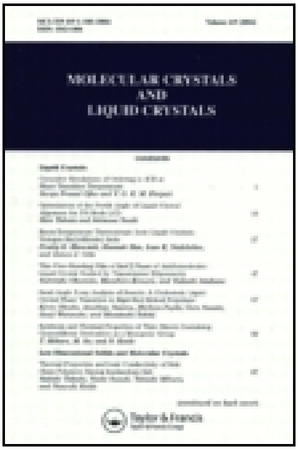

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Titania Modified Layered Silicate for Polymer/Inorganic Nanocomposites

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Sodium montmorillonite, from purified Romanian bentonite, and quasiamorphous TiO_2 aerogel were used for obtaining binary hybrids by solution intercalation method. In the nanohybrid, TiO_2 results in crystalline-anatase form. The morphostructural properties of the TiO_2 modified layered silicate were studied by X-Ray Diffraction, FTIR Spectroscopy, High Resolution Transmission Electron Microscopy and Thermogravimetric Analysis. By uniform dispersing of binary nanohybrid in a collagen matrix, nanocomposite with intercalated lamellar structure was obtained. The basal spacing (d_{001}) increases from 14.8Å in the binary hybrid to 18Å in the nanocomposite with collagen. Applications in regenerative medicine of hard tissue are foreseen.

Keywords: binary nanohybrid; collagen nanocomposite; layered silicate; titania aerogel

INTRODUCTION

Titania (TiO_2) has various catalytic applications in which it strongly interacts with metals. The clay/TiO_2 nanocomposites are well known as adsorbents and (photo) catalysts [1]. A special attention was awarded to obtain titania films because of its multiple uses [2].

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Recently, porous composite materials are frequently used to photocatalytic decompose toxic chemical substances from environment (exp.: volatile organic compounds – VOC's). In order to increase the adsorption capacity, attempts to obtain titania/zeolite or titania/clay composites, have been made [3,4]. At the same time, the uses of TiO_2 are known in biomedicine, to increase the biocompatibility between the metallic implant (of Ti) and the tissue [5]. The titania layer formed on the implant surface helps increasing the corrosion resistance of Ti and diminishes the immune rejection of the implant.

Lately, the use of collagen as biomaterial, biocompatible and bioresorbable, as prosthesis for connective tissues, in which is the main protein, became notorious [6,7]. The modification of the structure and the composition of matrix to obtain the osteoconductive and osteoinductive effect is necessary when using collagen as scaffold support to healing the bone tissue. This may be achieved by obtaining biocomposites with SiO_2, TiO_2, clays or hydroxyapatite [5,8]. The layered silicate improves the thermal and mechanical properties of the collagen and has a biostimulating effect on the cellular metabolism [9].

In this work, the morphostructural properties of TiO_2-modified layered silicate binary hybrids are presented and collagen-binary hybrids nanocomposites are obtained.

EXPERIMENTAL

Materials

Quasiamorphous TiO_2 aerogel, having 67% TiO_2, 460 m^2/g BET specific surface area and 12 nm the average diameter of the pores, was prepared by sol-gel synthesis and gel drying in supercritical carbon dioxide, at University "Babes-Bolyai", Cluj-Napoca Romania. Sodium montmorillonite was obtained by purification of Romanian bentonite (BVCUAP), with basal spacing d_{001}: 12.4 Å and 7% weight loss in the temperature range of $20 \div 120$°C (TGA).

Collagen gel (GECOL) with average molecular weight 300000 Da, was extracted from bovine (calf) skin at the National Research and Development Institute for Textile and Leather – ICPI Division, Bucharest, Romania.

Nanohybrids Obtainment

The binary hybrids were obtained, by solution intercalation method, from TiO_2 aerogel and purified bentonite at different layered silicate/TiO_2 aerogel ratios: 1/1, 1/2, and 2/1. Layered silicate, prior swelled 1% in distilled water over the night, was dispersed by a magnetic stirrer in a solution of 0.1% titania aerogel in distilled water, at 70°C, 10 min. After 24 h, at 70°C in an oven with air circulation, the mixture was centrifuge-separated. Both the sediment, "S", and the nanohybrid from the supernatant, "D", were dried 24 h, at 45°C.

By uniform dispersing of binary nanohybrid in the collagen matrix, nanocomposite with intercalated lamellar structure was obtained.

Characterization

The basal spacing was determined by means of X-ray diffraction (XRD) using a DRON-2.0 X-ray diffractometer with horizontal goniometer; it was utilized the CuKα radiation source ($\lambda = 1.5418$ Å) filtered with Ni for K_β component removing, in Bragg-Brentano system (by reflection); the patterns were automatically recorded at small angles (2θ: $2 \div 30°$). The diameters of the anatase nanoparticles (d) were calculated from XRD patterns by using the Scherrer equation. The specific surface area of the anatase nanoparticles was approximated by formulas:

$$S = \frac{6x10^4}{\rho d}, \text{ where, } \rho \text{ is anatase density} = 3.89\,\text{g/cm}^3.$$

The weight losses of analyzed samples, heated at constant rate, were determined as function of temperature with a THERMAL ANALYSIS DUPONT 2100. The working conditions were: heating rate of 20°C/min, under 50 cm^3/min airflow and the temperature range from 0 to 700°C. The temperature at the maximum rate of weight-loss, on the decomposition steps, was determined by DTA curves.

The interaction between components was investigated by infrared spectroscopy on FTIR Bruker VERTEX 70, with diamond ATR – HARRICK MVP2 device, in the range $4500 \div 500\,cm^{-1}$.

The shape and the size of the nanoparticles were observed by High Resolution Transmission Electron Microscopy (HRTEM), on Philips CM120ST instrument.

RESULTS AND DISCUSSION

The results obtained by TGA (Table 1) show enhanced thermal stability of the binary hybrids compared with that of the TiO_2 aerogel. In the range of the used temperature (20°C $\div$ 700°C), the resulted products exhibit four endothermic effects, same as TiO_2. For bentonite, the first step of decomposition is in the temperature range of

TABLE 1 TGA Results for BVCUAP Initial and After Modification with Different Ratios of TiO_2

Sample	T_{rdmax}[a] (°C)	The weight loss on the each step of decomposition (%) I 20°C ÷ 200°C	II 200°C ÷ 400°C	III 400°C ÷ 550°C	IV 550°C÷700°C
TiO_2 aerogel	195	13.1	14.5	1.1	0.6
BVCUAP	74	8.3	–	–	1.4
BVCUAP-TiO_2 (2:1)	84	10.9	1.8	0.6	0.8
BVCUAP-TiO_2 (1:1)	100	10.3	3.3	1.9	10.8
BVCUAP-TiO_2 (1:2)	102	10.7	2.3	0.8	0.95

[a]The temperature at the maximum rate on the first step of decomposition.

20°C ÷ 200°C and represents the loss of residual water from silicate. The quantity of eliminated water is higher in the binary hybrids. In nanohybrids the temperature at maximum rate of decomposition on the first step of decomposition (in the range of temperature 20°C ÷ 200°C) has higher values (84°C, 100°C and 102°C respectively, compared with 74°C, for silicate), proportional with the increase of TiO_2 concentration. For TiO_2 aerogel, the first step of decomposition (in the temperature range of 20°C ÷ 200°C) is characterized by 13.1% weight loss with the maximum rate of decomposition at 195°C. The weight loss on the second step of decomposition (in the range of temperature 200°C ÷ 400°C) is 14.5% with the maximum rate of decomposition at 277°C. In the range of temperature 400°C ÷ 550°C the weight loss is 1.1% with the maximum of the decomposition rate at 461°C. These results reveal that TiO_2 aerogel is a heterogeneous mixture from TiO_2 and organic compounds residues (revealed especially by the high weight loss in the range of temperature 200°C ÷ 400°C). In nanohybrids the weight loss percentages are diminished, with respect to TiO_2 content, probably because of the titanium-organic compounds intercalation between the silicate layers.

The XRD patterns presented in Figure 1 reveal that the diffraction peaks, characteristic for bentonite, decrease in intensity, proportional with the TiO_2 concentration increase. This decreasing in intensity is the consequence of the silicate layers surrounded by the TiO_2 particles. The basal spacing (d_{001}) increases from 12.4 Å in bentonite to approx. 15 Å in nanohybrids. These results proved that the titanium compounds intercalate between the silicate layers and partially exfoliate the layers. In nanohybrids TiO_2 results in crystalline anatase form ($2\theta = 25.37°$), compared to initial quasiamorphous structure, with crystals dimension of 53 Å and specific surface area of about 290 m^2/g.

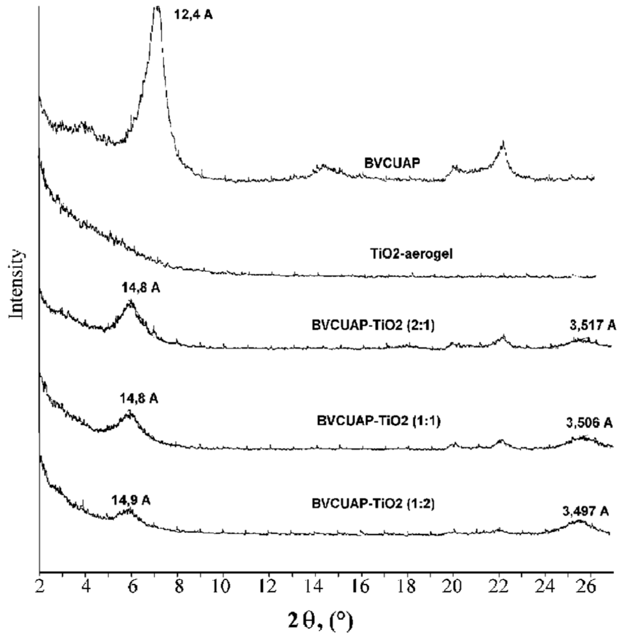

FIGURE 1 X-ray diffraction patterns for the binary hybrids vs. BVCUAP.

The X-ray diffraction patterns for nanohybrids after centrifugation are presented in Figure 2. TiO_2 crystallize selectively on the silicate layers. The layers on which TiO_2 crystallized are in form of sediment. From the elemental analysis of the solution separated after centrifugation resulted that in solution remains approximately 51% of the layered silicate and 3% of TiO_2 only.

The previous assumptions are sustained also by the FT-IR-ATR spectra (Fig. 3). TiO_2 aerogel presents bands characteristic for organic compounds (2875 cm^{-1}, 2930 cm^{-1} and 2973 cm^{-1}), residues from the sol-gel process. In nanohybrids, these bands become invisible, in the ATR spectra, proving the intercalation of these compounds between the silicate layers. The IR spectrum for the supernatant residue is similar with that for BVCUAP.

The HRTEM micrographs (Fig. 4) of BVCUAP (left) and binary hybrids (right) confirm that the silicate is surrounded by 5 nm – TiO_2 nanoparticles.

By uniform dispersing the binary nanohybrid in a collagen matrix, nanocomposite with intercalated lamellar structure was obtained. The XRD patterns presented in Figure 5 reveal that the basal

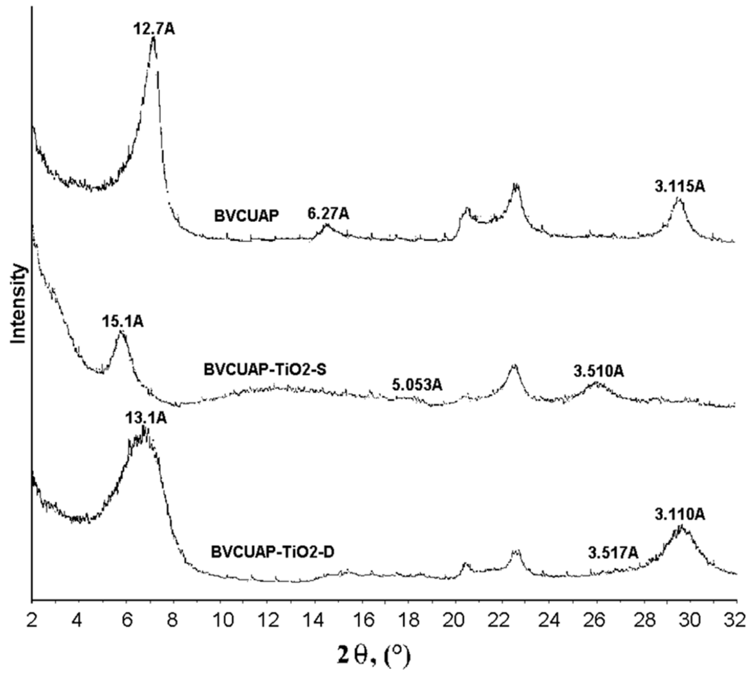

FIGURE 2 The X-ray diffraction patterns for nanohybrids after centrifugation.

spacing (d_{001}) increases from 14.8 Å in binary hybrid to approx. 18 Å in nanocomposites with collagen gel (GECOL), demonstrating the collagen intercalation. We observe that the morphology of the collagen

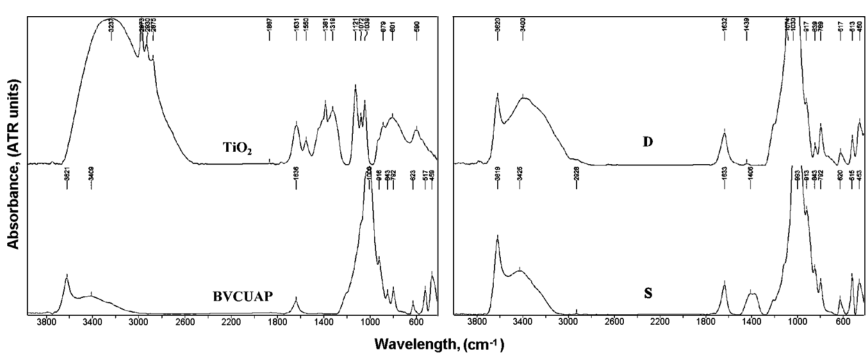

FIGURE 3 The FT-IR spectra for titania aerogel (TiO_2), bentonite (BVCUAP), nanohybrid in precipitate (S) and nanohybrid in supernatant (D).

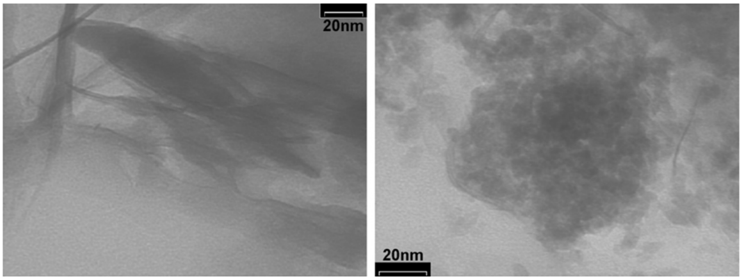

FIGURE 4 HRTEM images for BVCUAP (left) and 2/1 ratio layered silicate/TiO_2 binary hybrid (right).

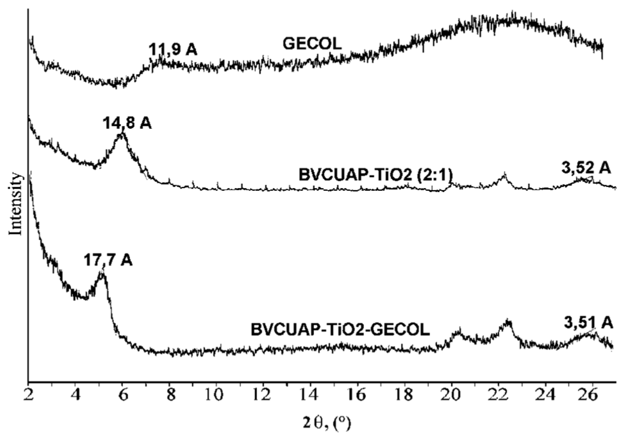

FIGURE 5 The X-ray diffraction patterns for collagen (GECOL), nanohybrid (BVCUAP-TiO_2) and collagen nanocomposite (BVCUAP-TiO_2-GECOL).

is modified, probably because of the interactions with the hydroxyl groups on the silicate surface.

CONCLUSIONS

Binary hybrids by solution intercalation method were obtained. In the nanohybrid, TiO_2 results in crystalline – anatase form, with crystals dimension of 53 Å and specific surface area of about 290 m^2/g. TiO_2 crystallize selectively on the silicate layers. The layers on which TiO_2 crystallized are in form of sediment. In the solution separated after centrifugation remains approximately 51% of the layered silicate. Between the silicate layers, titanium compounds intercalate and partially exfoliate the layers.

By uniform dispersing the binary nanohybrid in a collagen matrix, nanocomposite with intercalated lamellar structure was obtained. This nanocomposite can find applications in regenerative medicine of hard tissue.

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