New polymer inorganic-organic nano hybrids obtained through radical polymerization

Anita-Laura RADU[1], Andrei SARBU[1], Celina Damian[2], Stefan-Ovidiu DIMA[1], Anamaria LUNGU[1], Tanta-Verona NICOLESCU[1], Horia IOVU[2]

[1]National Research- Development Institute for Chemistry and Petrochemistry- ICECHIM Bucharest, ROMANIA

[2] The Faculty of Applied Chemistry and Material Science, University Polytechnica Bucharest, ROMANIA

raduanita@yahoo.com

INTRODUCTION

Hybrid nanocomposites are materials that contain monomer molecules, polymer segments or other organic species (guests) incorporated into host inorganic lattices. Hosts include both natural materials and synthetic compounds possessing well-defined intercalation properties. Rigid crystalline hosts (silica, zeolites) with a controllable system of interconnected nanometer-sized pores are capable of accommodating atomic or molecular guest species. The type of the forming nanocomposite depends on the concentration and the nature of the monomer as well as on the fabrication conditions.

New polymer inorganic-organic nanocomposites based on polyvinyl acetate were synthesized. Two types of silicate: 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.

METHOD

The inorganic powder (silica, HZSM-5) was soaked with vinyl acetate (containing 0.5% lauroyl peroxide based on monomer) in 10 mL glass ampoules. Vinyl acetate was introduced in different vol/wt ratios to silica (Table 1). For imbibitions (the penetration of monomer in silica pores), the ampoules were introduced in an ultrasonication bath 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°C, 24 hours. In these conditions the polymerization of vinyl acetate within the silica pores occurred. For zeolite HZSM-5 the same procedure was used and the samples were named P'1- P'5. The raw materials were analyzed by Chemical quantitative analysis and DLS. In order to prove the nanocomposite obtaining, the final products were characterized by XPS, XRD, and SEM.

RESULTS

Table 2 presents the chemical composition and Fig. 1 the content of significant elements of the silica and silicate samples, used to obtain the polymer hybrids. A rather similar composition of the two samples can be observed which can be explained by the fact that silica was obtained from a natural magnesium silicate: serpentinite. Silica has a higher silicon to aluminum ratio then ZSM-5. The average hydrodynamic diameter of the particles was determined, and is represented in Fig. 2. Greater average diameter values for the HZSM-5 inorganic compound with 2.136 μm value is probably due to the tendency of particles agglomeration in etylenglycol medium. Also, for silica, the presence of a bimodal particles size distribution can be observed. The XPS survey spectra (Fig. 3) were registered in order to identify the surface elements and showed distinct silicone and oxygen peaks which are the major constituents of the investigated HZSM-5 and the obtained composite. For the composite in was noticed an increased percentage of oxygen (69.29 to 71.2%) and the existence of carbon (10.87%), being is probably explained by the formation of polymer. XRD results of HZSM-5 and their composites (Fig. 4) showed the characteristic peaks of crystalline HZSM-5. In the composite pattern, an increase of peak intensities at 23.84° can be observed after the polymerization of the monomer in the composite, confirming the incorporation of polyvinyl acetate into zeolite. Imagine obtained from scanning electronic microscope (Fig. 5) give some useful information regarding the morphology and the dimensions of composite particles. A great percent of particles with diameters between 1-20 μm appears. The nano-structured particles exhibit typical aggregated elliptic shapes, which are due probably to the strong surface free energy of the small particles.

Table 1: The composition of the samples used for nanocomposites obtaining

Sample	Silica (g)	Vinyl acetate (mL)	wt/vol ratio
P1	2	1.5	1:0.75
P2	2	1.8	1:0.9
P3	2	2	1:1
P4	2	2.2	1:1.1
P5	2	2.5	1:1.25

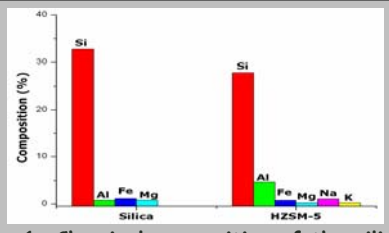

Fig. 1: Chemical composition of the silica and the synthetic zeolite used in this study

Table 2:The chemical quantitative analysis of the samples

Sample	Si %	Al %	Na %	K %	Fe %	Mg %	Cr %	Ni %	Cu %	Mn %	Ti %
Silica	32.75	0.76	-	-	1.16	0.80	0.71	0.008	0.028	0.012	0.02
HZSM-5	27.84	4.68	1.05	0.2	0.76	0.21	0.002	0.009	0.011	0.03	0.074

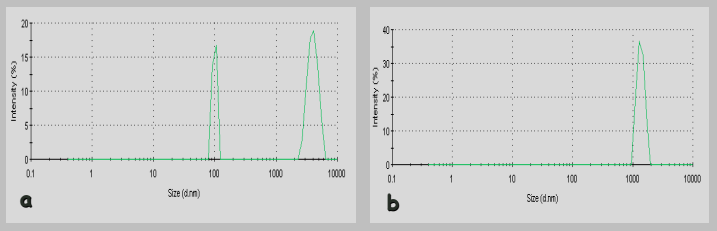

Fig. 2: Size distribution by intensity of silica (a) and HZSM-5 (b)

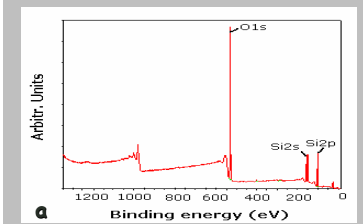

Fig. 3: XPS survey spectra for a) HZSM-5 and b) HZSM-5-Polyvinyl acetate composite

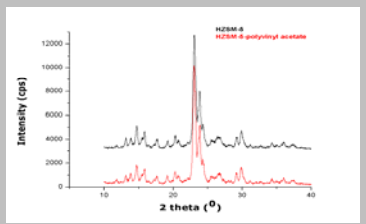

Fig. 4: XRD profiles of HZSM-5 and HZSM-5-polyvinyl acetate composite

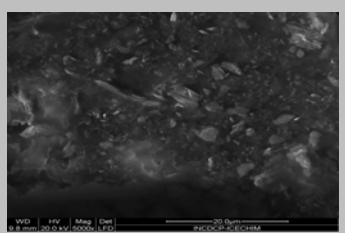

Fig. 5: SEM images of HZSM-5-polyvinyl acetate composite