Influence of the Ultrasonic Field on the Template Polymerization of Acrylonitrile in Inorganic Structures

ANITA-LAURA RADU[1]*, ANDREI SARBU[1], LUMINITA MARA[2], ALEXANDRA-SORINA GAREA[3], ANAMARIA LUNGU[1], STEFAN-OVIDIU DIMA[1], TANTA-VERONA NICOLESCU[1], HORIA IOVU[3]

[1]National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM, Polymers Department, 202 Independentei Spl., 060021, Bucharest, Romania

[2]National Research-Development Institute for Nonferrous and Rare Metals-IMNR, Pantelimon, Romania

[3] Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu, 011061, Bucharest, Romania

The present paper refers to the possibility of obtaining inorganic-organic nanohybrids, starting from nanoporous silica, in which the acrylonitrile template polymerization proceeds. In order to enhance the homogeneity between constitutive parts of the nanocomposite several methods were tested like increase of the imbibition period of the silica with the monomer, a better absorption capacity of the silica for the monomer and the use of the ultrasonication technique. The influence of the ultrasonic field on the template polymerization of acrylonitrile in inorganic structures was proved by FTIR and TG/DTG analyses. Ultrasonication was employed before the polymerization, in order to prevent the aggregation of particles, to well disperse the silica particles in the vinyl monomer and for a good imbibition. The results demonstrate that ultrasonication is effective in homogenizing the constitutive parts of the hybrid materials by yielding a fine microstructure of sintered nanomaterials.

Keywords: inorganic-organic hybrid, porous silica, ultrasonication, template polymerization, nanocomposites

Inorganic-organic hybrid composites are among the most important classes of synthetic engineering materials. By definition, a composite is a material composed of two or more physically distinct components, the intent of which is to achieve better properties than can be obtained by a single homogeneous material [1]. Aside from the intrinsic physical properties of the components, composite materials can also display special new properties as a result of the nature and degree of interfacial interaction between the two components. One of the frontiers in composites engineering is the development of viable methods for the synthesis of organic-inorganic composites with nanometer-scale architecture [2-4].

Inorganic and organic materials are usually quite different in their properties. Organic polymers generally suffer from some of the inherent drawbacks such as instability to heat and tendency of natural degradation upon aging. Inorganic species have good mechanical and thermal stability as well as other excellent properties. Organic moiety would provide flexibility, toughness, hydrophobic and new electronic or optical properties. Inorganic-organic hybrid materials could then have targeted properties by combining the features of both inorganic and organic components. Because of the new and various properties of these nanocomposite materials which the traditional macro scale composites do not have, the preparation, characterization and applications of inorganic/organic hybrid materials have become a fast expanding area of research in materials science. Looking to the future, there is no doubt that these new generations of hybrid materials, born from the very fruitful activities in this research field, will open a land of promising applications in many areas: optics, electronics, ionic, mechanics, energy, environment, biology, medicine for example as membranes and separation devices, functional smart coatings, fuel and solar cells, catalysts, sensors, etc [5-10].

The porous silica inorganic structures are generally prepared by the following methods: precipitation of alkaline solutions of soluble glass (Na_2SiO_3) in acid medium; sol-gel methods; micro silica deposition in vapors; hydrothermal procedures [11-13].

The preparation of porous silica by the hydrothermal procedure is a rather new approach and the serpentinite minerals utilization for this purpose represents a novelty, because until now the traditional methods for the silica gel obtaining consisted in the dissolution of soluble glass (sodium silicate) in mineral acids, especially with sulphuric acid, followed by final product calcinations [14-16]. The dissolution of sodium silicate soluble glass in a corrosive liquid allowed the removal of a phase (liquid) without destroying the three-dimensional structure of the remaining solid phase, namely the silica gel. Usually, microporous silica can be obtained by this method.

Ultrasonication involves the use of shear forces created by the implosion of cavitation bubbles of ultrasonic waves (sound waves in the kHz range) to alter material properties. However, it requires a medium such as water for radiation of the sound waves. Ultrasonication generates alternating low-pressure and high-pressure waves in liquids, leading to the formation and violent collapse of small vacuum bubbles. This phenomenon is termed cavitation and causes high speed impinging liquid jets and strong hydrodynamic shear-forces. These effects are used for the deagglomeration and milling of micrometer and nanometer-size materials as well as for the disintegration of cells or the mixing of reactants. In this aspect, ultrasonication is an alternative to high-speed mixers and agitator bead mills. Furthermore, chemical reactions benefit from the free radicals created by the cavitations as well as from the energy input and the material transfer through boundary layers. To obtain dense, fine-grained nanocomposites, fine particles and advanced powder

---

* *email: raduanita@yahoo.com; Tel.: 0213128501; 0723599783*

Table 1
CHEMICAL COMPOSITION OF THE SILICA OBTAINED BY THE ATTACK WITH HNO_3

Code	Parameters			SiO_2 %	Fe_2O_3 %	NiO %	Al_2O_3 %	Cr_2O_3 %	MgO %	Na_2O %	CaO %
	L:S	Temperature °C	Time min								
RN16	6	85	90	62.49	3.17	0.08	2.25	1.20	2.69	0.02	0.10
RN18	6	85	120	70.61	2.31	0.03	1.89	0.96	2.65	0.18	0.11
RN43	3.5	85	120	77.04	2.63	0.02	2.25	1.10	2.19	0.12	0.54

processing are needed. However, additional redispersion treatment such as ultrasonication is required to obtain dispersed suspensions because fine particles tend to agglomerate [17, 18].

The aim of our study was to obtain nanocomposite materials with improved properties based on nanoporous silica as inorganic matrix and polyacrylonitrile as polymer guest. In order to explain the influence of the ultrasonic field on the final composite we performed FTIR, TG/DTG analyses for advanced characterization of the nanocomposites.

Experimental part

Materials

Serpentinite from Dubova (Romania) dumps was an offer from Dubova Mineral Prod. Com. SRL- Romania. Nitric acid (HNO_3) 50%, azobisisobutyronitrile (AIBN) and acrylonitrile (AN), were purchased from Fluka, and were of analytical degree. AN was desinhibited by rectification.

Synthesis of the inorganic-organic nanocomposites

In order to obtain polymer hybrid inorganic-organic nanocomposites, by template polymerization, starting from nanoporous silica the next steps were applied:

<u>Preparation of nanoporous silica</u>

Silica must have a structure with holes so that the host-guest polymerization takes place in silica. The host cavities must offer conditions so that the monomer and the initiator penetrate it and finally allow the guest polymer to be obtain. We have chosen as inorganic material mesoporous silica.

Three different silica samples were obtained from serpentinite fine powders by the attack with HNO_3 50%, with different liquid: solid ratio (L: S). The synthesis conditions and chemical composition of the obtained silica are presented in table 1.

The reaction was carried out in an open thermo resistant vessel glass. The reaction temperature was maintained at 85°C and the reaction medium was stirred at 500 rot/min for the entire period of the reaction. The solvent level was maintained constant using distilled water. The reaction time was varied in the range 90-120 min.

The silica residue was separated at the end of the reaction by vacuum filtration. The residue had a gel appearance, the filtration being particularly difficult. The gel has been washed in two steps with hot distilled water (at about 90 - 95°C) and then it was dried at 60-80°C for 3 h in an oven.

<u>Preparation of the nanocomposites</u>

The next step of the study was the preparation of inorganic-organic nanocomposites by radical polymerization of vinyl monomers in the porous structures. The acrylonitrile (AN) was used as the vinyl monomer and azobisisobutyronitrile (AIBN) was utilized as the polymerization initiator.

The experiments were performed in glass ampoules which were broken after polymerization to recover the solid product. An ultra thermostat water bath was used as heat provider for the ampoules in order to maintain the reaction temperature (65°C).

The ampoules were purged with a low flow of nitrogen before polymerization (in order to remove the oxygen) and then were sealed with a rubber tube with Hoffman clamp.

The working procedure was the following: Silica and acrylonitrile (containing 0.5% initiator based on monomer) were introduced at 1:2 wt/vol ratio in 50 mL glass ampoules having a thin bottleneck. At the ampoules bottleneck a rubber tube with a Hoffman clamp was mounted. For imbibition (the penetration of monomer in silica pores), the ampoules were introduced in an Elma S10 Elmasonic ultrasonication bath, containing water, for various periods of time. After that, the ampoules were kept 22-72 h without ultrasonication. Finally a new ultrasonication was applied. The imbibition conditions are presented in table 2. Then the Hoffman clamp was demounted and a catheter tube was introduced in the ampoule through the rubber tube. The ampoule was purged about 10 min with a low flow of nitrogen. Quickly the catheter tube was removed at the end of the purging and the Hoffman clamp was remounted on the rubber tube of the ampoule and then was hardly tightened. The ampoule was introduced in ultra thermostat water bath and maintained at 65°C for 24 h.

Characterization of the nanocomposites

Silica purity was assessed by chemical analysis and the pore diameter was calculated from BET (Brunauer-Emmett-Teller) determinations.

Table 2
IMBIBITIONS CONDITIONS OF SILICA SAMPLES WITH ACRYLONITRILE

Composite Code	Period I of ultrasonication, min.	Time of imbibition without ultrasonication, hours	Period II of ultrasonication, min.
HRN16	0	72	0
HRN18	5	23	5
HPS1	0	22	60
HPS2	15	22	60
HPS3	30	22	60
HPS4	60	22	60
HPS5	30	22	30
HPS6	30	22	90

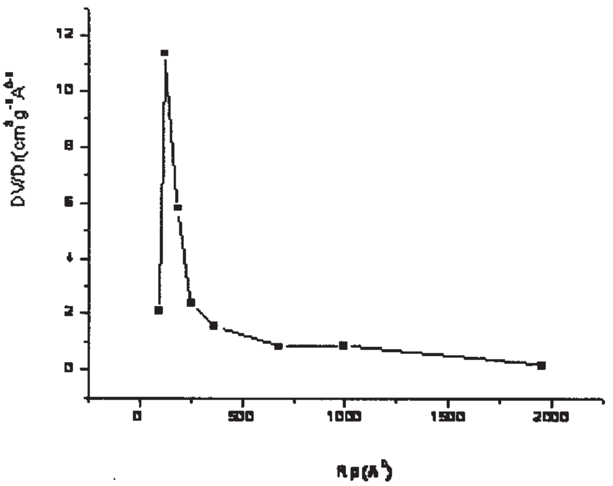


Fig.1. Distribution curve of pores volume as a function of the pores size for RN18 silica sample

FTIR measurements were performed on SHIMADZU 8900 equipment. The FTIR spectra were recorded in 400 ÷ 4000 cm^{-1} range with 4 cm^{-1} resolution. The samples were analyzed from KBr pellets.

Thermogravimetrical analysis (TGA) was done on a TA Instruments Q500 equipment, in nitrogen atmosphere from room temperature to 600°C with a heating rate of 10°C/min.

Results and discussions

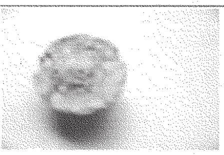
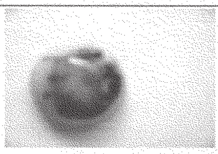
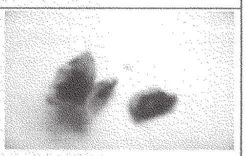
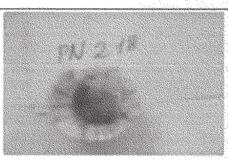
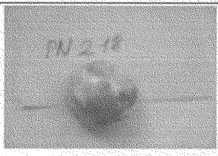
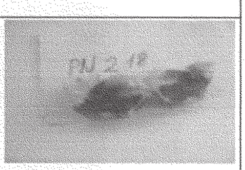
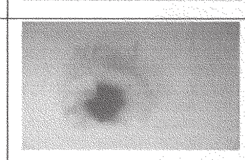
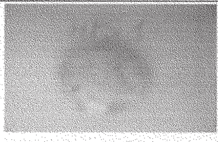
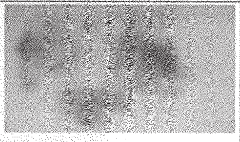
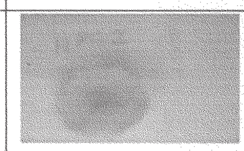
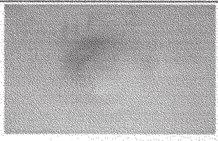
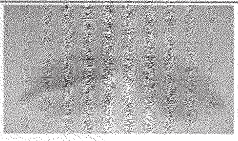
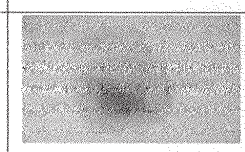
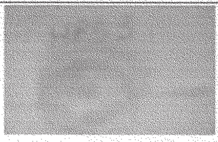
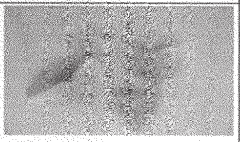
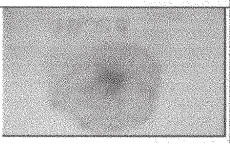
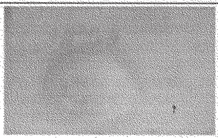
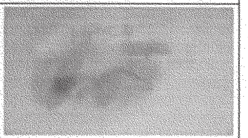
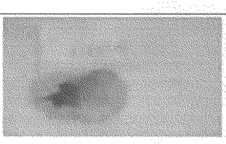
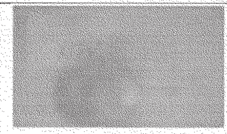
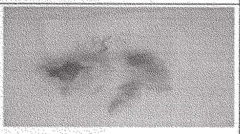
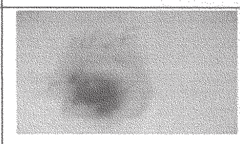
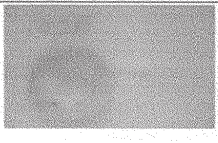
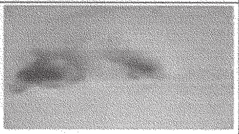
The silica samples displayed nanometric porosity, with pores diameter between 2-20 nm, as it appears in figure 1.

As one can see from table 1, the synthesis conditions, i.e. liquid: solid ratio (L: S), temperature and reaction time, influenced the purity of the obtained silica. The highest purity was obtained by the acid attack in the most drastic conditions: ratio L: S 6.0, temperature 85 °C and reaction time 120 min. This silica (RN18) presented the highest monomer absorption too; after the second ultrasonication the monomer is completely absorbed and no monomer film on top of the inorganic material was observed.

If the RN16 silica sample is statically imbibited with the monomer during 72 h and the ultrasonication is not applied, the monomer film is observed. This shows the favorable effect of the ultrasonication on the monomer absorption in the silica sample.

The composites aspect after polymerization is presented in table 3.

Table 3
TOP, BOTTOM AND IN CRACK ASPECT OF THE POLYMER NANOCOMPOSITES OBTAINED FROM DIFFERENT SILICA SAMPLES, WITHOUT AND WITH ULTRASONICATION

Silica sample Code	Aspect		
	The upper side	The bottom	The crack
HRN16			
HRN18			
HPS1			
HPS2			
HPS3			
HPS4			
HPS5			
HPS6			

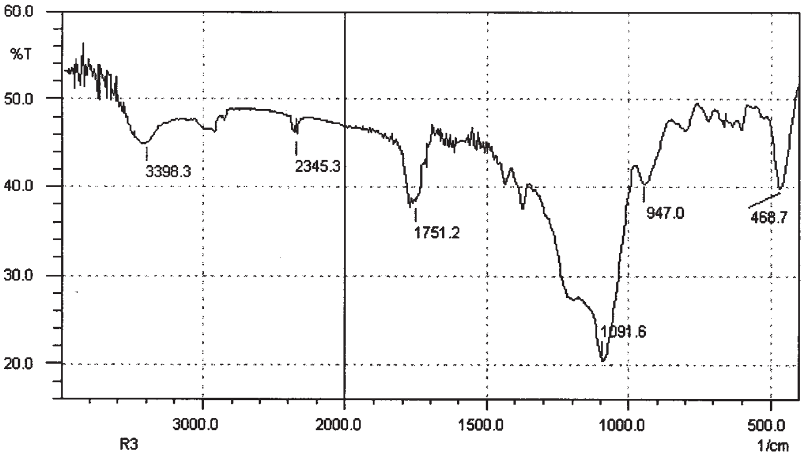


Fig. 2. FTIR spectrum of the reference (RN18 silica sample without polymer)

Comparing the pictures on table 3, one can observe that HRN16 and HRN18 composites, obtained without ultrasonication or with a short time ultrasonication display a surface with cracks, a glassy bottom with black spots, interior with black parts and an inhomogeneous aspect. The composites were compact and extremely firm.

In the case of the ultrasonicated samples (HPS1-HPS6) a great similitude of nanocomposites aspect was observed: the upper side smooth, white grey, the bottom glassy and inside white grey, with a homogeneous aspect. The composites, HPS1-HPS6 prepared from RN43 silica sample, were less compact and less firm.

All these facts show that the introducing of ultrasonication stages at the beginning and the end of the imbibition phase lead to uniform composite, even if the polymerization occurs in static conditions. It was found that the final stage of ultrasonication is very important. However it is recommended an initial period of at least 15 min of ultrasonication for a sufficient homogeneity of the nanocomposites. High purity and porosity of silica could also explain why we managed to obtain homogeneous samples in compositional terms.

The analyses performed on the obtained nanocomposites showed the presence of an organic compound, revealing that the silica pores were filled with polymer.

Figure 2 shows the FTIR spectrum of silica RN18 sample. It appears that SiO_2 is a three-dimensional polymer in which the SiO_4 units are linked in crystal, (796.0, 468.7, 457.1, 418.5 cm^{1}). The peak at 1091.5 cm^{-1} is generated by the asymmetrical stretching of Si-O-Si bridges in SiO_2. Otherwise, as the modes at 1087.8 and 1091.5 cm^{-1} appear only in porous silica structure with some oxidation degree, these frequencies can be related to the highly stressed SiO_2-Si interface. The bands at 3420 cm^{-1} and 1458.1 cm^{-1} can be associated with the molecular water. The presence of the water in the crystalline structure forms sharp bands, like in case of clays.

Comparing the FTIR spectra in figure 2 and 3, one can see in figure 3 the CN band appearing in the nanocomposite (at 2247 cm^{-1}) and the obvious modification of the spectra

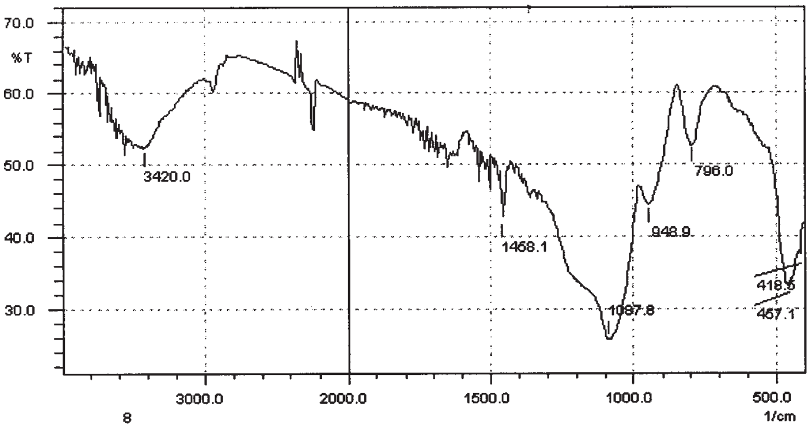


Fig. 3. FTIR spectrum of the composite prepared

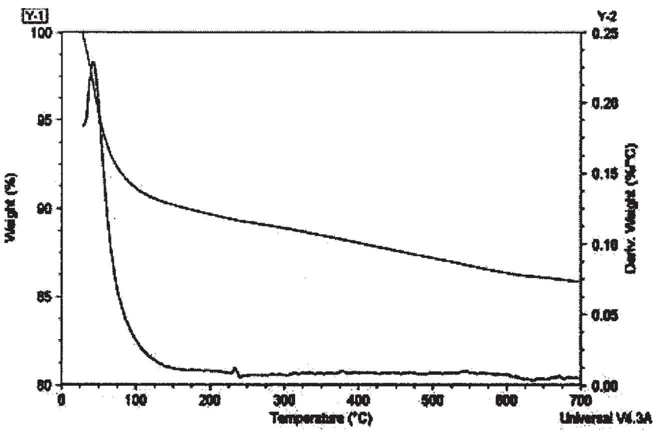


Fig. 4. The DTG curve for the silica sample obtained by the attack with HNO_3 50%

Table 4
MASS LOSS DETERMINED BY TGA ANALYSES

Sample	Mass loss %
Silica sample obtained by the attack with HNO_3 50%	14.13
Composite obtained from the silica sample	32.74

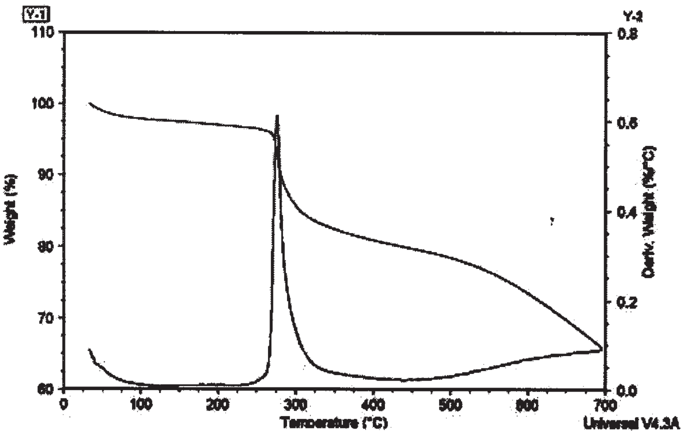


Fig. 5. DTG curve for the composite

in the 1800- 1100 cm^{-1} which could suggest the formation of a hybrid inorganic- organic nanocomposite. This band does not appear in the reference spectra (fig. 2).

In order to check the influence of the ultrasonic field, the thermostability of samples was studied by thermogravimetric analysis (fig. 4, 5). These analyses confirmed that between the polymer host and the silica matrix a good compatibility was obtained, leading to the formation of the hybrids. One may notice from Figure 4 that DTG curve of the reference (silica) exhibits only one maximum at 100°C, associated with molecular water. The composite exhibited also one peak in DTG, but this was assigned to the degradation of the polymer at about 300°C. The mass loss in TGA may be observed from Table 4. Thus the mass loss is higher for the composite than for the silica as it was expected due to the decomposition of the polymer, associated with the breakage of the organic part of the polymer hybrid. The analyses demonstrate the formation of hybrids because the PAN chains show improved thermal stabilities in the nanocomposites, than free PAN, which decomposes at around 200 °C [19].

Conclusions

Nanoporous silica was obtained through the hydrothermal procedure in order to synthesize inorganic-organic nanocomposites. The RN43 silica, obtained under drastical synthesis conditions, has a very high purity (over 77%). The silica samples were mesoporous with pore diameter of 2-20 nm.

The polymerization of acrylonitrile in the presence of the silica samples, after ultrasonication allowed obtaining composites. The inside aspect of the hybrid nanocomposite shows that ultrasonication readily improves the compositional homogeneity.

The influence of the ultrasonic field on the template polymerization of acrylonitrile in inorganic structures was also proved by FTIR and TG/DTG analyses.

Ultrasonication is a better way to homogenize the constitutive parts of the hybrid materials than the static imbibitions and the homogeneity of nanocomposites is influenced by the purity of silica samples. The monomer absorption in silica depends on the preparation conditions for silica samples.

References

1. (A) WEI, Y., YEH, J.-M., et. al, US Pat. 5, 1996, p. 868-966, (B) WEI, In Encyclopedia of mat.: Sci. and Techno. Elsevier Sci LTD., 2001.
2. SHARP, K. G., Adv. Mater., **10**, 1998, p. 1243
3. USUKI, A., HASEGAWA, N., KATO, M., Adv. Polym. Sci, **179**, 2005, p. 135–195
4. GOMEZ-ROMERO, P., CUENTAS-GALLEGOS, K., LIRA-CANTU, M. et. al, J. Mater. Sci., **40**, 2005, p. 1423–1428.
5. KICKELBICK, G., Progr. Polym. Sci., **28**, 2003, p. 83–114.
6. SANCHEZ, C., ARRIBART, H., GIRAUD-GUILLE, M. M., Nature Mater. **4**, 2005, 277.
7. SANCHEZ, C., JULIAN, B. et. al, J. Mater. Chem., **15**, 2005, p. 3559
8. SANCHEZ, C., GOMEZ-ROMERO, P., Wiley VCH, Weinheim, 2004
9. SANCHEZ, C., GOMEZ-ROMERO, P., New J. Chem., **1**, 2005, p. 57
10. BOURGEAT-LAMI, E., J. Nanosci. Nanotechnol., **2**, 2002, p. 1.
11. SAVARI, A., HAMOUDI, S., Chem. Mater., **13**, 2001, p. 3151
12. HOFFMANNN, F., CORNELIUS, M. et. al, J. Nanosci. Nanotechnol., **6**, 2006, p. 265
13. SHI, J-L., HUA, Z.-L., ZHANG, L.-X., J. Mater. Chem., **14**, 2004, p.795
14. OGOSHI, T., CHUJO, Y., J. Mat. Chem., **15** (2), 2005, p. 315
15. ONO, M., YOSHII, K., High pressure research, **20**, 2001
16. PASCAL, P., Nouveau Traite de Chimie Minerale, vol. VIII, Masson et C^{ie} Editeurs, Paris, 1965
17. CAO, G.Z., Imperial College Press, London, 2004.
18. ZHANG, Y.P., LEE, S.H. et. al, J. Appl. Polym. Sci., **104**, 2007, p. 2743
19. SURIANARAYANAN, M., PANDURANGA RAO, S. et. al, J. Hazardous Mat., **62** (2), 1998, p. 187

Manuscript received: 16.04.2009