



Unique polyvinyl acetate–mesoporous synthetic zeolite composites prepared in ultrasonic field



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ABSTRACT

The host–guest radical polymerization of vinyl acetate in the inorganic porous matrix improved both, thermal and mechanical properties of final modified material, relative to the polymer alone, which can be further used for various applications where stability in aggressive environments is required. The bulk material was characterized by various techniques i.e. elemental analysis, X-ray photoelectron spectroscopy (XPS), gel permeation chromatography (GPC), thermal gravimetric analysis (TGA), dynamic mechanical analysis (DMA), scanning electron microscopy (SEM) and porosity measurements (BET). XPS measurements indicated a preferential order of acetate groups at the surface of the hybrid and BET analyses highlighted the formation of a new porous structure derived from the mesoporous inorganic host. GPC results of the polymer extracted from the zeolite matrix showed variations of molecular weight and low polydispersity index relative to the pure polymer, which could be a consequence of a controlled polymerization mechanism induced by the presence of metal ions found in the zeolite matrix. Thermal stability and elasticity of the restrained polymer compared to that of pure PVAc was notably enhanced. Char formation in the sixth degradation stage and demethylation were additional steps compared to PVAc alone indicating some modifications of the thermal degradation mechanism for the entrapped PVAc.

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1. Introduction

Inorganic–organic hybrid is the collective term for materials including inorganic–organic, host–guest supramolecular materials, self assembled monolayers, nanocomposites, layered inorganic–organic compounds which can be formed by hybridization of inorganic structures and organic compounds [1–3]. These hybrids are formed by a synergetic combination of inorganic materials and organic polymers, both being highly attractive creating high-performance polymeric composites [4–6]. Advanced composite materials combine the unique properties of inorganic materials (hardness, rigidity and thermal stability) with those of organic polymers (flexibility, processability).

For the last decades, polymer composites have been receiving a considerable attention [7–9] due to the possibility of tailoring novel materials with improved thermal [10,11] and mechanical

[12,13] properties compared to those of polymers alone. Hence, designing organic–inorganic composites is an excellent way to induce other properties or improve the existing ones. The main difficulty in tailoring new composites refers to maintain raw materials’ properties of interest to a proper level while designing the new ones or improving the deficient ones. In this direction, considerable interest was focused upon encapsulation methods for polymers into host inorganic matrix as reinforcement component. Microporous zeolites and mesoporous silica have proven to be the most suited raw materials to allow insertion of various organic species within their highly porous structures [14–22]. Moreover, these molecular sieves are ideal host materials for supramolecular organized arrangements, providing high mechanical, chemical and thermal stability [23]. Zeolites, in particular, are crystalline oxides with regular porosity. Their pores have variable openings, usually presenting internal cavities of variable size and shape [24,25]. Poly (methyl methacrylate) [26,27], polystyrene [28], polyaniline [29] or polypyrrole [30] have been used so far as guest compounds in order to synthesize inorganic–organic composites with unique

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properties. The resulted hybrid materials presented potential for innovative applications i.e. ceramic filters, solar cell materials, protective and decorative coatings, and micro-optic articles [31–33]. Polymers synthesized under these special conditions have been intensively examined in order to properly correlate and control the morphology and the mechanical, electrical and photochemical properties of the final materials. However, most publications refer to polymer composites with small content of inorganic compounds (3–10%) [34,35]. Very few studies are actually debating the structure and properties of inorganic–organic polymer composites in which the inorganic content is exceeding 30–50%.

Therefore, this study proposes a new approach for designing new composite materials where the polyvinyl acetate was reinforced with mesoporous HZSM-5 inorganic host generating a unique class of hybrids with superior mechanical properties and higher thermal stability than similar materials. HZSM-5 zeolite is a well-known crystalline microporous solid consisting of tetrahedral primary building blocks linked through oxygen atoms; the three-dimensional networks contain pore and channel systems in the molecular size range of about 5 Å [36,37]. However, due to difficulties implying slow adsorption–desorption processes [38], basically governed by diffusion of particles in the microporous structure, our domain of interest referred to the influence of the mesoporous structure of the synthetic zeolite upon PVAc properties and global composite properties. As a result, the new mesoporous inorganic–organic composites based on HZSM-5-polyvinyl acetate can be further used as precursors for advanced ceramic powders–silicon carbide–obtained by a carbothermal reaction at high temperatures.

2. Experimental details

2.1. Chemicals

The synthetic zeolite, HZSM-5, employed in this study was received from Petroleum-Gas University (Ploiesti, Romania) as a pilot plant product. The zeolite presented the following characteristics according to the technical report: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1/45$ (mole/mole), mean particle size = 1369 nm (± 10 nm), crystallinity degree = 100%, BET specific surface area = $418 \text{ m}^2 \text{ g}^{-1}$, mean pore volume = $0.19 \text{ cm}^3 \text{ g}^{-1}$, pore size distribution in the ranges 5–20 Å (micro) and 20–300 Å (meso) were 89% and 11%, respectively. Vinyl acetate (VAc, 99%) and lauroyl peroxide (LP, 99%) were purchased from Sigma Chemical Co (St. Louis, USA). The monomer was distilled in order to remove the polymerization inhibitor and stored in the freezer (under 5 °C) before use.

2.2. Preparation of hybrid composites via host–guest polymerization

The hybrid composites were prepared by an original approach. A typical run consisted into the following steps: (i) impregnation/adsorption of VAc in the zeolite pores assisted by ultrasonication; (ii) polymerization of VAc assisted by ultrasonication. Primarily, a specific quantity of zeolite–HZSM-5 (2 g), increasing amounts of monomer–VAc (64 wt.%, 66 wt.%, and 68 wt.% monomer content relative to the zeolite) and the radical initiator–LP (1 wt.% relative to the monomer), were added in 10 mL glass vials. Afterward, the vials were purged with dry nitrogen gas, for about 3 min, in order to remove any existing oxygen and sealed with rubber caps. Subsequently, the glass tubes were ultrasonicated in an Elmasonic bath type Elma S10 for 24 h at room temperature in order to disperse the VAc homogeneously in the entire mesoporous network of HZSM-5 synthetic zeolite. The polymerization process was carried out in ultrasonic field in the same Elmasonic bath for 24 h at 80 °C. Similar procedures were applied for the polymerization of VAc

alone, used as reference. The obtained inorganic–organic composites were grinded and dried in an oven at 105 °C to a constant weight.

2.3. Characterization methods

2.3.1. X-ray fluorescence (XRF)

The elemental compositions were determined using a Rigaku ZSX Primus XRF device. Samples were prepared as flat disks, using a weighed mixture of sample powder and lithium tetraborate flux.

2.3.2. X-ray photoelectron spectra (XPS)

The X-ray photoelectron spectra (XPS) were recorded on a K-Alpha instrument from Thermo Fisher Scientific, fully integrated, using a monochromated Al $K\alpha$ source (1486.6 eV). The charging effects were compensated by an argon flood gun. The pass energy for the survey spectra was 200 eV and 20 eV for high resolution. Deconvolution of C 1s peaks was accomplished after subtraction of a Shirley background.

2.3.3. X-ray diffraction (XRD)

Powder XRD patterns were collected with a Rigaku Ultima IV diffractometer equipped with Cu $K\alpha$ radiation. The scanned range was $2\theta = 10\text{--}90^\circ$, with a scan speed of $5^\circ/\text{min}$.

2.3.4. Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halanda (BJH) methods

The BET surface area and pore measurement (BJH method) for the HZSM-5 synthetic zeolite and obtained composites were carried out by nitrogen adsorption using a Micromeritics ASAP 2020 V3.05 H analyzer. Nitrogen sorption isotherms at -196°C were recorded after all the samples were outgassed at 100°C for 3 h under vacuum prior to N_2 adsorption. The area of interest referred to the mesoporous/macroporous domains of zeolite and composites ($>2 \text{ nm}$ pore size distribution).

2.3.5. Scanning electron microscopy (SEM)

SEM images were registered using a FEI Quanta 3D FEG with Focused Ion Beam (FIB) instrument equipped with energy dispersive X-ray spectroscopy. The X-ray energy dispersive spectrometer was set at 20 kV acceleration voltage (SE-secondary electrons).

2.3.6. Gel permeation chromatography (GPC)

Gel permeation chromatograms were registered using the HPLC 1200 Series with refractive index detector (RID) from Agilent Technologies equipped with a PLGel Mixed-C ($300 \times 7.5 \text{ mm}$) Column and isocratic pump. Dimethylformamide (DMF) was used as mobile phase at a 1 ml/min flow rate. The column was calibrated using polystyrene EasiCal standards in the 162–5,000,000 g/mol range of molecular weight (M_n). Approximately 0.047 g of composite material was dispersed in 5 mL DMF and kept for 24 h at 25°C so that polymer dissolution from the zeolite pores to take place. The zeolite was separated from the resulted suspension through a specific HPLC 0.45 μm filter and the filtrate, containing solubilized PVAc was degassed for 15 min before being analyzed by GPC.

2.3.7. Thermogravimetric analyses (TGA) and differential thermal gravimetry (DTG)

TGA and DTG tests were performed on Q500 TA equipment, under nitrogen atmosphere using a $10^\circ\text{C min}^{-1}$ heating rate, from room temperature to 700°C .

2.3.8. Dynamic mechanical analysis (DMA)

DMA curves were recorded on a Q800 TA instrument. Each sample was heated from 25 to 180°C , using a 3°C min^{-1} heating rate

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