Summary of Doctoral Thesis

The effect of selected synthesis parameters on properties of porous polymer-silica gel systems

M.Sc. Patrycja Anna Krasucka

Fast development of technology, science and industry cause increased demand to produce new materials with well-defined structure and specific properties tailored for various applications. For this reason, hybrid materials, which include polymer-silica composites, have been of great interest over the last years. Unique properties combining the features of both components are characteristic of this type of materials. Depending on the chemical composition and morphological form, polymer-silica composites are used as fire-resistant materials, components of optical and electronic devices, sensors, anti-corrosion coatings, adsorbents, catalyst supports and membranes in diffusion processes. In addition, they can be applied as biomaterials used in medicine, e.g., as artificial tissues and in pharmacy, e.g., as drug carriers. An important feature of polymer-silica composites used in these areas determining their utility is the homogeneous mixing of both components. However, the organic polymer and inorganic silica oxide (SiO_2) have extremely different properties. Thus combining them into a composite material is a huge preparative challenge.

The dissertation presents results of research on the preparation, modification and characterization of polymer-silica composites, obtained using porous polymer matrix and silica gel produced by sol-gel reaction of a silica precursor (tetraalkoxysilane, TEOS) introduced into a polymer via the swelling method. Furthermore, the silica materials obtained by calcination of synthesized composites is analysed. Also, study on the swelling process of the used Amberlite polymers in TEOS is presented. In addition, the obtained materials were examined for potential use as drug carriers of modified release. The studies involved a number of advanced research methods, including low-temperature nitrogen sorption, scanning and transmission electron microscopy, optical microscopy, atomic force microscopy, thermogravimetry, X-ray diffraction, optical profilometry, positron lifetime spectroscopy and FT-IR ATR infrared spectroscopy.

The dissertation is divided into two parts: theoretical and experimental. The first is devoted to well-known polymers, silica materials and polymer-silica nanocomposites. For the selected materials the methods of their synthesis, characteristic morphological and structural features, as well as potential application are presented. Moreover, the standard methods of

composite materials characterization are described. In the experimental part own research in the field of preparation of new materials, followed by discussion of the obtained results and summary are presented.

The studies confirmed that the introduction of the silica gel precursor into the porous polymer matrix by swelling is an effective and simple method for preparing highly porous, spherical grains of polymer-silica composites. Both gaseous and liquid tetraethoxysilane are very good swelling agents for Amberlite XAD7HP. It has been proved that morphology and structural properties of composite materials, as well as silicas obtained by the calcination process, can be easily modified by changing the synthesis parameters and the composition of the reaction mixture.

First, the effect of the polymer matrix type on the obtained composites and their derivatives was examined. In the studies a commercially available polymer matrices differentiated in both the chemical nature and the pore structure were used. All obtained materials (composites and pure silicas) were marked by sphericity of grains and high porosity parameters.

In the next part of the research, various modifications of the composite materials synthesis were used. It was found that heating the XAD7 matrix to the glass transition temperature results in the relaxation of the polymer network and facilitates penetration of the precursor in the interior of the grain. Due to that, materials of different structure and high porosity were obtained in comparison to unmodified samples. Moreover, the obtained silica gel was marked by a unique morphology and extremely high sorption parameters.

It has been proved that it is possible to synthesize the composite in the presence of a polymeric network relaxant (the so-called expander). In that study a linear silicone oil which cause a high swelling of the polymer network was used. As a result, the obtained composite material was marked by wider pores and higher sorption parameters compared to the material obtained in classic way.

The presented research also confirmed the possibility of synthesis of the composites in the presence of a surfactant with varying concentration in the reaction mixture. Furthermore, the use of various catalysts as well as silica gel precursors also leads to obtaining this type of materials. It was found that addition of the surfactant into the reaction mixture results in two products with different morphology, i.e., (I) polymer-silica composite with spherical grains, similar in size to the those of XAD7 and (II) fine particles SiO_2-CTAB. Both after calcination gave two highly porous products: spherical grain silica and small-particle silica with regular pores of MCM-41/SBA-3 type. Morphology and structural features of all obtained products

are variable and highly dependent on surfactant concentration, type of silica precursor, and reaction mixture.

The subject of research in this dissertation was also systems composed of porous polymer-silica gel and porous polymer-tetraethoxysilane in terms of their potential use as modified-release drug carriers. It has been proved that the release of drugs from the group of non-steroidal anti-inflammatory drugs (NSAIDs) from the XAD7 matrix can be modified by the addition of tetraethoxysilane to the polymer-drug system, and the final effect depends on the method of transforming the precursor into silica gel. On the one hand, the transformation of tetraethoxysilane to silica gel at the preparation stage results in a ternary composite composed of polymer, drug and silica gel, and the formed silica acts as a membrane that delays the release of the drug. On the other hand, the transformation of TEOS in the buffer solution during the release of a poorly-water soluble drug (i.e., Naproxen) causes a rapid acceleration of its desorption. It results from the increased of solubility of the drug due to in situ produced ethanol during the transformation of TEOS and the swelling of the polymer in alkoxysilane, which facilitates the diffusion of the solvent into the matrix.

The results presented in this dissertation prove that the preparation of polymer-silica composites by the sol-gel method combined with the swelling of the polymer in the silica precursor is efficient, simple and easily modifiable. The obtained polymer-silica composites and silica gels exhibit interesting structural and morphological properties, which enable a wide range of practical applications.