Composites Science and Technology 90 (2014) 154–159

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Novel, highly-filled ceramic–polymer composites synthesized by a spouted bed spray granulation process ☆

M.F.H. Wolff [a], V. Salikov [a], S. Antonyuk [a], S. Heinrich [a,*], G.A. Schneider [b]

[a] Hamburg University of Technology, Institute of Solids Process Engineering and Particle Technology, Denickestr. 15, 21073 Hamburg, Germany
[b] Hamburg University of Technology, Institute of Advanced Ceramics, Denickestr. 15, 21073 Hamburg, Germany

ARTICLE INFO

Article history:
Received 26 March 2013
Received in revised form 4 November 2013
Accepted 9 November 2013
Available online 20 November 2013

Keywords:
Spouted bed
Granulation
Composite
Filling degree
B. Mechanical properties

ABSTRACT

We present a novel processing route to synthesize homogeneous ceramic polymer composites with ultra-high (~78 vol.%) packing density by using the spouted bed granulation technology and subsequent warm pressing. In the granulation process, two ceramic particle size fractions (α-Al_2O_3) and a thermoplastic polymer (polyvinyl butyral) are assembled to granules. In the process, μm-sized particles are coated with a layer of polymer which contains a second, nm-sized ceramic particles fraction. The mass fractions of each constituents can be adjusted independently. During the warm pressing, the nm-sized particle fraction along with polymer is pressed into the void volume of the μm-sized particles, thus achieving a homogeneous, isotropic composite structure with a very high packing density of ceramic particles. The material, which can easily be produced in large quantities, combines a high modulus of elasticity (up to 69 GPa), tensile strength (~50 MPa), and pronounced fracture strain (~0.1%) with an isotropic, biocompatible, metal-free composition. Possible failure mechanisms are discussed, including failure due to necking of the polymer, and failure due to limited polymer–particle-interfacial strength.

1. Introduction

Ceramic materials are intensively studied and used for applications in materials sciences and industries. The versatile use of this material class is a consequence of a number of useful properties such as high hardness and modulus of elasticity, and its abundance in nature. However, the structural applications of ceramic materials are often limited by their high brittleness and scatter of mechanical properties resulting in the lack of predictability of the material failure. On the other hand, polymeric materials in general exhibit a number of properties which are more or less complementary to the ones of ceramic materials, such as high ductility, adjustability, but relatively low modulus of elasticity and strength. These two materials classes are therefore often combined to form composite materials, and also both occur in many biological materials, in which large amounts of minerals are combined with small amounts of proteins or biopolymers. One of the most astounding findings in materials such as nacre has been, apart from discovering their hierarchical structure, the very high volume fraction of stiff constituents in a polymeric matrix, which is far beyond current technological capacities of materials design. Nacre for example consists of about 95 vol.% calcium carbonate and about 5 vol.% of polymeric material [1,2]. In general, the outstanding mechanical properties of these materials seem to be a complex interplay between their composite morphology, interface properties, and hierarchical assembly [3–8]. Inspired by nature's design principle, there has been much progress in synthesizing ceramic polymer composite materials [9–15], and exceedingly high values for toughness [16], dielectric constant [17], and strength [18] have been reported. However, the reported volume fractions for particles [13], platelets [19], and fibers [20] as reinforcing phase are always very much lower than in biological materials, resulting e.g. in a deficiency of the stiffness at least in one dimension. The stiffness of the polymeric phase can be slightly enhanced by cross-linking [18], but such techniques are tedious for bulk samples and have the tendency to be non-biocompatible. The way to achieve very high (isotropic) stiffness is therefore to achieve a very high packing density of the stiff phase in a composite. The isotropy is an inherent property of the composite when the filler material has a particulate nature (unlike e.g. fibers) and the filler material is homogeneously distributed within the polymer. It is known that in order to reach packing densities > 70 vol.% using nearly spherical particles, at least two particles size fractions have to be combined such that the void volume of one fraction is filled by the other (smaller) one [21,22]. This has proven to be very difficult to accomplish homogeneously for macroscopic amounts of material. Most of the experimental techniques and theoretical

* Corresponding author. Tel.: +49 40428783750.
E-mail address: stefan.heinrich@tuhh.de (S. Heinrich).

0266-3538/$ - see front matter © 2013 The authors. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compscitech.2013.11.006

investigations in the literature have therefore focused on small and medium filling degrees. At the same time the amount of polymer should be adjusted to exactly fill the free gap volume. This is vital for enhancing the fracture strain and avoiding large pores which would lower the strength of the material. While in the literature large enhancement factors for the stiffness are reported in composites, they are typically limited to one dimension (e.g. when fibers are used). However for particulate (low-aspect ratio-) filler particles, the composite material basically has the same modulus of elasticity in all spacial directions, which means that also two- and three-dimensional states of stress can be sustained, which is a considerable advantage for the design of structural elements, which often undergo complex states of stress. Another advantage of particulate filler particles as opposed to fibers is the generally much better biocompatibility, which opens up applications such as tooth implants, and which also simplifies the disposal of the material, a factor of ongoing increasing importance.

We developed a novel processing route combining the spouted bed technology [23,24] and subsequent warm pressing, with which it is possible to synthesize a microstructured ceramic–polymer composite material with very high filling degree and very small porosity, which is far more than reliably reported so far in the literature. In the granulation process, two ceramic particle size fractions (α-Al_2O_3) and a thermoplastic polymer (polyvinyl butyral) are assembled and then compressed to form a dense composite material. The material, which can easily be produced in macroscopic amounts, combines a high elastic modulus, tensile strength, and pronounced fracture strain with an isotropic, biocompatible, metal-free composition. As each of the components can be adjusted individually during the granulation process, the granules can be designed to have optimized properties (composition and morphology) for the subsequent uniaxial warm pressing. Spouted beds are in general known for their good mixing of the solid phase and are often used for the granulation and agglomeration of food powders, fine chemicals and pharmaceutical powders [25–29], but have not been used so far for the synthesis of microstructured composite materials. The technique consists of three basic steps: (1) preparation of the polymer solution, (2) spouted bed spray granulation, and (3) warm pressing. These processes as well as the structural and mechanical characterization methods are described in Section 2. In Section 3, the results of the granulation process and of the mechanical characterization are analyzed, and possible material failure mechanisms are discussed, including failure due to the propagation of cracks, and failure due to necking of the polymer.

2. Materials and methods

2.1. Materials

All ceramic particle fractions consisted of α-Al_2O_3, which has a modulus of elasticity of between 350 and 400 GPa, a density of about 3.98 g/cm^3, and no measurable fracture strain. The fluidized particles were fused alumina F360 (Kuhmichel Abrasiv GmbH) with a nominal $d_{50,3}$ of (22.8 ± 1.5) μm. The particle size distribution of these particles was measured with a camsizer XT (Retsch Technology GmbH). The particles used for the suspension were CT 3000 SG from Almatis Inc. ($d_{50,3} \sim 500$ nm), except for the lowest-filled samples, for which Alumina microgrid WCA 5 ($d_{50,3} \sim 4$ μm) from Pieplow & Brandt GmbH, Germany, was used. The used polymer was polyvinyl butyral (PVB) Mowital B 30 H, which was provided by Kuraray Europe GmbH. This polymer type has a medium degree of acetalization, a glass transition temperature of 68 °C, and, according to the manufacturer, a modulus of elasticity of approx. 2.5 GPa, a yield stress of 58 MPa, a tensile strength of 34.8 MPa, and an elongation at break of 57.9%. Ethanol was used as solvent, and diluted hydrochloric acid was used to adjust the pH value of the polymer–particle suspension. The ceramic Al_2O_3 is a versatile and frequently used technical ceramic, as it offers high hardness, strength, and modulus of elasticity, it is non-hazardous to health. The polymer (PVB) was chosen because it offers a good combination of properties, in particular it has a very good adhesion to hydrophilic surfaces and good solving properties.

2.2. Preparation of the polymer solution

To prepare the polymer solution, between 28 g and 42 g of the PVB were dissolved in ethanol with concentrations of 4–6 wt.%. 145 g of α-Al_2O_3 particles of the finer fraction were then added to the solution, and a heated ultrasonic bath was used for deagglomeration. For the stabilization of the suspension, diluted hydrochloric acid was added to reduce the pH value of the suspension from near the isoelectric point of alumina (pH $\sim$ 9) [30] to about pH 6. The suspension was then put on a heated magnetic stirrer and sprayed onto the fluidized alumina particles of the coarser fraction in the spouted bed apparatus using a peristaltic pump and a two-component nozzle.

2.3. Spouted bed spray granulation

300 g Of α-Al_2O_3 particles of the coarse fraction were fluidized in a prismatic spouted bed apparatus [31,32] (Fig. 1) with a small process chamber and a steep and large expansion zone (cross-section area ratio $\sim$13.8) described in [33], particularly constructed for the processing of fine and ultrafine particles (Geldart group C [34]) which cannot be fluidized in conventional fluidized beds [35]. The process gas (ambient air) was slightly heated to reach a temperature in the fluidizing zone of about 40 °C. The ceramic particles were fluidized in the dilute spouting regime (also called jet-spouting [36]) and were layered in the spray granulation process by the injected droplets containing the suspended ceramic particle fraction and the dissolved polymer, while the solvent evaporated and left the apparatus along with the process gas. Because of the small size and adhesion forces, a certain amount of agglomeration of the coated particles took place, which however did not significantly disturb the granulation process. Due to the intensive mixing as well as heat and mass transfer in the spouted bed spray granulation process, a homogeneous mixing of different particle sizes and the polymer was achieved, and segregation was avoided.

2.4. Uniaxial warm pressing

10–20 g Of the granules were then given into a steal die (inner diameter 4 cm) for warm pressing. At a pressure of 40 MPa the temperature was increased by $\sim$5 K/min to its final temperature of 160 °C. The pressure was then increased to 750 MPa. After 1 h, the sample was instantaneously unloaded and slowly cooled down to room temperature.

2.5. Compositional and mechanical analysis

The composition of the material was analyzed by measuring the geometrical density of the pressed sample and the non-volatile weight fraction. This was done by heating 5–10 g of the same granules to a temperature (600 °C) clearly above the decomposition temperature of the polymer (ash content of PVB < 0.1 wt.% at $T = 600$ °C) and measuring the relative weight loss. The ceramic volume fraction $p_{\mathrm{vol}}^{\mathrm{cer}}$ was then calculated via $p_{\mathrm{vol}}^{\mathrm{cer}} = w_{\mathrm{cer}} \cdot \rho_{\mathrm{press}}/\rho_{\mathrm{cer}}$, where $w_{\mathrm{cer}} = m_{600^\circ\mathrm{C}}/m_{\mathrm{room\ T}}$ is the residual mass fraction of the granules, $\rho_{\mathrm{press}} = m_{\mathrm{press}}/V_{\mathrm{press}}$ is the density of the pressed sample, and $\rho_{\mathrm{cer}} \simeq 3.98$ g/cm^3 the density of α-Al_2O_3. The polymeric volume fraction was calculated correspondingly by using