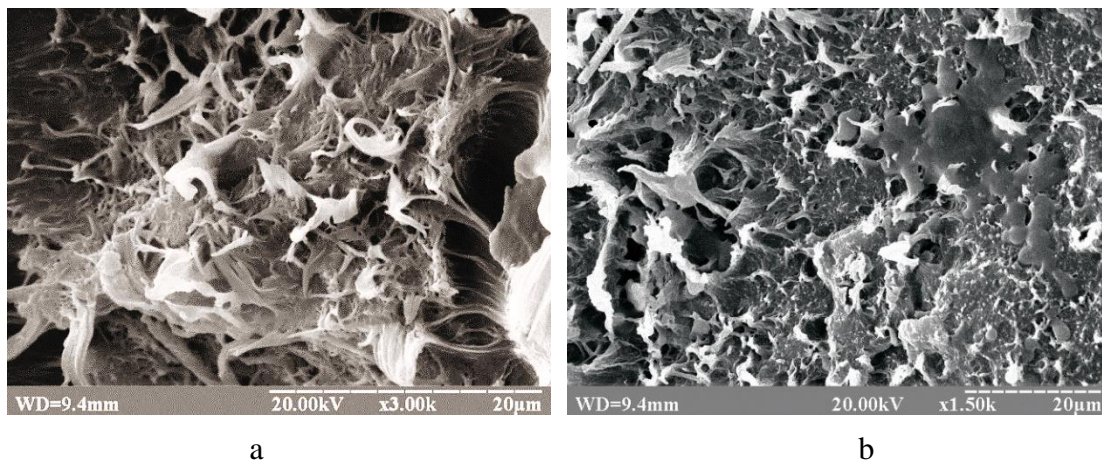


Fig. 10. SEM images of the fracture surface after exposure to nitric acid of HDPE nanocomposites with: unmodified HAP (a); HAP modified with 2 wt.% OA (b).

To confirm the stability of the obtained nanocomposites in the human body, the obtained specimens were soaked in water and saline for five days and then tested for the impact strength (Fig. 11) and surface hardness.

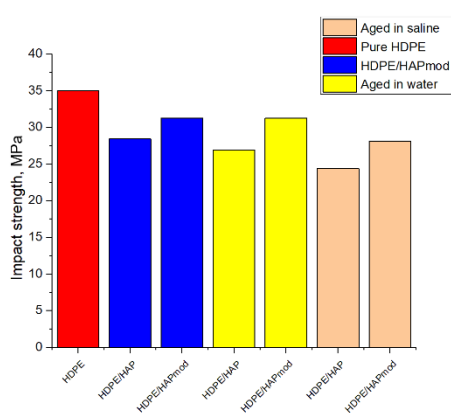


Fig. 11. The impact strength of nanocomposites filled with unmodified HAP and HAP with 2 wt.% OA.

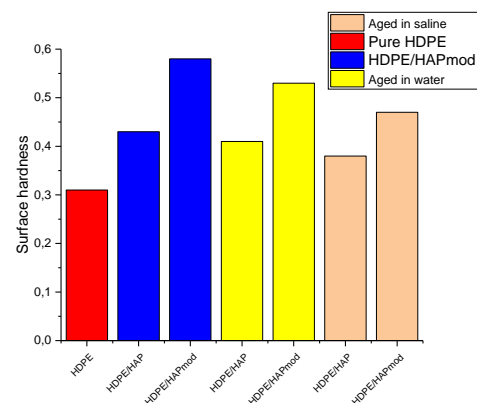


Fig. 12. Relative values of surface hardness of nanocomposites filled with unmodified HAP and HAP with 2 wt.% OA.

Analyzing these data, it can be concluded that the surface modification of HAp with 2 wt.% OA in all cases provides better nanocomposites performance compared with nanocomposites containing unmodified HAp, the impact strength increases by about 10%, and the surface hardness – by about 25-30%. There is no drastic deterioration in the nanocomposite properties after their exposure to water and saline.

Conclusions

HAp nanoparticles have been synthesized and surface-modified using OA. Chemosorption of OA brings about deagglomeration and lipophilisation of nanoparticles. The latter facilitates an even distribution of the HAp filler in the polymer matrix. HDPE-based nanocomposites have been obtained using both unmodified and surface-modified HAp nanoparticles for comparison. An increase in the performance of nanocomposites filled with HAp, modified by OA, compared with unmodified HAp, is shown. A significant increase in tensile strength and surface hardness is achieved by applying a small amount of modifier. 2 wt.% of OA chemisorbed at the surface of HAp nanoparticles brings about an increase in tensile strength by 66% and surface hardness by 31%. The obtained nanocomposites are quite stable when subjected to aqueous media with only a slight loss in the physico-mechanical properties. This makes them a good candidate to apply as bone substitute materials.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

References

- [1] Jaggi, H.S., Kumar, S., Das, D., Satapathy, B.K.R., Ray, A.R. (2015). Morphological correlations to mechanical performance of hydroxyapatite-filled HDPE/UHMWPE composites. *J. Appl. Polym. Sci.*, 132 (1), 1–10. DOI: 10.1002/app.41251.
- [2] Sloten, J. V., Labey, L., Van Audekercke, R., (1998). Materials selection and design for orthopaedic implants with improved long-term performance, *Biomaterials*, 19 (16), 1455–1459. DOI: 10.1016/s0142-9612(98)00058-1.
- [3] Shi, C., Yuan, Z., Han, F., Zhu, C., Li, B. (2016) /Polymeric biomaterials for bone regeneration. *Annals of Joint*, 1 (9), 27. DOI: 10.21037/aoj.2016.11.02.
- [4] Oladele, I. O., Agbabiaka, O. G. (2019). Structural performance of poultry eggshell derived hydroxyapatite based high density polyethylene bio-composites. *Heliyon*, 5 (10), 1-7. DOI: 10.1016/j.heliyon.2019.e02552.
- [5] Šupová, M. (2009). Problem of hydroxyapatite dispersion in polymer matrices: A review. *J. Mater. Sci: Materials in Medicine*, 20 (6), 1201–1213. DOI: 10.1007/s10856-009-3696-2.
- [6] Herman, V., González, G., Noris-Suárez, K., Albano, C., Karam, A., Romero, K., Yndriago, L., Marquez, A., Lozada L. (2009). Biocompatibility studies of HDPE–HA composites with different HA content. *Polymer Bulletin*, 62 (1), 45-55. DOI: 10.1007/s00289-008-1011-x.
- [7] Jaafar, C. N. A., Zainol, I., Khairani, M. I. I., Dele-Afolabi, T. T. (2022). Physical and Mechanical Properties of Tilapia Scale Hydroxyapatite-Filled High-Density Polyethylene Composites. *Polymers*, 14 (2), 251. DOI: 10.3390/polym14020251.
- [8] Yi, Z., Yubao, L., Jidong, L., Xiangn Z. (2007). Novel bio-composite of hydroxyapatite reinforced polyamide and polyethylene: Composition and properties. *Materials Science and Engineering: A*, 452 (3), 512–517. DOI: 10.1016/j.msea.2006.11.138.

- [9] Wang, Z.-P., Huang, Y.-F., Xu, J.-Z. (2015). Injection-molded hydroxyapatite/polyethylene bone-analogue biocomposites via structure manipulation. *J. Mater. Chem.: B* 3 (38), 1–9. DOI: 10.1039/C5TB00643K.
- [10] Wilson, O. C. (2009). Surface Modification of Hydroxyapatite: A Review. In R.J. Narayan, P.N. Kumta, W.R. Wagner (eds.). *Advances in Biomedical and Biomimetic Materials*. Publisher: WILEY. DOI: 10.1002/9780470538357.ch17.
- [11] Nabipour, H., Batool, S. Hu, Y. (2023). Chemical surface modification of hydroxyapatite for biomedical application: A review. *Emergent Mater.* 6, 31–44. DOI: 10.1007/s42247-021-00322-2.
- [12] Zhang, J., Feng, Y., Zhou, X., Shi Y., Wang, Li. (2021). Research status of artificial bone materials *International Journal of Polymeric Materials and Polymeric Biomaterials*, 70 (1), 37-53. DOI: 10.1080/00914037.2019.1685518.
- [13] Pu'ad, N. M., Haq, R. A., Noh, H. M., Abdullah, H. Z., Idris, M. I., Lee, T. C. (2020). Synthesis method of hydroxyapatite: A review. *Materials Today: Proceedings*, 29, 233-239. DOI: 10.1016/j.matpr.2020.05.536.
- [14] Wang, M., Bonfield, W. (2001). Chemically Coupled Hydroxyapatite-Polyethylene Composites: Structure and Properties. *Biomaterials*, 22 (11), 1311-1320. DOI: 10.1016/s0142-9612(00)00283-0.
- [15] Langmuir, I. (1917). The shapes of group molecules forming the surfaces of liquids. *Proceedings of the National Academy of Sciences of the United States of America*, 3 (4), 251-257. <https://www.jstor.org/stable/83667>.
- [16] Rafique, M. M. A. (2018). Hydrothermal Processing of Phase Pure and Doped Hydroxyapatite and its Characterization. *J. Encapsulation and Adsorption Sciences*, 8 (1), 18-37. DOI: 10.4236/jeas.2018.81002.
- [17] Ingham, B. (2015). X-ray scattering characterisation of nanoparticles. *Crystallography Reviews*, 21 (4), 229-303. DOI: 10.1080/0889311X.2015.1024114.
- [18] Winterer, M. (2002). *Nanocrystalline Ceramics: Synthesis and Structure*, Publisher. Springer-Verlag, Berlin. ISBN 3-540-43433-X.
- [19] HYDROXYLAPATITE "HIGH RESOLUTION" - Optional[ATR-IR] - Spectrum SpectraBase. <https://spectrabase.com/spectrum/G6i44b42hBS>.
- [20] Khan, H. M., Iqbal T., Ali C. H., Yasin S., Jamil F. (2020) Waste quail beaks as renewable source for synthesizing novel catalysts for biodiesel production. *Renewable Energy*, 154 (11), 1035-1043. DOI: 10.1016/j.renene.2020.03.079.
- [21] Liu, T., Huang, K., Li, L., Gu, Z., Liu, X., Peng, X., & Kuang, T. (2019). High performance high-density polyethylene/hydroxyapatite nanocomposites for load-bearing bone substitute: Fabrication, in vitro and in vivo biocompatibility evaluation. *Composites Science and Technology*, 175, 100-110. DOI:10.1016/j.compscitech.2019.03.012.10.1016/j.compscitech.2019.03.012.