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Polymer nano-encapsulation of templated mesoporous silica monoliths with improved mechanical properties

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Abstract

Macroporous (1–5 μm) monolithic silica aerogels consisting of both random but also ordered mesoporous walls have been synthesized via an acid-catalyzed sol–gel process from tetramethoxysilane (TMOS) using a triblock co-polymer (Pluronic P123) as a structure-directing agent and 1,3,5-trimethylbenzene (TMB) as a micelle-swelling reagent. Pluronic P123 was removed by Soxhlet extraction, and materials in monolithic form were obtained by extracting the pore filling solvent with liquid CO_2, which eventually was taken out supercritically. Although these monoliths are more robust than base-catalyzed silica aerogels of similar density, nevertheless, the mechanical properties can be improved dramatically by letting an aliphatic di-isocyanate (Desmodur N3200) react with the silanols on the macro- and mesoporous surfaces. As it turns out, the polymer fills the mesopores and coats conformally the macropores of templated samples, so that BET surface areas decrease dramatically, from 550–620 $m^2 g^{-1}$ to <5 $m^2 g^{-1}$. By comparison, polymer nano-encapsulation of non-templated acid-catalyzed aerogels preserves a large fraction of their mesoporous surface area, and BET values decrease from 714 $m^2 g^{-1}$ to 109 $m^2 g^{-1}$. Finally, since polymer nano-encapsulation preserves the macroscopic physical dimensions of the monoliths before drying, comparative analysis of the physical dimensions against XRD data of native versus polymer nano-encapsulated samples provides evidence that upon drying macropores (micron size regime) shrink less than mesopores (nanometer size regime).

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1. Introduction

The 1992 discovery [1] by scientists at Mobil Corporation of the M41S series of ordered mesoporous silicas has drawn great interest in those materials because of their large surface area, uniform pore size distribution [2] and their potential application in catalysis [3], sorption [4], and chromatography [5–7]. Typically, M41S type of materials have pore sizes in the 20–30 Å range and are made via an aqueous base-catalyzed process using micelles of cationic surfactants as templates [1]. As it turned out, however, pore size can be increased further by increasing the volume of the micelles. That was accomplished by two methods. First, pore sizes up to 40 Å were achieved by increasing the length of the hydrophobic tether of the cationic surfactant [8]. This route, however, is limited by the fact that the ratio of the volume of the hydrophobic tether to the area of the ionic head has to be within certain limits [9]. In the second approach, the pore size was increased up to 100 Å by using 1,3,5-trimethylbenzene (TMB) to swell the hydrophobic volume of the template (MCM-41

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material) [1,10a]. Higher concentrations of TMB, however, decrease the internal order in the material [9]. On the other hand, variable amounts of the template (surfactant) gave different pore morphologies, varying from a two-dimensional hexagonal (MCM-41 material) to three-dimensional cubic (MCM-48) to lamellar with poor structural integrity (MCM-50 material) [10].

In addition to their intrinsic practical interest, the M41S class of materials set a paradigm in the use of supramolecular assemblies (as opposed to single molecules) as structure-directing agents (templates), showing that pore structures and sizes can be controlled precisely and independently by the size and shape of the template [11]. Accordingly, a second major advancement in the pore size control came in 1998 with Stucky's introduction of large amphiphilic triblock copolymers as templates, as for example poly(ethyleneoxide)-*block*-poly(propyleneoxide)-*block*-poly(ethyleneoxide) (Pluronic 123) in acid media, yielding the so-called SBA-class of mesoporous silicas [12]. Such polymer-templated mesoporous silicas generally have pore sizes up to 300 Å and thicker walls than MCM-41-type materials. Again, pore sizes larger than 300 Å are achieved by using swelling agents like TMB [12,13]. But, if the amount of TMB is increased further, it takes all the amount of the surfactant to stabilize the emulsion of the swelling agent, leading to the destruction of the ordered mesoporous structure, and to the appearance of large interconnected voids in a new type of material referred to as mesoporous cellular foam (MCF) [14]. Originally, SBA and MCF type materials were received as precipitates in powder forms.

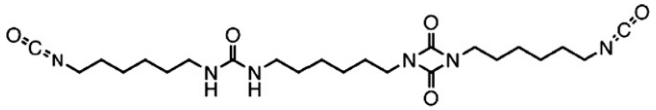
In the meantime, monolithic silicas with well-defined porous structures have been investigated for applications in separations [15]. HPLC columns based on such materials were first reported by Nakanishi and Soga in 1991, and are characterized by higher total porosity and permeability compared to packed columns, allowing operation at low pressures, yet at higher flow rates, thus reducing the analysis time drastically [16–19]. Recently, Nakanishi and co-workers worked out a modification of Stucky's method for SBA-15/MCF materials yielding, reportedly, monolithic periodic mesoporous silica with well-defined macropores [20]. Basically, Nakanishi's approach was to reduce the amount of solvent (aqueous acid) used in Stucky's process thus obtaining gels rather than precipitates. In Nakanishi's method, the gelation solvent (water) was removed at 60 °C under ambient pressure, and the templating agent (Pluronic P123) was removed by calcination at 650 °C, which can lead to up to 50% volume shrinkage of the monolith [21,22].

Concurrently with those advances, we have been developing a method where the native –OH surface functionality of typical base-catalyzed sol–gel silica is employed as a template that directs conformal polymerization of isocyanates on the mesoporous surfaces. The most remarkable property of the resulting materials is their mechanical strength: for a density increase by a factor of three we realize a strength increase by a factor of 300 [23]. Overall, the new material may combine the thermal conductivity of glass wool with a multiple of the specific ultimate compressive strength of graphite fiber reinforced epoxies. We refer to those materials as polymer cross-linked aerogels and the process as cross-linking. Here, we apply this approach on bi-continuous macro/mesoporous monolithic wet gels prepared along the line of Nakanishi's modification of Stucky's method, using Pluronic P123 (molecular weight 5,800) as a templating agent and 1,3,5-trimethylbenzene (TMB) as an expanding agent. The templating agent was washed off by Soxhlet extraction and the resulting wet gels were exposed to a solution of a di-isocyanate in acetone; unreacted di-isocyanate was removed and the samples were dried with CO_2 taken out supercritically. The effect of the polymer on the micro/nanostructure was characterized exhaustively and the material was evaluated for load-bearing applications. Overall, isocyanate-treated monoliths undergo minimal shrinkage, they maintain the macroporous structure of the native monoliths and are much more robust than the latter.

2. Experimental

2.1. Materials

Acetone, acetonitrile, and alcohol were all purchased from Pharmaco Chemical Company (Brookfield, CT 06804), Nitric acid was purchased from Seastar Chemical Inc. (Pittsburgh, PA 15275), tetramethylorthosilicate (TMOS) and 1,3,5-trimethylbenzene (TMS) were purchased from Sigma–Aldrich (St. Louis, MO 63103), while Pluronic P123 (tri-block co-polymer: $PEO_{20}PPO_{70}PEO_{20}$) was supplied by Acros Organics (New Jersey). Research samples of Desmodur N3200, a hexamethylene diisocyanate oligomer, were provided by Bayer (Pittsburgh, PA 15205). All chemicals were used as received.



diisocyanate main component

2.1.1. Preparation of templated samples

All templated mesoporous materials of this study were made using the same amount of TMOS and Pluronic P123 and are labeled as MP4 ('P4' stands for 4 g of Pluronic P123) following Nakanishi's notation [20]. In a typical procedure, 4.0 g of Pluronic P123 was dissolved in 12 g of a 1.0 M aqueous solution of nitric acid, and a given amount of TMB (see below) was added under magnetic stirring at room temperature. Solutions after addition of Pluronic P123 are clear but after addition of TMB look turbid. After stirring for 30 min at room temperature, samples were cooled to 0 °C and 30 min later TMOS (5.15 g) was added under vigorous stirring. Table 1 summarizes the nomenclature for the samples as it corresponds to the