



## Polymer/silica composite of core–shell type by polymer swelling in TEOS

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### ABSTRACT

Monodisperse polymer/silica composite material with a polymer as the core and hydrophilic silica gel as the shell was prepared by a two-stage procedure. In the first stage, the swelling of Amberlite XAD7HP particles in tetraethoxysilane (TEOS) was performed. Subsequently a portion of the XAD7HP particles impregnated with TEOS were transferred to acidic aqueous solution to facilitate a sol–gel process of the silica precursor. This procedure is assessed as a potential route to a composite material with a core–shell morphology. Scanning electron microscopy and  $^{29}\text{Si}$  MAS NMR indicated the formation of silica microfibers on polymer beads. The silica microfibers were anchored in the polymer matrix. In consequence, the silica shell exhibited relatively high mechanical stability. The swelling of the polymer and the formation of the silica phase substantially changed the porosity of the initial polymer material. The final composite surprisingly exhibited very homogeneous porosity. The textural characteristics of the investigated materials were defined by nitrogen adsorption–desorption at 77 K.

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### 1. Introduction

Polymer/silica composite materials have been extensively studied for a long time due to the combined advantages of silica (e.g., thermal stability) and organic polymers (e.g., pH stability, chemical functionality). The techniques necessary for the synthesis of composite materials containing a wide variety of silica and organic species arranged in different ways are well documented [1–5]. The most general approach consists in introducing the preformed silica particles, pure siliceous or chemically modified, to enhance the compatible interactions between the polymer and silica in blending and *in situ* polymerization. High dispersion of silica within the polymer matrix is achieved by using very small nanoparticles of silica, colloidal silica, or silica precursors such as tetraethoxysilane (TEOS) that hydrolyze and condense as silica deposits within the polymer matrix [6–9]. Another approach depends on filling silica pores (or other mineral porous materials) with a monomer of the polymer precursor and polymerizing it within these pores [10,11].

In general, polymer/silica nanocomposites can be divided into four groups: (i) polymer with dispersed silica particles of various morphology [12–18], (ii) silica with incorporated polymer inside silica pores [11,19,20], (iii) polymer particles as the core and silica as the shell [21–23], and (iv) silica core with polymer shell [15,16]. All these types of composites have promising properties for application as catalysts [24–26], specific sorbents [27,28], components in electronic devices [29,30], or advanced drug delivery systems

[31,32] or in chemical sensing [33]. In many cases, the addition of inorganic component causes improvement of the mechanical and thermal stability of the polymer matrix [34–36]. A relatively simple route for preparation of polymer core/silica shell nanocomposites is adsorption of silica particles onto preformed polymer particles [37]. The chemical structure and microscale morphology of composite materials can be tailored by adjusting polymer and silica precursors and their concentration.

This paper presents our attempt to investigate the synthesis route of polymer–silica composites based on polymer swelling in TEOS. The proposed approach was used to construct a uniform microstructure of polymer with incorporated silica species. The initial results of the applied swelling method for preparing polymer/silica composites with well-defined geometry of pores and core–shell morphology are described.

### 2. Experimental

#### 2.1. Sample preparation

The composite sample was prepared by swelling of commercial Amberlite XAD7HP (a nonionic aliphatic acrylic ester, Rohm and Haas) beads (0.2–0.5 mm) in TEOS (Sigma–Aldrich, 98%), followed by hydrolysis and condensation of the silica precursor in acid solution. Initially the XAD7HP beads were wetted with TEOS. The amount of TEOS was adjusted so that the beads started to stick together, preserving a loosely packed structure. Polymer beads rapidly swelled to more than three times their dry volume. The polymer/TEOS ratio was 0.5 w/w. It can be assumed that part of the added TEOS takes part in filling pores, and part in the swelling

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process. It is worth noting that the amount of absorbed TEOS markedly exceeded the pore volume of a pure polymer examined by different methods. Next the Amberlite XAD7HP particles saturated with TEOS were transferred to acidic aqueous solution (270 cm<sup>3</sup> of aqueous HCl, 0.2 M, per 6 g of sample) and kept at room temperature for 24 h for gelation and aging. The solid product in the form of spherically shaped particles was filtered, washed with water, and dried at 110 °C under vacuum. No aggregation of these particles is observed. The drying procedure was performed over 12 h. It should be stressed that due to the location of the silica source in the polymer, the solution outside the solid product does not contain the silica precursor or any additional silica species.

In order to remove the external silica shell part of composite sample was processed by mechanical abrasion.

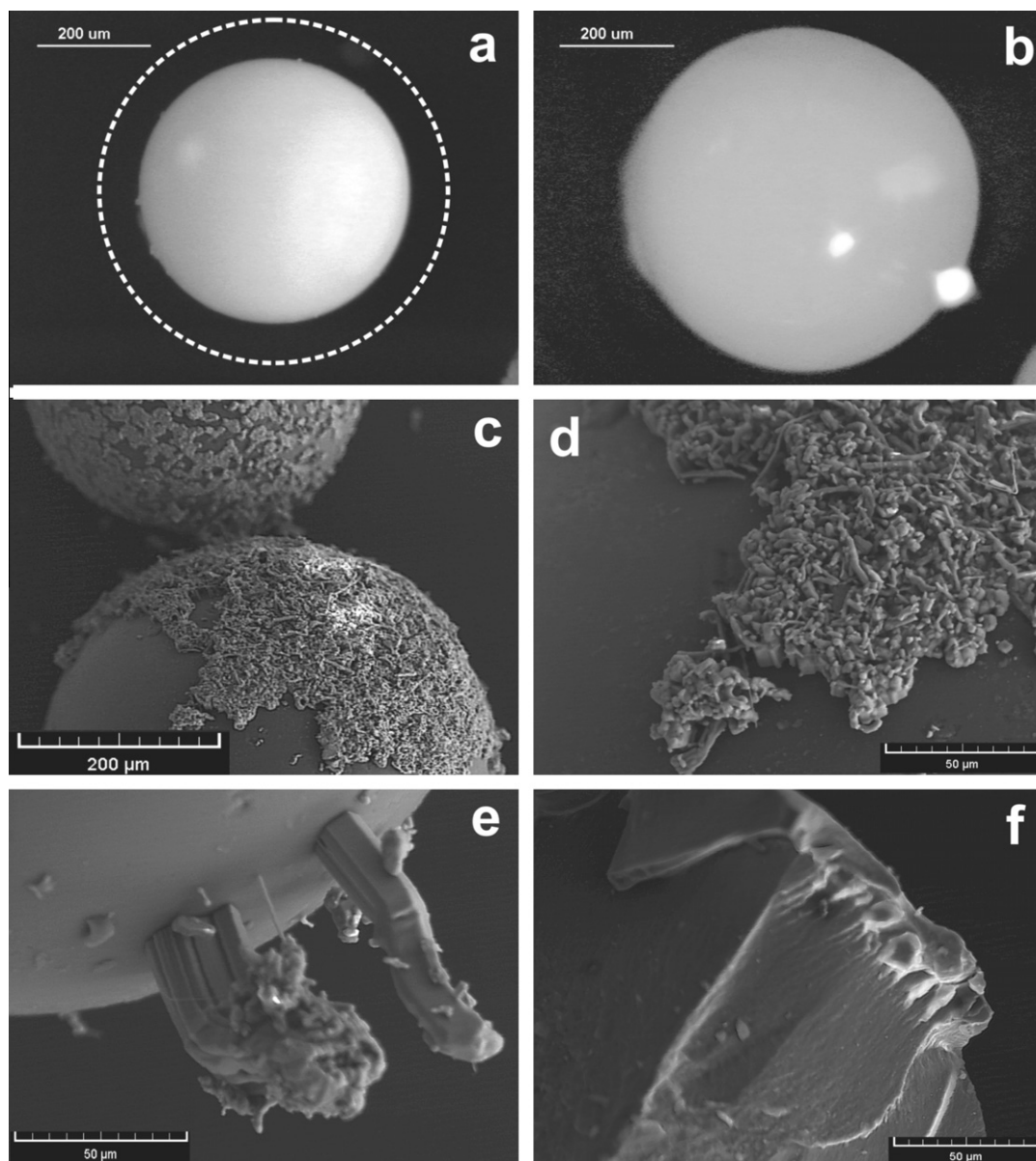
## 2.2. Sample characterization

Textural characterization of the samples was carried out by the low-temperature nitrogen adsorption–desorption method.

Nitrogen adsorption–desorption measurements were made at 77 K using an ASAP 2405 volumetric adsorption analyzer (Micromeritics, Norcross, GA). The specific surface areas,  $S_{\text{BET}}$ , of the investigated samples were evaluated using the standard Brunauer–Emmett–Teller (BET) method for nitrogen adsorption data in the range of relative pressure  $p/p_0$  from 0.05 to 0.25. The total pore volumes were estimated from single-point adsorption at a relative pressure of 0.985. The pore size distributions were obtained from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) procedure [38].

<sup>29</sup>Si magic-angle spinning (MAS) NMR spectra of the solid samples were obtained at the resonance frequency of 59.6 MHz on a Bruker Avance-300 spectrometer. For <sup>29</sup>Si NMR, 4-mm zirconia rotors spun at 8 kHz were used. About 8000 scans were applied until a satisfactory signal-to-noise ratio was achieved. The spectra were recorded using the HPDEC pulse program. The chemical shifts are given in ppm and referred to Q<sub>3</sub>M<sub>8</sub> as standard material.

SEM studies were conducted on a Tesla BS-301 microscope operating at 15.0 keV.



**Fig. 1.** (a and b) The polymer beads before and after swelling; dotted line illustrate the dimensions of the swollen bead. (c and d) SEM images of the composite beads with silica coverage on the external surface. (e) SEM image of the silica fibers anchored into polymer beads. (f) The cracked bead surface after abrasion of the external part of the silica fiber.

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