Polymer–silica composites and silicas produced by high-temperature degradation of organic component

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ABSTRACT

Highly porous polymer–silica nanocomposites and silica gels were prepared using cross-linked copolymer resins of various chemical character as organic templates. Tetraethyl orthosilicate (TEOS) was successfully introduced into the template by the swelling of the preformed polymer particles. The silica source introduced into the resins was transferred into the silica gel by the means of the sol–gel method. After the organic component had been removed during a high temperature treatment of the polymer–silica nanocomposites, the spherically shaped silica particles were obtained. The pore structure of nanocomposites and calcined pellets was investigated through the conventional adsorption method so as to study the evolution of the porosity in the polymer templates of various character. The analysis of the porosity parameters characterizing the investigated materials within micro- and mesopores indicates a varying extent of the penetration of silica component into polymer templates, depending on their geometrical structure and hydrophobicity.

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1. Introduction

The preparation of the nanostructured solid particles of the desired size and morphology for specific applications is an important challenge for materials science. Multicomponent inorganic–organic composites play an important role in this field due to their particular thermal, mechanical and chemical properties [1–5]. It is well recognized that polymer–silica composites exhibit unusual and, very often, unique properties which cannot be observed for polymer and inorganic phase separately [6–9]. Much attention is focused particularly on the controlled embedding of silica nanoparticles in the polymer matrices. The development and improvement of various methods of synthesis have made it possible to prepare the silica–polymer nanocomposite particles exhibiting various interesting morphologies [10–12] and with potential applications including catalysis, separation of gas and liquid compounds, encapsulation of bioactive substances, chemical sensing, etc. [12–15]. Generally, there are three most commonly used ways of the silica–polymer nanocomposite preparation: first, the method consisting in the dispersion of the silica particles as fillers within the polymer matrix [6,8,9,15–19]; second, the in situ polymerization of monomers in the presence of silica [19–22]; finally, the

sol–gel processes of silica precursor in the presence of polymer or monomers [13,15]. The fusion of the silica species with polymer component may lead to an inhomogeneous distribution of inorganic particles within the resulting final nanocomposite material due to its aggregation. Therefore, the chemical modification of silica is a common practice resulting in a larger compatibility of the components and the enhancement of the interaction between them [7,10,12,22–25]. The adsorption of small silica particles onto polymer particles is assumed to be an efficient method for preparation of nanocomposites particles with core–shell morphology [15,24].

Recently, a novel approach has been proposed for the synthesis of a polymer–silica nanocomposite with particles of various sizes. This method consists in the swelling of the preformed polymer particles of desired pore structure in tetraethoxysilane (TEOS) as a silica gel precursor [18,26–31]. The swelling process consists in filling the pores with TEOS, which subsequently penetrates the spaces between the chains of polymer matrix. The spherically shaped beads of polymer–silica nanocomposite are obtained after the transformation of the inorganic precursor in aqueous solutions of the desired pH into a silica gel [29–31]. This approach represents an efficient route in the preparation of polymer–oxide composites applying a cross-linked polymer matrix swollen in oxide precursor. The pores of polymer are precipitation environment for oxide component. This route is in some way similar to previously used the mixing of the nanoparticles with monomer followed by polymerization or simultaneous polymerization of both components. The

final polymer–inorganic materials exhibit a relatively high porosity of pore volume, exceeding 1 cm^3/g, and pores within mesopore range. Moreover, after the removal of the organic component during a high temperature treatment of the nanocomposites, the spherically shaped porous particles of silica gel have been obtained. It should be stressed that their internal structure strongly depends on the conditions of the silica precursor condensation [29]. The procedure resembles the preparation of carbon adsorbents on the silica template, in which the final carbon material contains pores formed after the removal of the silica component [32]. A similar approach was also applied for the synthesis of specific titanium sorbents for the removal of arsenic from water systems [33,34].

Continuing our previous work, we presented the advantages of the swelling method in preparation of the polymer–silica nanocomposites. Commercially available porous polymer insoluble beads Amberlite P-4, P-16 and P-7 were used as templates in the preparation of polymer–silica nanocomposites. All the three templates are highly porous and differentiated in respect of the arrangement of the basic structural polymer species. Therefore, the aim of this study was to investigate the influence of the porosity and chemical character of the skeleton of polymer templates on the porosity of the polymer–silica nanocomposites and, finally, the silica spheres. As it was demonstrated elsewhere [18,31], the calcination of such organic-inorganic composites allows to obtain silica gels in the form of spherical beads of a unique internal structure. Thus, the structural differences in the pure silica gel obtained after high temperature treatment of our composites were studied with respect to structural characteristics of applied polymer templates. These investigations are very useful in evaluating the materials for possible applications as specific sorbents of desired porosity or as a sustained drug release systems. The investigated materials were tested at different stages of their preparation with the use of scanning electron microscopy (SEM) and low temperature nitrogen adsorption and thermogravimetry (TGA). In order to illustrate that our swelling method facilitate the preparation of highly porous silica microspheres using porous polymer template, we perform the preparation changing the template.

2. Experimental

2.1. Synthesis procedure

Commercially available Amberlite P-4 and P-7 supplied by ROHM & HAAS (now Dow Chemical Co.) were used as a polymer porous template for the fabrication of polymer–silica nanocomposites. Both P-4 and P-16 polymeric adsorbent are hydrophobic nonionic cross-linked polystyrene-divinyl benzene copolymer resins, but their porosity differs substantially. In contrast, P-7 is a non-ionic acrylic polymer of moderately polar character. The polymer–silica composites were synthesized according to the procedure which has recently been described in detail in Refs. [30,31]. First, in accordance with the manufacturer's suggestion, the polymers were rinsed very carefully with distilled water and dried in air for 10 h at 80 °C. Thereafter, the dry polymer templates were soaked with tetraethoxysilane (TEOS, Sigma-Aldrich, 98%). The amount of added silica source was adjusted so that the beads started to stick together but still preserved a loosely packed structure of individual particles. It should be stressed that the amount of absorbed TEOS varied considerably between polymer templates (see Table 2). Next, the samples were treated with 200 cm^3 of 2 M HCl solution and left for 24 h at room temperature for gelation and aging. Afterwards, the spherically shaped polymer–silica composites were rinsed with distilled water and dried for 8 h at 80 °C. The fabricated composites were named: P–Si-4, P–Si-16 and P–Si-7, respectively. In order to prepare pure SiO$_2$, a part of the samples, P–Si-4, P–Si-16 and P–Si-7 were calcined in air at 550 °C for 10 h. The remaining incombustible

residues, being the pure SiO$_2$ component of the composites, were designated as P–Si-4, P–Si-16 and P–Si-7, respectively. Moreover, the residual organic content in the P–Si-4, P–Si-16 and P–Si-7 samples was determined and estimated to be approximately little higher that 1% w/w for carbon, nitrogen and hydrogen. The elemental analysis was performed using a CHN analyzer (Perkin-Elmer CHN 2400).

2.2. Characterization methods

2.2.1. Scanning electron microscopy

The morphology of the polymers and their derivatives was examined with the use of scanning electron microscope (FEI Quanta 3D FEG) working at 5 and 30 kV. Before the examination, all samples were coated with high-purity Au/Pd alloy with the use of high vacuum sputter coater to eliminate the charging of the specimen.

2.2.2. Nuclear magnetic resonanse

The ^{29}Si magic-angle spinning (MAS) NMR spectra of the solid samples were carried out on a Bruker Avance 300 spectrometer at resonance frequency of 59.6 MHz. For ^{29}Si NMR 4 mm circonia rotors spun at 8 kHz was used. About 8000 scans were applied until a satisfactory signal-to-noise ratio was achieved. The spectra were recorded by using HPDEC pulse program. The chemical shifts are given in ppm and referenced to tetramethyl silane as a standard material (dTMS = 0).

2.2.3. Low-temperature nitrogen adsorption

Nitrogen adsorption/desorption isotherms were measured at −196 °C using a volumetric adsorption analyzer ASAP 2405 (Micromeritics, Norcros, GA). The standard Brunauer-Emmett-Teller (BET) method was used to evaluate the specific surface area [35]. The total pore volume was estimated from single point adsorption at $p/p_0 = 0.985$. The pore size distributions were calculated from the desorption branch of the isotherms by using the Barrett–Joyner–Halenda (BJH) procedure [36].

2.3. Swelling of polymers in TEOS

The measurements of swelling ratios (SW) of polymers P-4, XAD7 and P-16 in TEOS were used by volumetric swelling method. To three graduate cylinders, 2 cm^3 of each polymer were added (earlier washed with deionized water and dried under vacuum); subsequently 4 cm^3 of TEOS were added. After 1 h, the volumes of swelled polymers were noted.

Swelling ratios (SW) were calculated from equation:

$$SW = \frac{V_F - V_I}{V_I} \times 100\%$$

where: V_F—final volume of swollen polymer, V_I—initial volume of polymer before swelling.

2.4. Thermal Analysis TG

n-Heptane was used as wetting liquids. Thermodesorption experiments were made with Derivatograph C (MOM, Hungary), using the quasi-isothermal program developed by Paulik and Paulik [37,38] at the heating rate of 3°/min within the linear heating range. The samples in the form of paste were prepared by adding an excess of liquid adsorbate to the dry adsorbent and were placed in a conical platinum crucible. Prior to the experiment, the silica gels were outgassed to facilitate the penetration of liquid adsorbate into pores.