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ABSTRACT

Sonochemistry is a widely used method for obtaining nanostructure composite materials due to resulting chemical effects, like surface influence of radicals, and physical effects, like intensive dispersion, homogenisation and emulsification. Ultrasonic effects are produced by interaction of ultrasonic waves with liquid-solid medium and cavitation process in intensive ultrasonic field. This method was applied for preparation of DLPLG-HAp biocomposite material. Size, shape, morphology and spatial arrangement of obtained nanoparticles processed at low temperature during the synthetic process were determined. Polymeric parts of sonochemically processed materials obtained at different bulk temperatures (low-8°C and high-25°C) and with different phase constitution (DLPLG:HAp weight percent ratios were 100:0, 90:10 and 75:25) were further analysed. Influence of ultrasound on degradation of DLPLG polymeric chains, changes of molecular mass distribution and relationship between this degradation and some synthetic parameters, like temperature and share of ceramic phase, were evaluated. Samples were characterized using X-ray powder diffraction (XRD) and infrared spectroscopy (IR) - for identification, scanning electron microscopy (FE SEM and SEM) - for morphology analysis and size exclusion chromatography (SEC) - for degradation determining.

MATERIALS and METHODS

HAp was synthesized using $\text{Ca}(\text{NO}_3)_2 \times 5\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ as Ca and P precursors and urea as precipitation agent by homogeneous precipitation method in the field of ultrasound using the following parameters: $T_{\text{max}} = 90^\circ\text{C}$, $t = 2$ h and ultrasonic field power = 600 W. After preparation, HAp was mixed with ethanol and additionally treated with ultrasound for 10 min for breaking down obtained agglomerates. Apatite treated in this way was than mixed and dispersed within polymer solution comprising DLPLG (2% DLPLG in acetone) in an ultrasonic field. The additional precipitation of polymer was initiated by adding ethanol dropwise into the reaction vessel. The applied value of ultrasonic field power was 142.5 W. Temperature of the bulk was $T = 25^\circ\text{C}$. In some cases reaction vessel was cooled by ice with the aim to decrease bulk temperature to $T = 8^\circ\text{C}$ during precipitation process. DLPLG:HAp wt%/wt% was either 90:10 or 75:25. Sonochemical treatment was continued until all the ethanol as non-solvent was added. Final volume of ethanol was twice the volume of acetone. When the precipitation was finished, the obtained colloid mixture was mixed with PVP (100 mL, $2 \cdot 10^{-4}\%$) as surfactant solution. The reaction mixture was than shortly centrifuged at 4000 rpm to spin down the pellet, which was air-dried afterwards. Experimental parameters are summarized in Table 1.

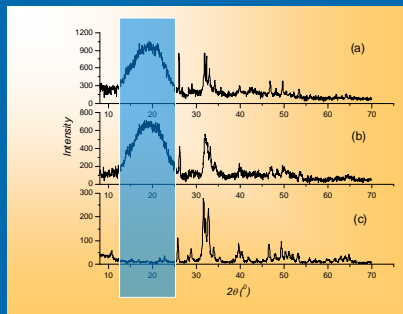


Figure 1: XRD spectra of composite materials with DLPLG:HAp ratio: 90:10 (a), 75:25 (b) and pure HAp (c)

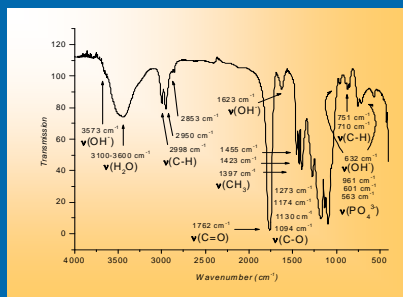


Figure 2: IR spectrum of DLPLG/HAp composite material

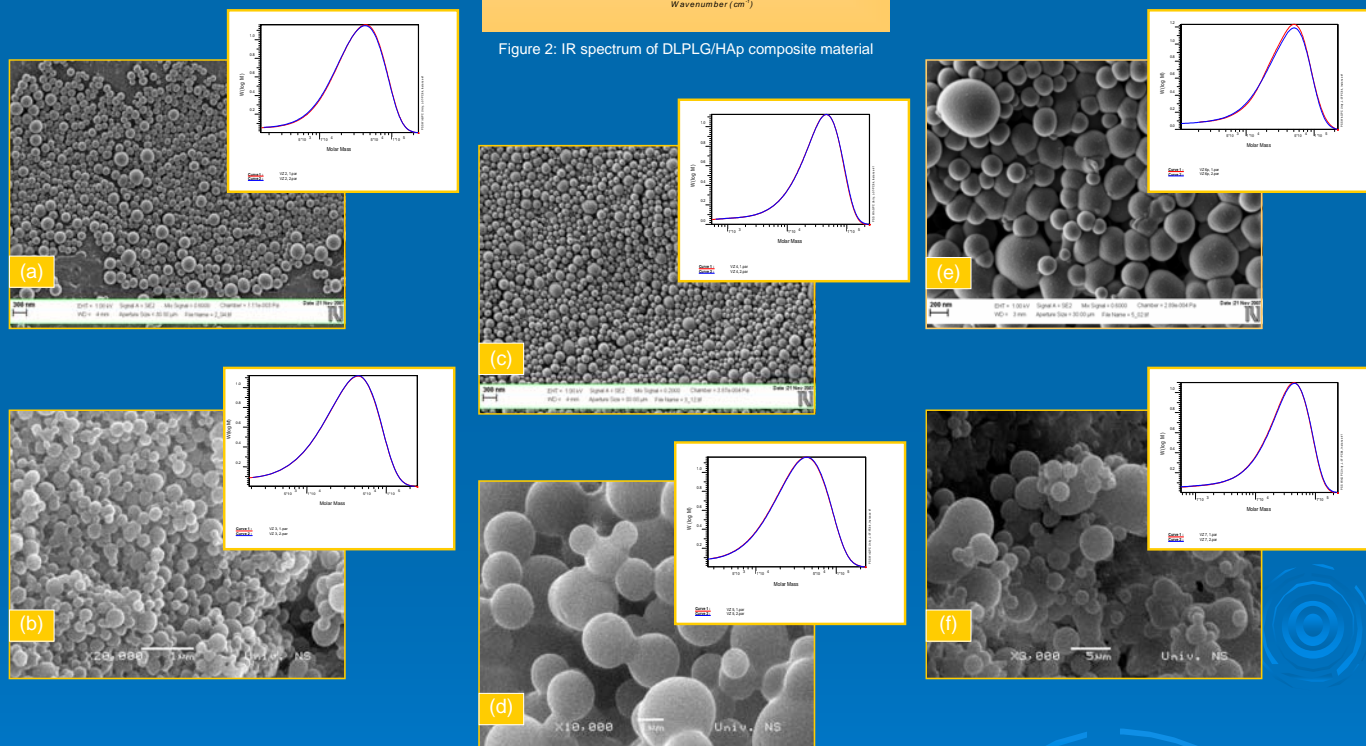


Figure 3: SEM images of sonochemically processed DLPLG polymer (a) and (b) and DLPLG/HAp composites (c), (d), (e) and (f) and corresponding molecular mass distributions obtained by SEC

RESULTS and DISCUSSION

Generally, particles were spherical in shape and with smooth surface. The most regular morphology was obtained for DLPLG/HAp composite with 90:10 weight percent ratio fabricated at lower (8°C) bulk temperature. These spheres were in the range between 50 and 300 nm in size and they had highly regular spatial arrangement. Results showed the existence of DLPLG degradation in the field of ultrasound, decrement of average molecular mass and change in molecular mass distribution width. These effects were accentuated at higher processing temperature. Chain degradation effect in the field of ultrasound was enhanced with higher ceramic (HAp) content. The greatest average molecular mass change was recorded at processing temperature of 25°C and higher (25 wt %) content of hydroxyapatite. These changes were less pronounce in DLPLG/HAp composite with lower (10 wt %) HAp content and in materials obtained at lower (8°C) temperature. Minimum change of molecular mass distribution was determined in pure polymer treated by ultrasonic field. These results indicate acceleration of DLPLG degradation stimulated by interactions between polymeric chains and ceramics in the field of ultrasound.

Table 1: Experimental conditions and SEC calculated results of DLPLG average molecular mass

	DLPLG:HAp	T (°C)	$\overline{M}_w \cdot 10^{-4}$	$\overline{M}_n \cdot 10^{-4}$	$\overline{M}_w / \overline{M}_n$
(a)	100:0	8	4.2211	1.4384	2.93
(b)	100:0	25	3.9560	1.7658	2.24
(c)	90:10	8	4.0374	1.9929	2.03
(d)	90:10	25	3.9192	1.0696	3.67
(e)	75:25	8	4.0181	1.9123	2.10
(f)	75:25	25	3.8376	1.1069	3.47

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