



Amberlite XAD copolymers as an environment for silica deposition



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ABSTRACT

Polymer-silica composites are one of the most important and popular groups of functional materials. Thanks to their unique properties combining the features of both polymer and silica components, they are increasingly used in many areas of life. Amberlite-silica composites were prepared via swelling of a polymer in tetraethoxysilane TEOS. The influence of the character of the polymer and temperature on the composite structure is discussed. A systematic study of the structure of the polymer-silica composites was carried out using various techniques. The pore system of the investigated materials was examined by nitrogen adsorption measurements. The mesopore structure of initial polymers is substantially changed after incorporation of the silica component. Thermal transformation of the silica and polymer network was investigated by positronium annihilation lifetime spectroscopy PALS. Morphological features of the bulk material were studied using SEM and a profilometer. Mechanical resistance of spherical composite materials and silica produced by combustion of the polymer in the composite was determined in a compressive stress experiment. Beside conventional information, structural characterization is supplemented with discussion of the structural stability of the studied materials in a wide temperature range. Characterization of the composite materials on a molecular scale allows optimal use and further development of the new synthesis route discussed.

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1. Introduction

Polymer-silica composites with specific porosity and morphology are of great importance due to numerous applications such as high selective sorption, catalysis, controlling systems for drug release, chemical sensing, or membranes [1–4]. Thus, the production of these materials has been a great challenge for many years. The most popular seem to be composites obtained by controlled embedment of the silica component into a polymer representing various morphological forms such as microemulsion or preformed polymer rigid particle [5–7]. In such a case, the shape and size of the final particles may be tuned in advance. A great advantage of polymer-silica composites is that they may be used as an intermediate product, calcination of which offers pure silica a unique pore structure and a highly developed surface. This is a useful method for production of porous silica materials with desired morphology, which uses polymer as a hard template and pore creating agent [8–11].

Recently, the polymer-silica composite has been prepared by swelling of cross-linked polymers such as Amberlites XAD in silica precursors, e.g. tetraethoxysilicates [7,8,12]. Among commercially available porous polymers, the Amberlites are very popular and widely used in separation processes. Amberlite XAD7 has been most intensively studied during the recent decades [13–16]. The pores of the polymer used and any free volumes in the polymer matrix are a good precipitation environment for the oxide component [17].

In our earlier application of this approach, we focused on the Amberlite XAD7-silica composite [18,19]. Mutual relations between both components in the composite were discussed in terms of their sorption properties. The objective of the present work is to gain a better description of the composite structure and the derived silica material.

All members of the Amberlite's family are polymers composed of small spherical particles, which in turn are assembled into larger spheres. Their characteristic porosity represents the space between these primary particles. The distribution of their dimensions is rather narrow, as suggested by the data presented earlier [8,20]. Thanks to the existence of this nanometer-size free space, all

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polymers easily swell in organic solvents. The substantial uptake of the solvent occurs via infiltration of the polymer network by solvent molecules, but also due to the capillary forces present between the primary particles. This is the main cause of the very high uptake of most solvents by Amberlites. More than double uptakes have been recorded, inter alia, for Amberlite XAD7 and such solvents as propanol, water, and chloroform [21]. Similarly high uptakes have been observed in the case of liquid silanes, e.g. tetraalkoxysilanes. Interestingly, the solvent uptake is different for polymers with an identical chemical character, but different porosity and total pore volume, e.g. XAD4 and XAD16 [8,21]. This effect suggests that the pore structure plays an important role in polymer swelling and solvent uptake. Thus, this factor has fundamental relevance in preparation of silica(oxide)-polymer composites.

The porosity of the composite is influenced by intermolecular interactions of the silica precursor and the polymer component. After mixing of both organic and inorganic components, a new material with a mixed chemical composition is obtained. Usually, this new product displays a modified mechanical, thermal, and structural character in comparison to the pure components. Although the chemical character is in great part maintained after mixing, the physical features of components are usually changed. The physical parameters, mainly structural ones, of both components are not additive due to the specific conditions of silica condensation and, very probably, a different degree of the mutual infiltration of both components. Hydrolysis and, first of all, 3D condensation of the silica precursor inside the pores of a polymer may be expected to have a different course than in the bulk solution, as in conventional synthesis. It is hard to predict the interactions between TEOS and a given polymer network. TEOS is assumed as a hydrophobic agent, which is confirmed by its weak solubility in water. On the other hand, crosslinked polymers are also dominantly hydrophobic due to the presence of numerous hydrophobic segments, mainly with a hydrocarbon character, in their structure. Among Amberlites, mesoporous resins Amberlite XAD4 and Amberlite XAD16 are highly hydrophobic. Both are composed of styrene-divinylbenzene and are characterized by a different pore structure. In turn, as a crosslinked acrylic polyester, Amberlite XAD7 is assumed to be a moderately polar polymer [16,22]. The synthesis strategy, which consists in application of swelling in the preparation of the polymer-silica composite, is particularly attractive for the latter polymer because it yields mechanically stable spheres with high silica content (up to 20%). The structure of the composites prepared by wetting and swelling with silica precursors was widely discussed earlier [7,8]. However, there are several questions concerning the relationships between both components that should be explained. The main ones are: (i) whether the silica precursor infiltrates only the free space of pores or the polymer network as well (in the latter case, the polymer network should be permanently deformed in the composite), (ii) whether, at the absence of polymer infiltration, the properties of both components are preserved and identical to the properties of the pure components, and (iii) whether the composite porosity is a sum of the porosity of the silica component inside pores and the porosity of the polymer, i.e. whether their porosities are additive.

2. Experimental

2.1. Materials

Amberlites XAD4, XAD7, and XAD16, 20–60 mesh (Rohm & Haas Co), and tetraethoxysilane (TEOS, 98%) were purchased from Sigma Aldrich. Hydrochloric acid (33–35%) and ethyl alcohol (99.8%) were supplied by POCH (Poland). All reagents were used without further purification. Prior to sample preparation, all

Amberlite resins were washed with deionized water and dried at 353 K under vacuum.

2.2. Sample preparation

Polymer-silica composite samples were prepared according to the procedure described earlier [7,8]. Dry commercial polymers XAD4, XAD7, and XAD16 were initially washed in the manner recommended by the manufacturer. Then, the polymers were soaked with TEOS until all beads were swollen but did not stick to each other (1.3 g TEOS/1 g XAD4, 1.9 TEOS/1 g XAD7, and 2.1 g TEOS/1 g XAD16). Next, the samples saturated with TEOS were immersed in 200 cm³ of 2 M HCl solution and left for 24 h at room temperature. After that time, the polymer-silica materials obtained were filtered, rinsed with deionized water, and dried at 373 K. The prepared polymer-silica composites were labeled as X4-Si, X7-Si, and X16-Si. After calcination of a part of each composite sample at 823 K for 12 h, pure silica materials named Si-4, Si-7, and Si-16 were obtained. The amounts of pure silica in the composite samples (determined gravimetrically after calcination) were 19%, 25%, and 9% for X4-Si, X7-Si, and X16-Si, respectively.

Analogously to the procedure described above, two other types of XAD7 polymer-silica composites and pure silica samples were prepared. The first one was synthesized in the same way as the X7-Si sample, but the polymer saturated with TEOS was rinsed with ethanol and dried at 373 K before immersing in the acid solution. The further procedure was unchanged. The composite and calcined samples were named analogously X7-SiE for the composite and Si-7E for pure silica. The amount of pure silica in the X7-SiE composite sample was estimated at 18%. The second sample was prepared in a similar manner but at elevated temperature. The pure XAD7 polymer was immersed in an excess of TEOS (3.8 g TEOS/1 g X7), then the mixture was heated up to 423 K (above the glass transition temperature of XAD7) with stirring for 3 h. The polymer structure becomes flexible at this temperature. Thermal energy is sufficient to change the amorphous rigid structure to the flexible one, which is more accessible for TEOS molecules. Finally, the sample was washed with ethanol. The composite sample and calcined silica sample were labeled as X7-SiT and Si-7T, respectively. The amount of pure silica in the X7-SiT composite was 12%.

2.3. Characterization methods

The morphology and internal structure of the selected samples were analyzed under a scanning electron microscope (FEI Quanta 3D FEG) working at 5 and 20 kV and with an optical profilometer. Profilometric measurements were carried out in the Vertical Scanning Interferometry VSI operation mode using a Contour GT (Bruker) equipped with Vision 64 ver. 5.41 software. The scan area was 62.5 × 46.9 μm with 50× objectives used. The resolution of the scans was 640 × 480 pixels.

The nitrogen adsorption/desorption isotherms at 77 K were measured with a volumetric adsorption analyzer ASAP 2405 (Micromeritics, Norcross, USA). The specific surface area, S_{BET} , was calculated from the linear form of the BET equation in the relative pressure range from 0.05 to 0.25 [23]. The pore size distributions (PSDs) were calculated using the BJH [24] and NLDFT [25] methods. Both calculating procedures are incorporated into the software of the instrument.

Alternatively, the PSDs were obtained using positron porosimetry, i.e. a technique based on positron annihilation lifetime spectroscopy (PALS) [26]. A fast-slow delayed coincidence spectrometer composed of Ortec and Polon modular electronics was used for collecting PAL spectra. Its scintillation detectors were equipped with BaF₂ crystals. The activity of the ²²Na positron source was ca.

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