



Macroporous alumina with cellular interconnected morphology from emulsion templated polymer composite precursors



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ABSTRACT

Macroporous polymer composites with included alumina particles were prepared via an emulsion templating procedure by photopolymerising the monomer containing continuous phase. Methyl methacrylate and multifunctional acrylate monomer Sartomer SR 492 were used for the polymer matrix. Composites with open porous cellular morphology with cavities around 15 μm were obtained and further processed by a calcination and sintering process to form alumina ceramic material with the same morphology as the polymer composite precursors. Emulsion composition was optimised in order to obtain monolithic type of the final material with macropores on a micrometer scale connected by a number of interconnecting channels. Mechanical and thermal properties both of precursor composites and ceramic materials were evaluated.

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1. Introduction

Porous ceramic materials find a number of applications, such as filtration, catalysis, biomedical applications, solar energy conversion, acoustic transfer and others [1]. While for many standard applications porosity within the material is considered problematic, a porous ceramic with a high degree of control over morphology and pore size is advantageous for numerous uses.

Preparation of cellular porous ceramics can be implemented typically using a foaming procedure, and even the use of polymeric precursors is well-known; however, relatively large pores are usually obtained (200–1700 μm) [1]. There is less known on obtaining open porous cellular ceramics with pore sizes in the range of several micrometers.

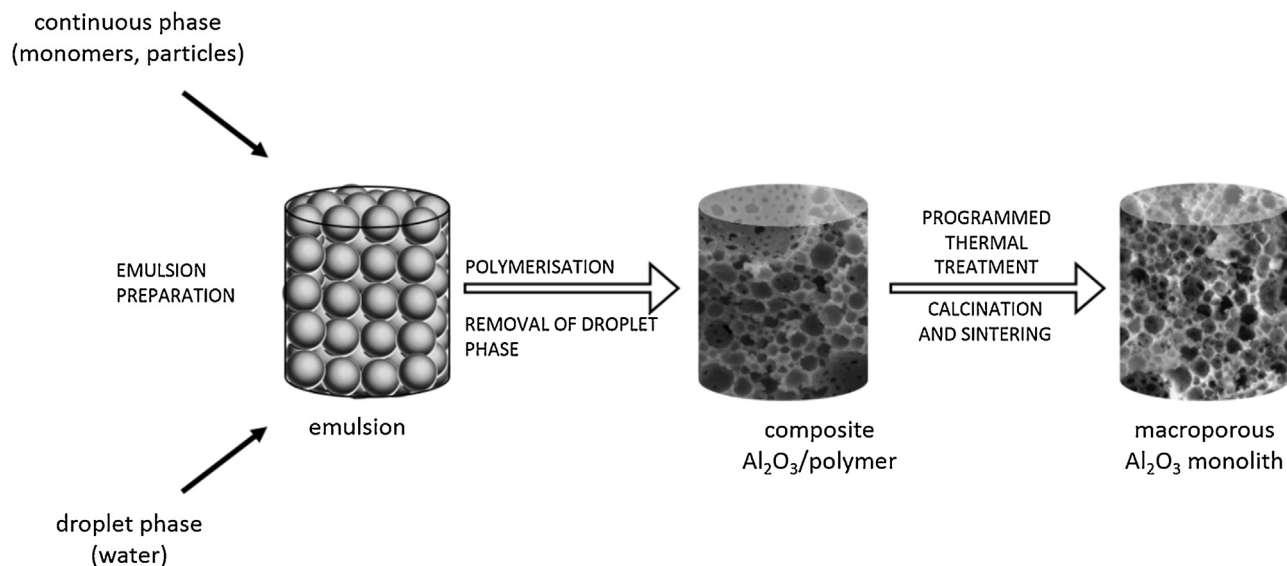
Emulsions with a high volume share of droplet phase and monomers containing continuous phase can be effective templates for the production of macroporous polymeric materials with interconnected pores. Polymerization of monomers in the continuous phase can lead to a polymer with an interconnected macroporous morphology. A wide variety of polymers with an interconnected cellular morphological structure have been prepared in this manner

[2–4]. Recently, research work has also been devoted to composite and inorganic material prepared by emulsion templating. Imhof and Pine report the use of emulsion templating for the preparation of titania-based ceramics with good control over pore size distribution [5]. In this case, a non-aqueous emulsion is used for templating the pores in the material and a sol–gel process to deposit the metal alkoxide at the exterior of the droplets of emulsion. Similarly, Akartuna et al. describe the preparation of porous ceramics by an emulsion templating procedure incorporating metal oxide particles in the aqueous or oil phase without any monomer/polymer matrix [6]. However, the use of emulsions as templates for porous ceramics presents problems regarding the use of aqueous phase due to the reactivity of most metal alkoxides towards water and the challenging sol–gel process for the deposition of particles in the continuous phase of emulsions.

Another possibility is to use a polymer matrix for the dispersion of metal oxide particles. Several methods for the preparation of either composite or inorganic porous materials involving an emulsion templating step have been reported. Silverstein et al. prepared a hybrid polyHIPE material that combines an inorganic polysilsesquioxane network with an organic polystyrene network [7], while Carn et al. report about emulsion-templated silane based materials [8]. Zhang et al. prepared inorganic/polymer beads by O/W/O sedimentation polymerisation [9]. Polymer scaffolds were immersed in an inorganic precursor solution sol–gel condensation

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Scheme 1. Schematic of polymer emulsion templating approach.

in air and calcination of the polymer was performed. Macro porous alumina monoliths were prepared by filling polystyrene foam templates with alumina hydrosols [10]. Polystyrene templates were subsequently removed by calcination at different temperatures. Maekawa et al. have prepared meso- and macrostructured inorganic solids using a two-step process in which a polystyrene foam served as a scaffold for imbuing a block-co-polymer/sol-gel mixture into the macroporous foam [11]. Subsequent elimination of organic structure by solvent extraction or calcination resulted in an inorganic framework.

Recently, Ngai et al. have described the use of emulsion templating for the preparation of silica and titania materials where poly(*N*-isopropylacrylamide) microgels are used as stabilizers and freeze drying procedure for the removal of solvents [12,13]. Similarly, Kovačič et al. report the preparation of zinc oxide based material however resulting porous material could not retain monolithic form [14]. There are also examples of using air foaming for obtaining macropores and subsequent sintering of solid phase [15].

The approach described herein utilizes the emulsion templating directly; no step other than the preparation of a stable emulsion with inclusion of metal oxide particles dispersed in the monomer phase is needed. Heating of the particle-included polymer results in sintering and removal of polymer, yielding a ceramic monolith with the morphology closely resembling the precursor polymer. The use of a polymer matrix for the dispersion of metal oxide particles allows for tuning of morphology and better control of process scale-up, as the morphology of the final product is determined by the polymer composite derived from polymerisation of the continuous phase of the emulsion. The porosity of the final product can be tailored by varying the volume fraction of the emulsion's droplet phase however a compromise between porosity and mechanical properties of the final product must be achieved.

2. Materials and methods

2.1. Chemicals

Propoxylated trimethylolpropane triacrylate (SR 492, Sartomer), aluminum oxide (Al_2O_3 , particle size average 290 nm, Sigma-Aldrich), Disperbyk-111 (BYK-111, BYK-Chemie), toluene (TOL, anhydrous, 99.8%, Sigma-Aldrich), calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, 98%, Sigma-Aldrich) and Irgacure 819 (I-819,

BASF) were used as received. Methyl methacrylate (MMA, 99%, Sigma-Aldrich), ethylene glycol dimethacrylate (EGDMA, 98%, Sigma-Aldrich) were passed through a basic alumina column prior to use in order to remove the inhibitors.

2.2. Preparation of porous composites by emulsion templating

Oil phase was prepared with aluminum oxide particles (4 g in the case of 4:1 ratio), monomer (1 g, either SR 492 or a mixture of MMA and EGDMA in wt. ratio of 2:1) and toluene (1.5 mL), which were placed in a round darkened reactor vessel, fitted with an overhead stirrer with a D-shaped PTFE blade and stirred at 150 rpm for 10 min. After that, the dispersing agent (240 mg; 6 wt% with regards to Al_2O_3 particles) was added and the mixture stirred for another 10 min followed by the addition of the photoinitiator (2 wt% I819 with regards to monomer) and stirring for additional 10 min. The aqueous phase was prepared separately by dissolving 1 wt% of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in degassed deionized water and was added drop-wise via a dropping funnel over a period of 5 min to the organic phase while stirring at 250 rpm. Stirring was continued for another 60 min after the addition of the aqueous phase. The prepared emulsion was transferred to rectangular silicon molds (50 mm × 4 mm × 3 mm) and polymerized in a UV chamber (Intelliray 600, Uvitron) at 100% intensity for 120 s with a distance between the sample and light source of 80 mm. Samples cleaned in ethanol bath for 24 h and dried in vacuo at 40 °C for 24 h.

2.3. Sintering process

Composite polymer samples were placed in a tubular type oven and heated in air to reach a temperature of 1400 °C at a rate of 0.5 °C/min.

2.4. Characterization

Morphology of the samples was investigated with FEI Quanta 200 3D SEM microscope (20 kV). Prior to SEM analysis the samples were gold coated using ion sputter Jeol JCF-1100E for 3 min at 40 mA. TGA analysis was made on Mettler Toledo TGA/SDTA 851 (heating rate 1 °C/min). Aluminum oxide particle size was determined by Zetasizer Nano ZS (Malvern). Indentation testing was done using two different devices, a Hysitron Ubi 750L equipped

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