U.P.B. Sci. Bull., Series B, Vol. 73, Iss. 1, 2011 ISSN 1454-2331

NEW POLYMER INORGANIC-ORGANIC HYBRIDS OBTAINED THROUGH RADICAL POLYMERIZATION

Anita-Laura RADU[1], Andrei Sârbu[2], Celina Damian[3], Anamaria Lungu[4], Luminiţa MARA[5], Raluca MUNTEANU[6], Liliana SÂRBU[7], Horia IOVU[8]

Au fost sintetizate noi nanocompozite polimerice anorganic-organice pe bază de poliacetat de vinil. Ca matrice anorganică s-au utilizat 2 tipuri de compuşi: o silice mezoporoasă şi un zeolit modificat (HZSM-5). Polimerizarea radicalică a monomerului vinilic s-a realizat în porii structurii anorganice. Materiile prime au fost analizate cu ajutorul analizei chimice cantitative şi prin difuzia dinamică a luminii (DLS). Pentru a dovedi obţinerea de nanocompozite, produsele finale au fost caracterizate prin spectroscopie în infraroşu cu transformata Fourier (FTIR) şi spectroscopie cu fotoelectroni de raze X (XPS) pentru structura chimică, difracţie de raze X (XRD) pentru cristalininitate, microscopie electronică de baleiaj (SEM) pentru analiza microstructurală şi calorimetrie diferenţială de baleiaj (DSC) pentru determinarea tranziţiilor termice.

New polymer inorganic-organic nanocomposites based on polyvinyl acetate were synthesized. Two types of compounds: mesoporous silica and a modified zeolite (HZSM-5) were used as inorganic matrix. The radical polymerization of the vinyl monomer took place in the pores of the inorganic structure. The raw materials were analyzed by chemical quantitative analysis and dynamic light scattering (DLS). In order to prove the nanocomposite obtaining, the final products were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) for chemical structure, X-ray diffraction (XRD) for crystallinity, scanning electron microscopy (SEM) for microstructural analysis and differential scanning calorimetry (DSC) for thermal transitions assessment.

---

[1] PhD student, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania, e-mail: raduanita@yahoo.com

[2] PhD Eng., National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM, Romania

[3] PhD student, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania

[4] PhD student, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania

[5] Eng., National Research-Development Institute for Nonferrous and Rare Metals-IMNR, Bucharest, Romania

[6] PhD Eng., National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM, Romania

[7] Chim., National Research and Development Institute for Chemistry and Petrochemistry-ICECHIM, Romania

[8] Professor, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, Romania

Keywords: radical polymerization, inorganic-organic nanocomposite, hybrids

1. Introduction

Hybrid nanocomposites are materials that contain monomer molecules, polymer segments, solvents, or other organic species (guests) incorporated into host inorganic lattices [1]. Hosts include both natural materials and compounds prepared by various synthetic techniques and possessing well-defined intercalation properties. Rigid crystalline hosts (silicates, zeolites etc) with a controllable system of interconnected nanometer-sized pores are capable of accommodating atomic or molecular guest species. The resulting supramolecular structures have a unique molecular architecture [2]. The most important issues pertaining to the interpenetration into mesoporous hosts are sorption and phase transitions. Chemical analysis and structural characterization of hybrid materials prepared via in situ condensation, polymerization, or by incorporation of presynthesized macromolecules into mesoporous channels could reveal this aspects [3]. Aluminosilicate-polymer nanocomposites offer enhanced mechanical strength and thermal stability, interesting barrier properties for gas separation, and high thermal stability [4]. Layered aluminosilicates are often used as hosts for the polymerization of vinyl monomers [5]. The type of the forming inorganic structure/polymer nanocomposite depends on concentration and nature of the monomer as well as on the fabrication process and conditions [6]. Organic-inorganic hybrid materials [7], especially the composites consisting of nano-inorganic particles and polymers, have received considerable attention [8, 9] due to the fact that resultant materials are supposed to have better mechanical and/or thermal properties. These materials consist in more then 95 % organic polymer and less then 5 % inorganic silicates. Less studied are the inorganic- organic polymer nanocomposites in which the inorganic content is over 40-50 %. For instance, recently, considerable efforts have been devoted to the synthesis and application of mesoporous hybrids, because they can exhibit a synergistic combined performance of the individual components [10]. In particular, mesoporous silicate/polymer hybrids [11] are capable of providing combined advantages such as diverse functionality, flexibility, mechanical stability, chemical inertness, and high surface area. For this reason, there is a strong demand for the facile fabrication of mesoporous silicate/ polymer materials. Mesoporous silica is one of the most important porous inorganic materials, because it can find many potential applications such as in catalysis, sensing, adsorption electrochemistry and nanocasting for porous carbon [12–15].

The aim of this study was to explore new polymeric nanocomposites, in which mesoporous silica or a synthetic zeolite: molecular sieve zeolite in protonated form (HZSM-5), are the inorganic matrix. The main novelty is the use of such matrices as hosts for the radical polymerization of vinyl acetate, which opens new perspectives in the field. The raw materials were analyzed by chemical quantitative analysis and DLS.

The products were characterized by a combination of spectroscopic (FTIR, XPS), X-ray diffraction (XRD), thermal (DSC) and microscopy techniques (SEM). This paper is an attempt to put together the intercalation properties of inorganic hosts, the chemistry of the forming polymer guests, and the basic properties of the resultant hybrid nanocomposites.

2. Experimental part

2.1. Materials

Mesoporous silica was obtained in laboratory. The serpentinite from Dubova (Romania) dumps was grounded and attacked with concentrated mineral acid: HCl 6M, at 4.6 vol/wt ratio at 90 ^{o}C, during 90 min. A silica gel and a liquid were produced, which were separated by filtration. The silica gel was washed with water and dried yielding a grey silica powder, as a mesoporous material with pore dimensions of 2-20 nm [16]. HZSM-5, the synthetic zeolite, was supplied by UPG Ploiesti and used as received. Lauroyl peroxide (LP) and vinyl acetate (VA), were purchased from Fluka and were of analytical degree. VA was used disinhibited by rectification.

2.2. Inorganic-organic composite synthesis

The inorganic powder (silica, HZSM-5) was soaked with vinyl acetate (containing 0.5% lauroyl peroxide based on monomer) in 50 mL glass ampoules. Vinyl acetate was introduced in different vol/wt ratios to silica (Table 1) and to HZSM-5 (Table 2) and the ampoules were purged with nitrogen, in order to avoid the possible inhibition effect of oxygen.

Table 1

The composition of the silica samples used for nanocomposites obtaining

Sample	Silica (g)	Vinyl acetate (mL)	wt/vol ratio
P1	2	1.8	1:0.9
P2	2	2	1:1
P3	2	2.2	1:1.1
P4	2	2.5	1:1.25
P5	2	2.8	1:1.4

Table 2

Composition of synthetic zeolite samples used for nanocomposites obtaining

Sample	HZSM-5 (g)	Vinyl acetate (mL)	wt/vol ratio
P’1	2	4.5	1:2.25
P’2	2	4.8	1:2.4
P’3	2	5	1:2.5
P’4	2	5.2	1:2.6
P’5	2	5.5	1:2.75

Then, the ampoules were sealed with a rubber tube, tightened with a Hoffman clamp. For silica, the samples were named P1-P5 and for HZSM-5 zeolite, the samples were named P’1- P’5. Imbibitions, were performed in the sealed ampoules in an Elma

S10 Elmasonic ultrasonication bath, containing water, for 1 hour. After that, the ampoules were kept 24 hours at room temperature, without ultrasonication. Finally, a new 1 hour ultrasonication was applied. Composite materials were obtained by the introduction of the glass ampoules in an ultra thermostat water bath at 80 ^{o}C. Because the minimum decomposition temperature of lauroyl peroxide is around 80 ^{o}C and the boiling point of vinyl acetate is about 73 ^{o}C a low supra pressure in the sealed ampoules appeared. Although after 10 hours the initiator concentration becomes practically 0, the ampoules were kept 24 hours for polymerization, in order to be sure that the monomer conversion is practically total, eliminating any doubt of the monomer existence in the composite. In these conditions the polymerization of vinyl acetate within the silica or HZSM-5 pores occurred.

2.3. Analysis

The chemical quantitative analysis of silica and HZSM-5 was performed on an Atomic emission spectrometer Spectroflame, Germany.

Average diameter of silica or zeolite particles was determined with a Zetasizer Nano ZS ZEN 3600 instrument (Malvern) for diluted samples within ethylenglycol solution (0.1 %).

FTIR measurements of the final products, in KBr pellets, were performed on Bruker Vertex 70 equipment. The FT-IR spectra were recorded in 400÷4000 cm^{-1} range with 4 cm^{-1} resolution and 32 scans.

The XPS Spectra were recorded on Thermo Scientific K-Alpha equipment, fully integrated, with an aluminum anode monochromatic source.

The XRD spectra were registered on a Rigaku Ultima IV difractometer, with CuK α radiation. The scanned range was 2θ = 10 - 90°, with a scan speed of 5^{o}/min.

Differential scanning calorimetry (DSC) tests were performed on LINSEIS Pt 10 equipment using a rate of 5^{o}C/min, from room temperature to 300^{o}C.

Surface morphology of inorganic structures and nanocomposites was studied with scanning electron microscope type Quanta 200 applying an accelerating voltage between 10 and 15 kV.

3. Results

3.1. Silica and silicates analysis

Zeolites are micro porous crystalline solids with well-defined structures. Generally they contain silicon, aluminum and oxygen in their framework and cations, water and/or other molecules within their pores. The morphology and Si/Al ratio in the zeolite structure are influenced by different variables such as initial chemical composition, silicon and aluminum source. Silica was a mesoporous material with pore dimensions 2-20 nm [16].

In Fig. 1 one can see the content of significant elements in silica and zeolite samples, which were used to obtain the polymer hybrids. A rather similar composition of the two samples can be observed. It can be explained by the fact that silica was obtained from a natural magnesium silicate: serpentinite. The silicon to aluminum ratio was higher for silica compared with HZSM-5. The Si/Al ratio varies depending on their particular structure, and it is a result of the electrostatic interactions arising from $[AlO4]^{5-}$ adjacent tetrahedral. The sample HZSM-5 has a relatively low content of Ca, Na, K, and Mg, and in silica Na and K are missing. Also, the zeolite sample has 0.5% carbon in composition. An important feature of the used silica and silicate is the iron presence in their composition in amount of about 1%.

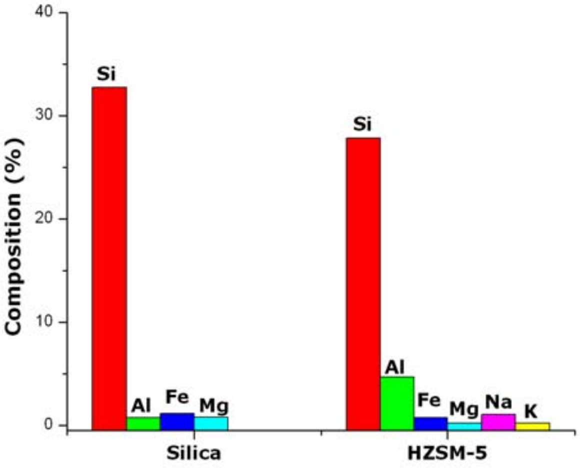


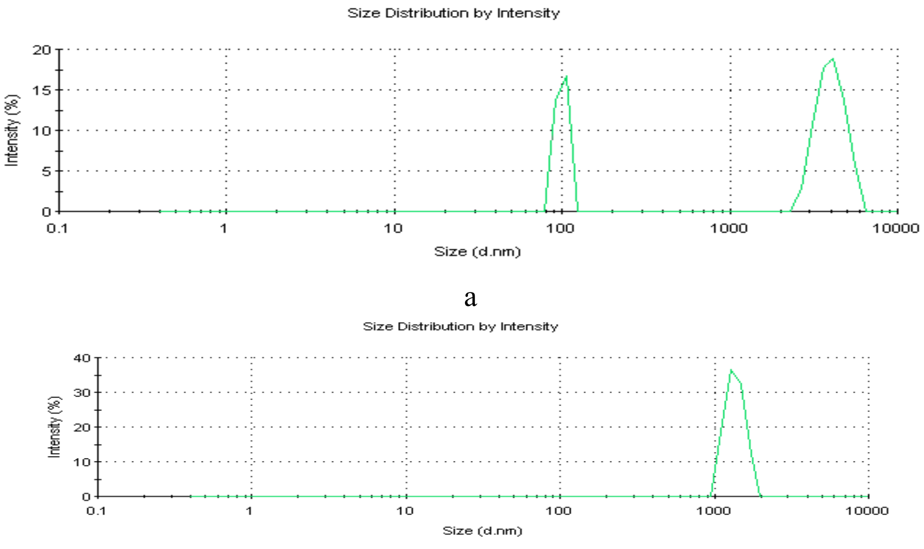
Fig. 1. Chemical composition of the silica and synthetic zeolite used in this study

The dynamic light scattering data are presented in Table 3 indicating a particle size distribution of the silica particles ranging from 99 nm to 4.0 µm. The diameter for the HZSM-5 particles is 1369 nm. The particle size distributions of the two host particles are presented in Fig. 2. For silica, a bimodal particles size distribution can be observed proving the existence of two types of silica particles of two different sizes. The two types of inorganic materials have different particle distributions as it can be seen from Fig. 2. It is bimodal for silica and unimodal for HZSM-5.

Table 3

DLS data concerning the diameter particles of inorganic materials

Sample	Diameter (nm)		Intensity (%)	
	Peak 1	Peak 2	Peak 1	Peak 2
Silica	4023	99.19	69.5	30.5
HZSM-5	1369	-	100	-



a

b

Fig. 2. Particle size distributions measured by DLS for silica (a) and HZSM-5 (b)

3.2. Nanocomposites characterization

Because the polymerization conversion cannot be measured in such complex systems, different analytical techniques were used in order to highlight the polymer nanocomposite formation. The FT-IR spectra of silica and HZSM-5 nanocomposites in the range of 400-4000 cm^{-1} are presented in Fig. 3 and Fig. 4 respectively.

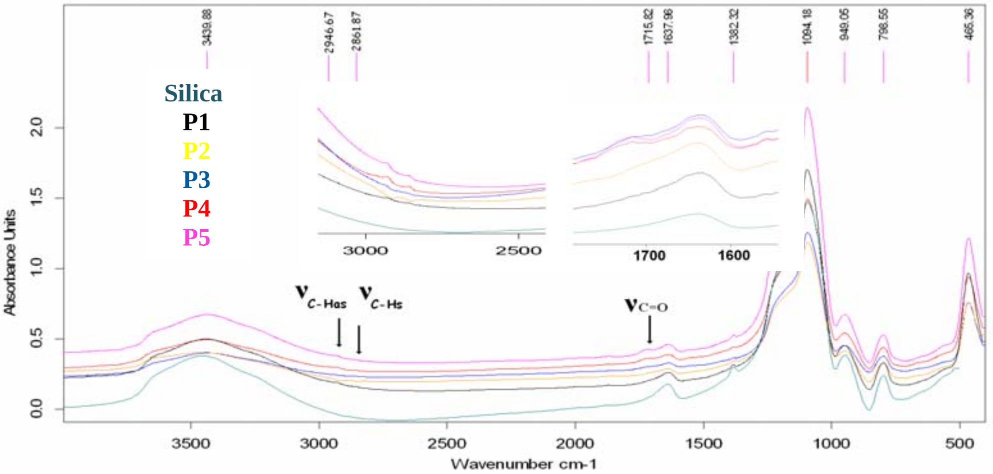


Fig. 3. FT-IR spectra for silica-polyvinyl acetate composites (P1-P5)

The FT-IR spectra of silicates-polymer nanocomposites show bands at 465, 798, 949, 1094 cm^{-1} (Si-O-Si - stretching vibration) for silica and at 446, 548, 1095, 1229 cm^{-1} for HZSM-5 which are assigned to different vibrations of tetrahedral and framework atoms in silicates. FT-IR spectra also showed the corresponding wavelength of C=O group, (stretching vibration) at 1715 cm^{-1} for P samples at 1741 cm^{-1} for P' samples, and 2900-2800 cm^{-1} for methyl groups (stretching vibration), which may be assigned to the vibration of C-H bonds from the organic radicals formed inside the inorganic pores. Additionally, the adsorptions bands at 1382 and 1400 cm^{-1} belong to the C–H bending vibrations which arise upon the reduction of the C=C double bond intensity. The C-H bonds, better seen in detail, are weak, probably due to the dispersion of the polymer in silica pores.

The FT-IR analysis is a good proof that the polymerization occured with the formation of the inorganic-organic nanocomposite compounds.

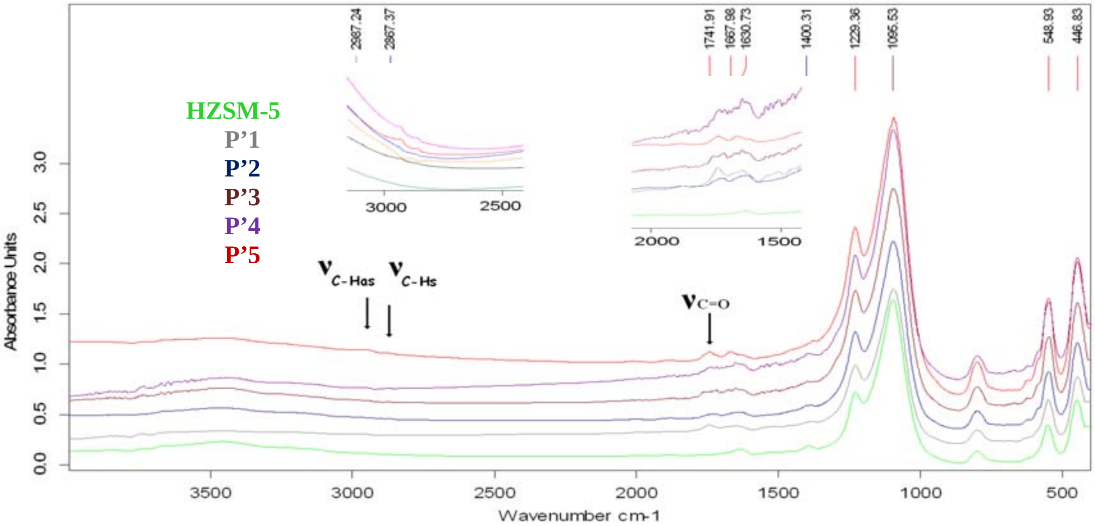


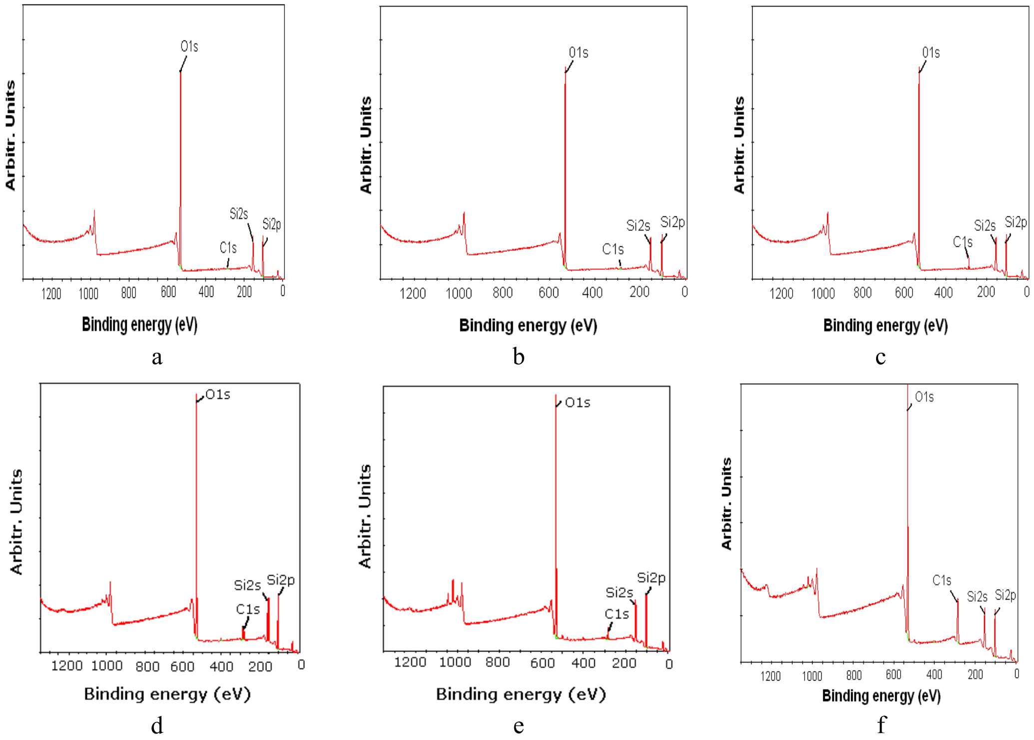
Fig. 4. FT-IR spectra for HZSM-5-polyvinyl acetate composites (P'1-P'5)

The XPS survey spectra were registered in order to identify the surface elements. They showed distinct silicon, oxygen, and carbon peaks which are the major constituents of the investigated silica, HZSM-5 and the obtained composites. No other major elements were detected. The XPS survey spectra for silica are shown in Fig. 5a, b, c, for HZSM-5 in Fig. 5d, e, f, and the relative atomic concentrations (At %) for silicon, oxygen, and carbon are listed in Table 4. As one can see, the carbon percentages of the composites (2.17 to 4.29% for P and 7.05 to 24.98 % for P' samples) slightly increase with the monomer concentration, which is probably explained by the formation of higher amount of polymer. In the same time, it appears that the polymerization of vinyl acetate occurs better in HZSM-5 micropores then in silica nanopores. The XPS data support the FT-IR results, proving again the hybrid host-guest material obtaining.

Table 4

Relative atomic concentrations (AT %) of the elements from XPS survey spectra

Sample	Si (%)	O (%)	C (%)
Silica	25.22	72.60	2.17
P3 silica-polyvinyl acetate composite	25.13	71.93	2.94
P5 silica-polyvinyl acetate composite	24.15	71.56	4.29
HZSM-5	23.62	69.32	7.05
P’3 HZSM-5-polyvinyl acetate composite	22.71	66.42	10.87
P’5 HZSM-5-polyvinyl acetate composite	16.05	54.11	24.98



a b c d e f

Fig. 5. XPS survey spectra for a) silica, b) P3 silica-polyvinyl acetate composite, c) P5 silica-polyvinyl acetate composite d) HZSM-5, e) P’3 HZSM-5-polyvinyl acetate composite, f) P’5 HZSM-5-polyvinyl acetate composite

XRD analysis was used in order to identify the possible changes in silicates crystalline phases by the polymerization of the vinyl monomers in the pores.

XRD results of HZSM-5 and their P’composites (Fig. 6) showed the characteristic peaks of crystalline HZSM-5 at 2θ = 13.19, 13.87, 14.77, 15.92, 17.74, 19.2, 20.23, 23.09, 23.84, 26.70, and 29.19^0 which correspond to Bragg distances of 6.70, 6.37, 5.98, 5.56, 4.99, 4.61, 4.38, 3.84, 3.72, 3.33 and 3.05 Å. These values show that the sample exhibits the typical ZSM-5 structural characteristics (MFI). Thus the polymerization in micropores does not disturb the crystalline structure of the HZSM- 5 host.

There are no significant shifts of characteristic peaks in the zeolite indicating that no strong specific chemical interactions occurred between the polymer and zeolites. However, non-specific interactions between the external hydroxyl groups or extra framework cations of zeolites and the polyvinyl acetate could occur.

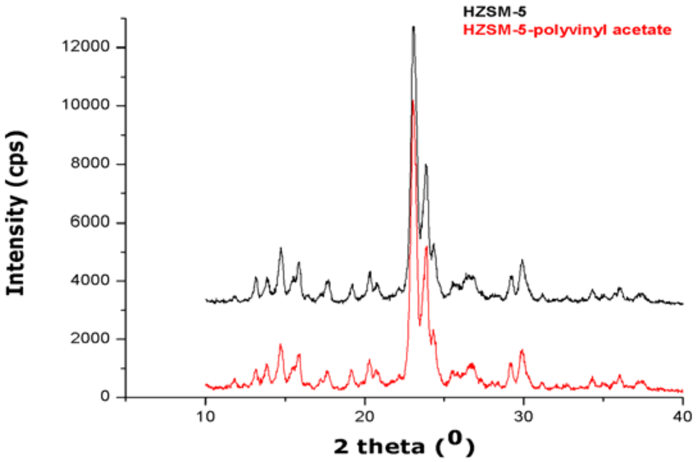


Fig. 6. X-ray diffraction profiles of HZSM-5 (a) and HZSM-5-polyvinyl acetate composite (b)

DSC is an analytical tool which helps to understand the thermal behavior of the silica-polyvinyl acetate nanocomposite having various polymer contents (Fig. 7). As the radical polymerization takes place in mesoporous silica particles, strong physical bonds have formed between silica particles and macromolecule network, and the movement of polymer chains at high temperature was restrained.

As one can see in Fig. 7, the increase of the vinyl acetate content in synthesis, leads to a displacement of the endothermic peak from 100 °C for P3, to 80 °C for P4, and 70 °C for P5 wich was a simultaneous attenuation. Because these endothermic peaks are most probably due to the water evaporation, and if we consider that the water in zeolite is retained in the pores, this means that the pores are filled with more polymer. As the monomer content increase in the synthesis, the free volume becomes lower, leading to a capillary effect on the water evaporation temperature.

The DSC data further support the formation of the hybrid polymer nanocomposite by the vinyl acetate polymerization in silica mesopores.

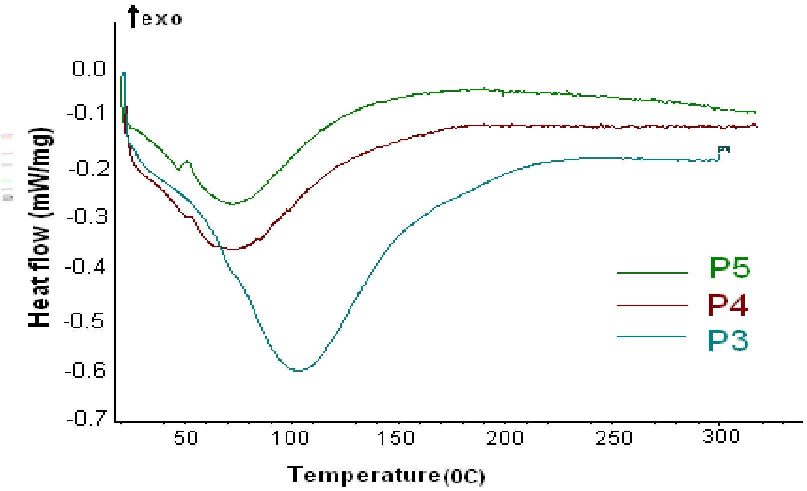
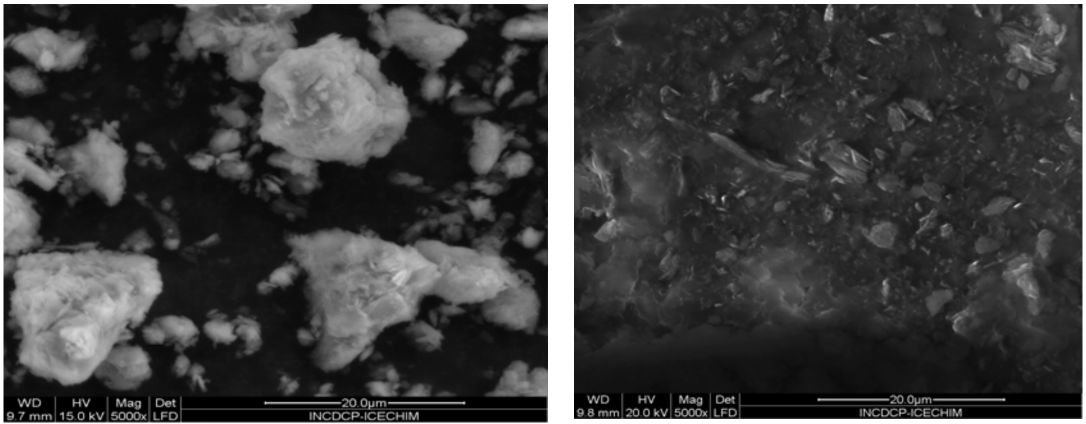


Fig. 7. The DSC curve for the silica-polyvinyl acetate composite

Pictures obtained by scanning electron microscopy give some useful information regarding the morphology and the dimensions changes of inorganic (HZSM-5) particles in the composite (Fig. 8). A great percent of particles with diameters between 1-20 µm appears in the raw material, as well in the composite.

The crystals with micro sizes show a rectangular shape (image (a)), while the composite particles exhibit typical shapes elliptic aggregated (image (b)). On Fig. 8 b), the pores covering with polymer can be also observed.



a b

Fig. 8. SEM images of HZSM-5 (a) and HZSM-5-polyvinyl acetate composite (b)

4. Conclusions

FT-IR spectra proved the formation of new inorganic-organic nanocomposite compounds. The XPS survey spectra allowed the identification of the surface elements and showed distinct silicon, oxygen, and carbon peaks which are the major constituents of the investigated silica, HZSM-5 and their composites. Polymer formation was proved by increasing the amount of carbon in the composites. XRD results proved that the polymerization in micropores does not disturb the crystalline structure of the HZSM- 5 host. The DSC analysis showed the filling of the silica pores with polymer. The SEM results showed the presence of a great percent of particles with diameters between 1-20 µm and the covering of pores with polymer. The radical polymerization of vinyl acetate organic monomer in inorganic (silica or HZSM-5) porous materials allowed the obtaining of a new hybrid material with high inorganic content (up to 40%). Taking into account the previewed depletion of oil in next decades, this result is very important because it opens the perspective of new composites obtaining with less organic material.

REFERENCES

[1] *A.D. Pomogailo*, Hybrid Intercalative Nanocomposites, Inorganic Materials, **vol. 41**, Suppl. 1, 2005, S47–S74

[2] *K. Mogyorosi, I. Dekany, J.H. Fendler*, Preparation and Characterisation of Clay Mineral Intercalated Titanium Dioxide Nanoparticles, Langmuir, **vol. 19**, no. 7, 2003, pp. 2939–2946

[3] *K. Moller, T. Bein*, Inclusion Chemistry in Periodic Mesoporous Hosts, Chem. Mater., **vol. 10**, no. 10, 1998, pp. 2950–2963

[4] *P. Gomez-Romero*, Hybrid Organic–Inorganic Materials— In Search of Synergic Activity, Adv. Mater., **vol. 13**, no. 3, 2001, pp. 163–174

[5] *D.W. Kim, A. Blumstein, S.K. Tripath*, Nanocomposite Films Derived from Exfoliated Functional Aluminosilicate through Electrostatic Layer-by-Layer Assembly, Chem. Mater., **vol. 13**, no. 5, 2001, pp. 1916–1922

[6] *Z. Vuluga, D. Donescu, C. Radovici, S. Serban, H. Paven*, Coupling and compatibilizer agents effects in polystyrene/layered silicate nanocomposites, U.P.B. Sci. Bull., Series B, **vol. 66,** no. 1, 2004

[7] *M.T. Runa, S.Z. Wu, D.Y. Zhang, G. Wu*, A polymer/mesoporous molecular sieve composite: Preparation, structure and properties, Materials Chemistry and Physics, **vol. 105**, 2007, p. 341–347

[8] *S.H. Kim, A.S. Hoon, H. Toshihiro*, Polymer, **vol. 44**, 2003, p. 5625

[9] *X.F. Li, W.C. Guan, H.B. Yan, L. Huang*, Mater. Chem. Phys., **vol. 88**, 2004, p. 53–58

[10] *X.B. Liu, F.X. Chang, L. Xu, Y. Yang, P. Tian, L.H. Qu, Z.M. Liu*, Microporous and Mesoporous Materials, **vol. 79**, 2005, p. 269

[11] *J. Jang, J. Bae*, Fabrication of mesoporous polymer/silica hybrid using surfactant-mediated sol–gel method, Journal of Non-Crystalline Solids, **vol. 352**, 2006, pp. 3979–3984

[12] *J. Yao, H. Wang, K.-Y. Chan, L. Zhang, N. Xu*, Incorporating organic polymer into silica walls: A novel strategy for synthesis of templated mesoporous silica with tunable pore structure, Microporous and Mesoporous Materials, vol. 82, 2005, pp.183–189

[13] *D. Donescu, R. Somoghi, C. Petcu, M.C. Corobea, R. Ianchis, C.L. Nistor*, Silica hybrid particles synthesized through sol-gel processes, U.P.B. Sci. Bull., Series B, **vol. 70**, No. 2, 2008, p. 39

[14] *B. Yuliarto, H.S. Zhou, T. Yamada, I. Honma, Y. Katsumura, M. Ichihara*, Anal. Chem., **vol. 76**, 2004, p. 6719

[15] *A.-L. Radu, A. Sarbu, L. Mara, A.-S. Garea, A. Lungu, S.-O. Dima, T.-V. Nicolescu, H. Iovu,* Influence of the ultrasonic field on the template polymerization of acrylonitrile in inorganic structures, Materiale Plastice **46**(4), 2009, pp. 399-403

[16] *A.-L. Radu, A. Sarbu, S. Motoc, L. Mara, V. Fruth-Oprisan, S. A. Garea, S.-O. Dima, G. Nechifor, L. Sarbu, H. Iovu*, New method for silicon nitride synthesis via hybrid polymer nanocomposites, Materiale Plastice, **47**(2), 2010, pp. 167-172