Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Development of New Ternary Nanostructured Hybrids

Roxana Mioara Piticescu [a], Laura Madalina Popescu [a], Aurelia Meghea [b], Viorel Badilita [a] & Eugeniu Vasile [c]

[a] National R&D Institute for Non-ferrous and Rare Metals, Pantelimon, Judetul Ilfov, Romania

[b] National Consultancy Centre for Environmental Protection - UPB, Bucharest, Romania

[c] METAV C-D, Bucharest, Romania

Version of record first published: 16 Jun 2008

To cite this article: Roxana Mioara Piticescu, Laura Madalina Popescu, Aurelia Meghea, Viorel Badilita & Eugeniu Vasile (2008): Development of New Ternary Nanostructured Hybrids, Molecular Crystals and Liquid Crystals, 483:1, 216-227

To link to this article: http://dx.doi.org/10.1080/15421400801918104

Mol. Cryst. Liq. Cryst., Vol. 483, pp. 216–227, 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801918104

Taylor & Francis
Taylor & Francis Group

Development of New Ternary Nanostructured Hybrids

Roxana Mioara Piticescu[1], Laura Madalina Popescu[1], Aurelia Meghea[2], Viorel Badilita[1], and Eugeniu Vasile[3]
[1]National R&D Institute for Non-ferrous and Rare Metals, Pantelimon, Judetul Ilfov, Romania
[2]National Consultancy Centre for Environmental Protection – UPB, Bucharest, Romania
[3]METAV C-D, Bucharest, Romania

Ternary systems based on hydroxyl apatite-purified montmorillonite-organic polymer were synthesized in situ in hydrothermal conditions at high pressures and low temperatures. Complex nanostructured materials were obtained. The possibility of the formation of strong chemical bonds under high pressures, between organic–inorganic phases, has been investigated by Fourier Transform Infrared Spectroscopy (FT-IR). Microstructure and morphology have been investigated by High Resolution Transmission Electron Microscopy (HRTEM). Studies to understand the influence of the synthesis conditions on the final form of nanocomposite have been performed.

Keywords: hydrothermal synthesis; microstructure; morphology; organic–inorganic nanocomposites

INTRODUCTION

Hybrid organic–inorganic materials retained the attention of the scientific community due to their unique properties allowing the development of innovative industrial applications. Nanostructured organic–inorganic hybrids could be use for optical, mechanical,

This article is a result of experimental works performed in the frame of TECOR-EMED project no.16/2005 financed by the National Agency for Scientific Research-Research for Excellence Programme. The authors thank to Dr. Maria Giurginca for performing FT-IR spectra of composites, Dr. Zina Vuluga for providing natural purified montmorillonite and Dr. Gabrielle Chitanu for providing synthetic polymers.

Address correspondence to Roxana Mioara Piticescu, National R&D Institute for Non-ferrous and Rare Metals, 102 Biruintei Blvd., Pantelimon, Judetul Ilfov, PC 077145, Romania. E-mail: roxana@imnr.ro

thermal, electrical or magnetic applications due to their novel physical and chemical properties [1]. Hybrid materials already entered on the market are synthesised by different processes routes based on soft chemistry, namely: copolymerisation of organosilanes and metal alkoxides, encapsulation of organic components within sol-gel derived silica or metallic oxides, organic functionalisation of nanofillers, nanoclays or other compounds with lamellar structures [2]. Bio-nanocomposites represent an emerging group of hybrid materials based on organic naturals or synthetic polymers and inorganic phases which interact at nanometric scale. Among inorganic phases a special attention is paid to layered materials which have the ability to intercalate different bio-polymers leading to hybrids with functional properties [3]. The formation of a strong chemical bonding between organic–inorganic phases could enhance for e.g., the mechanical properties of nanocomposites. One method to form such strong chemical bonding is to functionalise the organic polymer backbone with different groups by a sol-gel process. Polystyrene–SiO_2, PMMA-SiO_2, polyethylene oxide-SiO_2 hybrids were obtained through this method [1]. Sol-gel process creates homogeneous composites with wide range of properties and composition at low temperatures, but it has some drawbacks which limit its technological applications, namely: large volume shrinkage due to the evaporation of large amount of solvent, small molecular hydrolysis by-products and poly-condensation reactions [4]. Development of biomaterials and their synthesis techniques contribute to the broadening of the application field for different biocompatible materials. Bone defects, which appear in different clinical situations, and their reconstruction to restore the backbone integrity is a very important step in patients' recuperation. Recently, new materials, cellular transplant and bioactive molecules were explored to solve bone deficiencies. Development of hybrid polymers systems (copolymers, complexes, hydro gels, etc.) based on natural or synthetic macromolecules and applications large spectrum in biomaterials science was a challenge for the scientific community in the last years. Today, many materials are available for bone replacement (e.g., hydroxyl apatite, calcium phosphate, calcium carbonate, etc.) and their clinical efficiency was already tested by researchers. However, it is still unclear which material could be the best choice for bone replacement. It is well known that mineral phase of the bone is formed from calcium phosphates with structure and composition similar to the natural apatite. Mineral nature of the bone suggests that its properties, density and hardness, are in principal influenced by the formation process of solid crystalline apatite. Thus, the formation of mineral apatite requires the presence of calcium, phosphor, oxygen

and filling ions (Cl^-, F^-, or HO^-). Apatite is one of the flexible minerals which can be easily chemically substituted. Na^+, K^+, Fe^{2+}, Zn^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, etc. are the most known and use ions for calcium substitution in bone mineral phase [5]. On the other hand anionic complexes like AsO_4^{3-}, SO_4^{2-}, CO_3^{2-}, SiO_4^{4-} could replace PO_4^{3-} from mineral apatite structure. The presence of Si^{4+}, SiO_4^{4-} ions in hydroxyl apatite network has an important role in the bony calcification process, improves the osteoblasts activity, and accelerates the formation of mature bone in the crystalline network defects [6].

In the article a new ternary nanostructured hybrid is developed. Nanostructured organic–inorganic hybrids of layered silicates (purified montmorillonite), hydroxyl apatite and phosphorilated polysaccharide were obtained under hydrothermal conditions at high pressures and low temperatures. It is expected that phosphorilated polysaccharide may improve the mechanical properties of hydroxyl apatite and to introduce side chains in the presence of layered silicates.

EXPERIMENTAL

Materials

Purified montmorillonite was obtained from National R&D Institute for Chemistry and Petrochemistry – ICECHIM, Romania. Phosphorilated polysaccharide was synthesised in Institute for Macromolecular Chemistry Petru Poni, Yassi, Romania. Soluble salts of calcium (analytical purity, Merck) and phosphorous (purity $> 99\%$, Merck) were used as starting materials for in situ hydroxyl apatite synthesis under hydrothermal conditions.

Hydrothermal Synthesis of Ternary Nanostructured Hybrids

Soluble salts of calcium and ammonium phosphate aqueous solutions were used as starting materials for hybrid nanocomposite synthesis. These solutions were mixed with an appropriate amount of mineralising reagent (ammonia solution), purified montmorillonite and/or synthetic polymer. Synthesis of complex ternary nanostructured systems was performed in situ under hydrothermal conditions at low temperatures (to avoid degradation of synthetic polymer) and high pressures (> 2 MPa to promote chemical interactions between all the species in the reaction system) in a CORTEST, USA autoclave. The precipitates thus obtained were filtered, washed and dried for several hours in an oven. Some examples of the synthesised samples are presented in Table 1.

Characterisation of the Binary and Ternary Nanostructured Systems

Chemical volumetric and gravimetric methods as well as spectroscopic methods (inductively coupled plasma – ICP; direct coupled plasma-DCP; atomic absorption spectrometry – AAS) were used to determine the composition of binary and ternary systems. X ray diffraction phase analysis (XRD) for binary and ternary systems was performed by Bragg-Brentano diffraction method, coupling $\Theta - \Theta$, on planar samples, with a BRUKER type D8 ADVANCE diffractometer, using characteristic radiation CuKα 1&2. Dismissing CuKβ was performed with SOL X detector. Experimental data were digitally collected, step by step scanning method in the range $2\Theta = 2-74$ grade with a step $\Delta(2\Theta) = 0.020^{\circ}$ and a measure time/step $\tau = 3$ sec. Experimental data were processed with the soft DIFFRACplus BASIC Evaluation Package, version EVA12, 2006 and data base ICDD PDF-2 Release 2006. The bonding nature between organic and inorganic phase was analysed by Fourier Transform Infrared spectroscopy (FT-IR) on a FT/IR 620 JASCO spectrometer. Microstructure characterization by high resolution transmission electron microscopy (HRTEM) and electron diffraction (SAED) was performed on a Philips CM 12 microscope (resolution 2 Å). Small quantities of samples were milled in a mortar and immersed in absolute ethylic alcohol, suspension being homogenized by ultrasonication. Fine particles from homogenized suspension were collected on a copper grid covered with an amorphous porous carbon layer. Thus assayed samples were examined by transmission electron microscopy in bright field (TEMBF), electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM).

RESULTS AND DISCUSSIONS

Representative samples synthesized in hydrothermal conditions (Table 1) were subject of characterization.

Figure 1 shows a representative area of the diffraction pattern used for phase analysis of sample HBP 1, HBP 2, HBP, HBP 4 and FBP1-HT respectively. It can be observed that the peak (001) at $2\Theta = 7.2^{0}$ from montmorillonite is slightly shifted in hydrothermal treated samples, probably due to the interaction of hydroxyl apatite with the top layer of montmorillonite and as the consequence an exfoliated structure could be formed. In Table 2 the results of XRD analysis are summarised. The crystallite sizes of hydroxyl apatite of about 20 nm in samples HBP 1 and HBP 3 could be explained taking into account kinetic considerations: in the first hour the process is diffusion controlled

TABLE 1 Representative Samples Synthesised in Hydrothermal Conditions

No	Sample type	Sample name	Hydrothermal synthesis parameter	Calculated composition
1	Hydroxyl apatite-montmorillonite	HBP 1	150°C/1h p > 2 MPa	95 weight % Hap 5 weight % montmorillonite
2	Hydroxyl apatite-montmorillonite	HBP 3	150°C/2h p > 2 MPa	95 weight % Hap 5 weight % montmorillonite
3	Hydroxyl apatite-montmorillonite	HBP 2	150°C/3h p > 2 MPa	95 weight % Hap 5 weight % montmorillonite
4	Hydroxyl apatite-montmorillonite	HBP 4	150°C/3h p > 2 MPa	50 weight % Hap 50 weight % montmorillonite
5	Hydroxyl apatite-montmorillonite-phosphorilated polysaccharide	FBP 1-HT	150°C/3h p > 2 MPa	85 weight % Hap 5 weight % montmorillonite 10 weight % polysaccharide
6	Hydroxyl apatite	Hap 7	150°C/3h p > 2 MPa	–

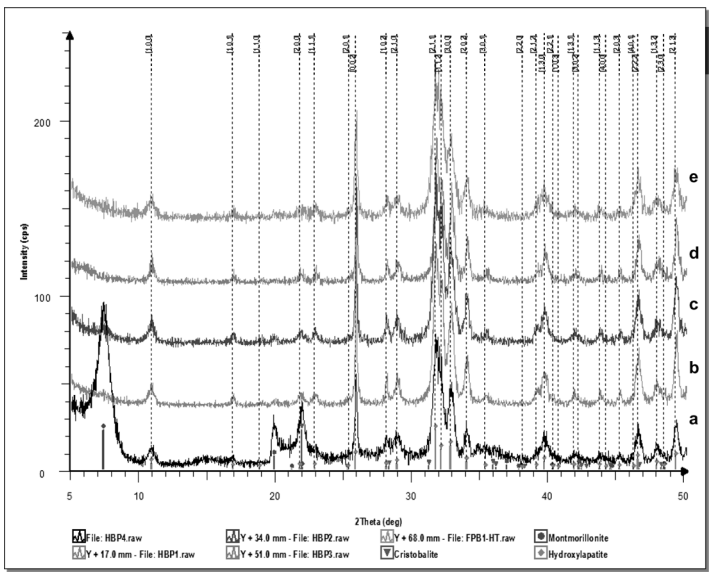

FIGURE 1 Representative area of diffraction pattern for phase analysis of samples: a) HBP 4; b) HBP 1 c) HBP 2; d) HBP 3; e) FBP 1-HT.

TABLE 2 XRD Analysis Results for Binary and Ternary Systems Synthesised in Hydrothermal Conditions

	Crystallite sizes [nm]			Semiquantitative analysis [%]		
Sample name	HAp	Montmorillonite	Cristobalite	HAp	Montmorillonite	Cristobalite
HBP 1	20	–	–	97.4	2.0	0.6
HBP 3	18	–	–	94.4	5.0	0.6
HBP 2	21	–	–	95.6	4.2	0.2
HBP 4	18	11	9	45.5	48.4	6.0
FBP 1-HT	15	–	–	86.2	3.5	0.3

and the interaction with top layer of montmorillonite is very slow; after three hours the grain growth is predominant. It can be assumed that the optimum hydrothermal treatment time for binary systems is about two hours (the interaction of hydroxyl apatite with montmorillonite is probably predominant and the semi-quantitative phase analysis corresponds to the calculated composition). Hydroxyl apatite crystallite sizes in sample FBP1-HT are lower (15 nm). A possible explanation could be the predominant interaction of hydroxyl apatite with both top layer of montmorillonite and polymer and as a consequence the grain growth is diminished. FT-IR spectra of purified montmorillonite, samples.

HBP 4 and FBP 1-HT are presented in Figures 2–5. In the hydroxyl stretching region montmorillonite is characterised by bands at 3635 cm^{-1} and 3451 cm^{-1} assigned to M-OH and OH stretching modes from interlayer H_2O (Fig. 2). In sample HBP 4 new bands can be observed at 3571 cm^{-1} and 3631 cm^{-1}, while OH stretching mode from the interlayer H_2O is shifted to 3224 cm^{-1}, probably due to the interaction between purified montmorillonite and hydroxyl apatite. In the hydroxyl stretching region phosphorilated polysaccharide is characterised by bands at 3432 cm^{-1} assigned to OH stretching vibration, while in ternary system FBP 1-HT (Fig. 5) it can be observed that the band corresponding to OH stretching vibration is shifted to 3424 cm^{-1} (probably due to the interaction between hydroxyl apatite and phosphorilated polysaccharide) and a new band at 3571 cm^{-1} assigned to M-OH from montmorillonite could be also observed. The band at 2370 cm^{-1} assigned to the stretching vibration of P-H group can be observed both in phosphorilated polysaccharide and in ternary system (Fig. 5). The band at 1457 cm^{-1} assigned to distortion vibration of CH_2 group of piranozic ring from phosphorilated polysaccharide is slightly shifted to 1437 cm^{-1} in ternary system due to the interaction

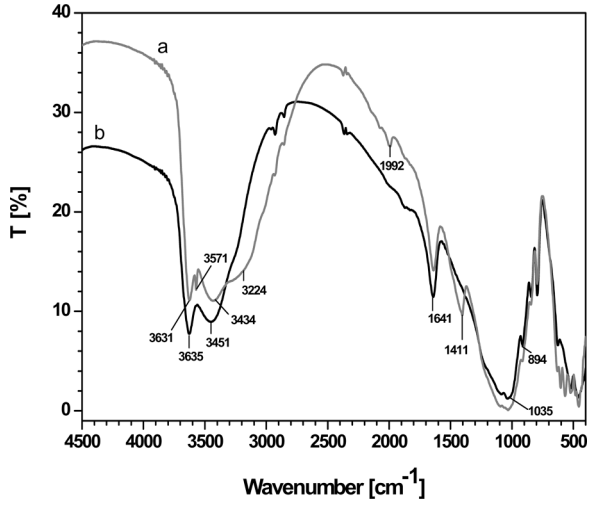

FIGURE 2 Comparative FT-IR spectra for HBP 4 sample (a) and purified montmorillonite (b).

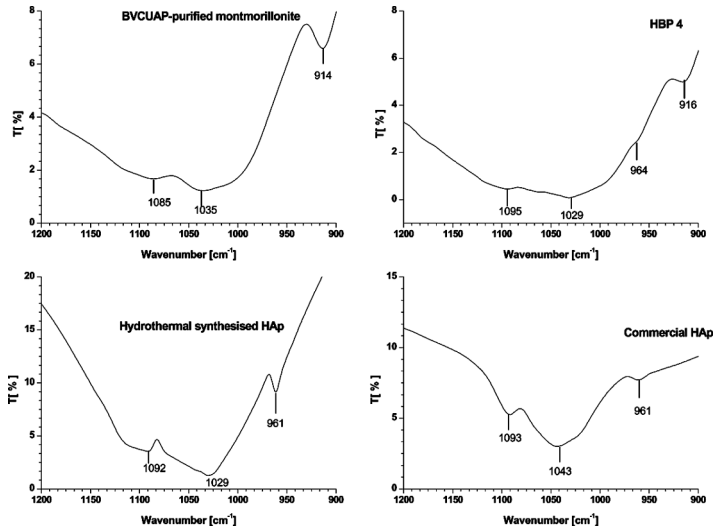

FIGURE 3 Comparative FT-IR spectra for purified montmorillonite, HBP 4, hydrothermal synthesised hydroxyl apatite and commercial hydroxyl apatite sample in the region 900–1200 cm^{-1}.

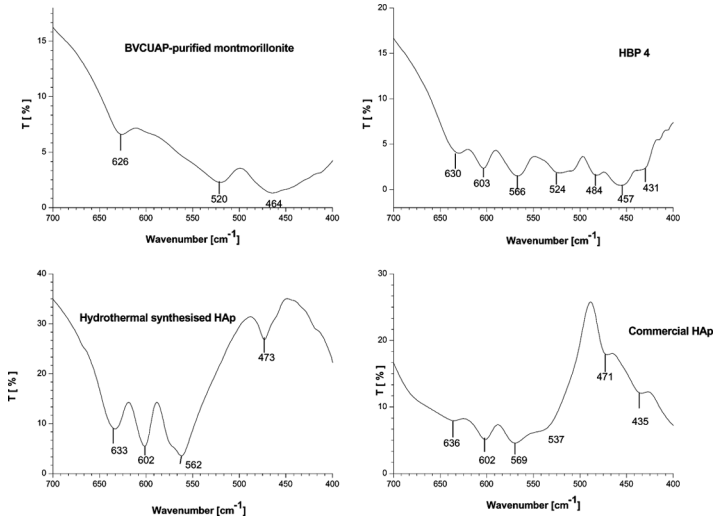

FIGURE 4 Comparative FT-IR spectra for purified montmorillonite, HBP 4, hydrothermal synthesised hydroxyl apatite and commercial hydroxyl apatite sample in the region 400–700 cm^{-1}.

between organic phase and hydroxyl apatite (Fig. 5). In the low frequencies region (900–1200 cm^{-1}) (Fig. 3) it can be observed the bands at 1035 cm^{-1}, 1085 cm^{-1} that can be assigned to Si-O vibrations [7,8]. The band that changes with the orientation of specimen is that at 1085 cm^{-1}. The region 900–1200 cm^{-1} also contains symmetric (ν_1) and asymmetric (ν_3) P-O stretching vibrations of phosphate group.

The ν_1 absorbance occurs at 962 cm^{-1} while other two components of ν_3, at 1040 cm^{-1} and 1092 cm^{-1} were identified [9]. In the hydrothermal synthesised binary and ternary systems (Figs. 3, 5) it can be observed that the P-O symmetric vibration (ν_1) and asymmetric (ν_3) P-O stretching vibrations are overlapped to the Si-O vibrations and a broad band results in the region 900–1200 cm^{-1}. A possible explanation could be the modification of phosphate (PO_4) tetrahedron symmetry due to the interaction with montmorillonite and polymer respectively [10]. In the region 400–700 cm^{-1} could be also observed the bands that are assigned to ν_4 (asymmetric bending) vibrations of phosphate groups (Fig. 4). In this region the vibrations modes of hydroxyl groups from montmorillonite, hydroxyl apatite and phosphate groups are associated.

The morphology of a typical particle from the sample HBP2 was analysed by bright field transmission electron microscopy (Fig. 6). It can be observed the presence of hydroxyl apatite with rod-like

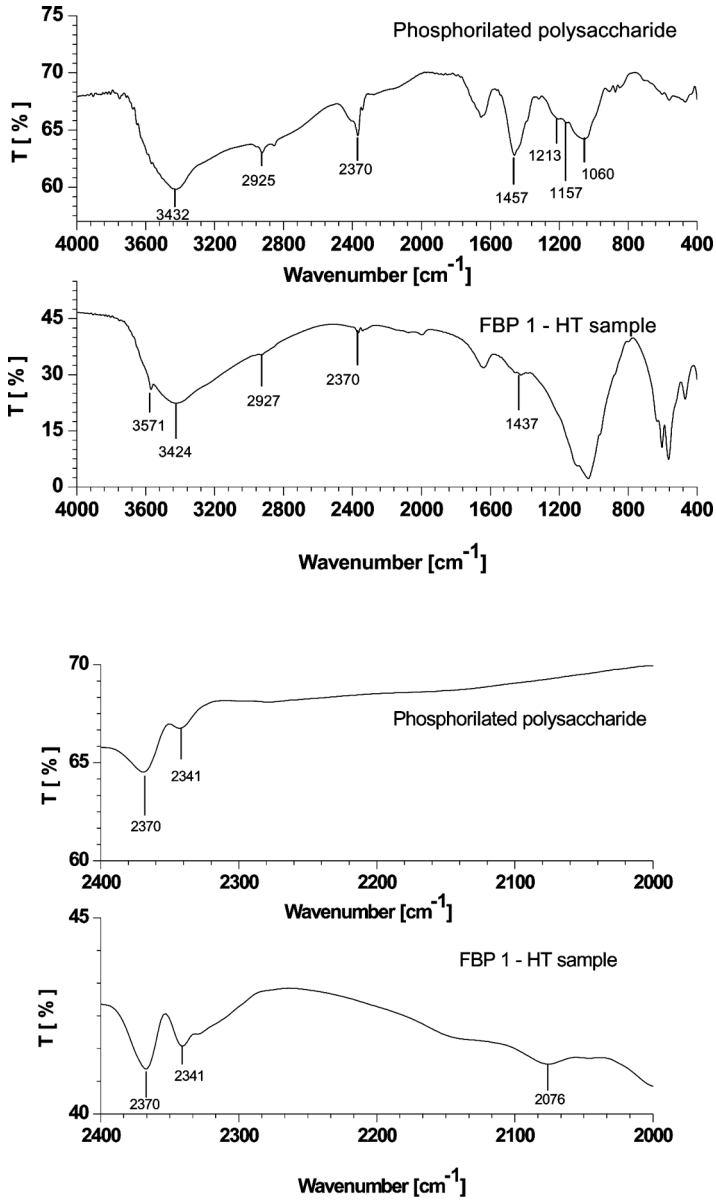

FIGURE 5 Comparative FT-IR spectra for FBP 1-HT sample and phosphorilated polysaccharide.

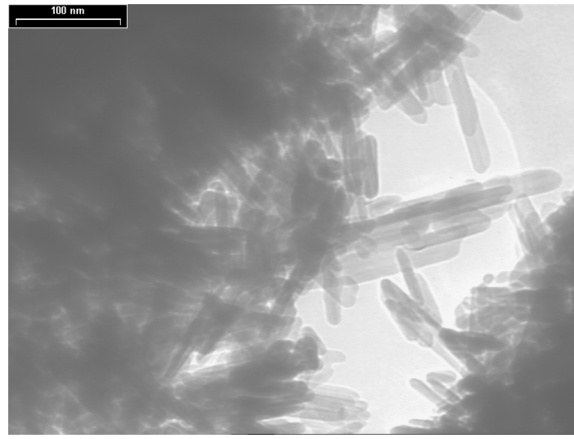

FIGURE 6 Bright field transmission micrograph of sample HBP 2.

shapes of lengths up to 100 nm. The (100) plane of crystalline lattice corresponding to hydroxyl apatite nanocrystals are revealed by the HRTEM analysis (Fig. 7).

The SAED image of HBP2 sample is presented in Figure 8. It can be observed the existing of both hydroxyl apatite (revealed by the diffraction rings corresponding to the inter-planar distances of the

FIGURE 7 High resolution transmission electron micrograph of sample HBP 2.

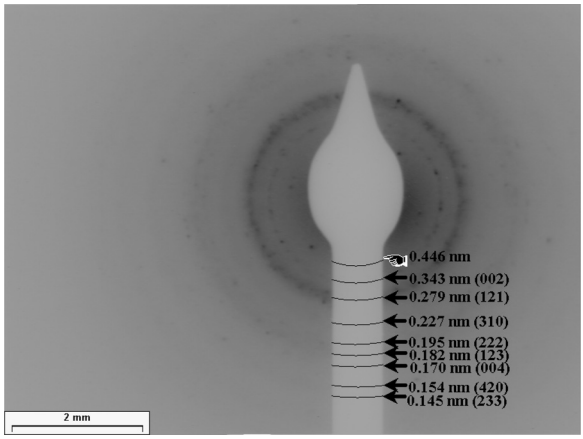

FIGURE 8 Secondary accelerated electron diffraction micrograph (SAED) associated to micro-area from Figure 6.

planar group with Miller index given in Fig. 7) and montmorillonite particles (revealed by the diffraction ring corresponding to interplanar distance 0.446 nm of the planar group with (100) Miller index of the hexagonal montmorillonite lattice).

CONCLUSIONS

Ternary systems based on hydroxyl apatite-purified montmorillonite-organic polymer were synthesized in situ in hydrothermal conditions at high pressures and low temperatures to avoid the decomposition of the organic phase. The process enables the formation of complex nanostructured materials with controlled phase composition. The possibility to form chemical bonding between phases was revealed by different methods. Analysis of XRD patterns shows a slightly shift of the peak (001) at $2\Theta = 7.2^{\circ}$ from montmorillonite in hydrothermal treated samples, possibly due to the interaction of hydroxyl apatite with the top layer of montmorillonite leading to the formation of an exfoliated structure. The FT-IR investigation of ternary samples shows new bands that can be observed at $3571\,cm^{-1}$ and $3631\,cm^{-1}$; while OH stretching mode of the interlayer H_2O is shifted to $3224\,cm^{-1}$, probably due to the interaction between purified montmorillonite and hydroxyl apatite. In the hydrothermal synthesised binary and ternary systems it can be observed that the P-O symmetric vibration (ν_1) and asymmetric (ν_3) P-O stretching vibrations are overlapped to the Si-O vibrations and a broad band results in the

region 900–1200 cm^{-1}. A possible explanation could be the modification of phosphate (PO_4) tetrahedron symmetry due to the interaction with montmorillonite and polymer respectively. Microstructure and morphology investigation by HRTEM shows the presence of both hydroxyl apatites with rod-like shapes of lengths up to 100 nm and montmorillonite forming a complex nanostructured material. Further works are in course to detail the mechanisms of formation of the ternary system.

Future goals include the extension of the study to demonstrate the biocompatible potential of these new nanostructured ternary materials for applications in regenerative medicine and tissue engineering.

REFERENCES

[1] Cuiming Wu, Tongwen Xu, & Weihua Yang, (2005). *European Polymer Journal*, *41*, 1901–1908.
[2] Clement Sanchez, Beatriz Julian, Phillippe Belleville, & Michel Popall. (2005). *J. Mater. Chem*, *15*, 3559–3592.
[3] Eduardo Ruiz-Hitzky, Margarita Darder, & Pilar Arranda. (2005). *J. Mater. Chem.*, *15*, 3650–3662.
[4] Jui-Ming Yeh, Chang-Jian Weng, Kuan-Yeh Huang, Chun-Che Lin. (2006). *Journal of Applied Polymer Science*, *101*, 1151–1159.
[5] Wopenka, B. & Pasteris, J. D. (2005). *Materials Science and Engineering C. 25*, 131–143.
[6] Porter, A. E., et al. (2003). *Biomaterials*, *24*, 4609–4620.
[7] Luc Lerot & Philip F. Low. (1976). *Clays and Clay Minerals*, *24*, 191–199.
[8] Theo Kloprogge, J., Ray L. Frost, & Robyn Fry. (1999). *Analyst*, *124*, 381–384.
[9] Nancy Pleshko, Adele Boskey, & Richard Mendelshon. (1991). *Biophys. J,-Biophysical Society*, *41*, 786–793.
[10] Melissa D. Lane, M. Darby Dyar, & Janice L. Bishop. (2007). *Lunar and Planetary Science* XXXVIII Conference, March 12–16, 2007, League City USA, abstract.