1 Introduction

The evolution of human civilization has always been strongly influenced by the materials available to build machines and tools of various kinds. Many periods of ancient civilization are even named after the predominantly used materials, such as the Stone Age, the Bronze Age, and the Iron Age. In modern times, a tremendous variety of different materials have been developed. Various ceramic materials can be fabricated with outstanding hardness and strength, an inconceivable number of different metal alloys are available, and many different types of polymers have been developed, which can be synthesized in different grades and modifications. Despite this abundance, it can still be observed that technological limitations are often set by the limited properties of materials.

Novel properties of materials can arise when different kinds of materials are combined on the microscale and/or nanoscale. Such materials are called composite materials, or composites. A lot of effort worldwide is put into developing novel composite materials with enhanced properties. Fig. 1.1 shows the basic concept of an envisioned multidimensionally designed hierarchical composite consisting of ceramic, metal, and polymeric particles. Different materials can be used on each length scale, which opens up a lot of possibilities to tailor the material properties.

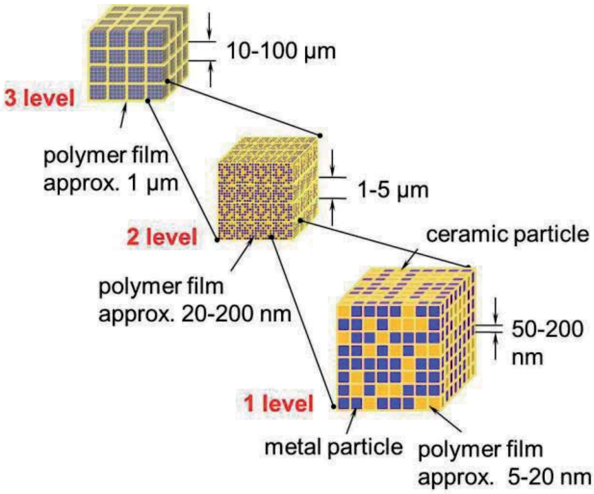

Fig. 1.1: Concept of a multidimensionally structured self-similar ceramic-metal-polymer composite (adapted from SFB986 research proposal).

The major motivation for the fabrication of such composites is the large observed discrepancy between artificially-made materials and load-bearing biological materials. Many biological materials, such as nacre, bones, or enamel, are made from constituents which are readily available in nature and which exhibit rather inferior mechanical properties. However, the observed macroscopic properties of the resulting composites are outstanding and much better than the properties of the constituents. Detailed observations and analyses of these materials in recent years have shown that the impressive mechanical properties of biological materials (high fracture toughness, high strength, high hardness etc.) are at least to some extent a result of the complex arrangement of the individual constituents. One important feature of many biological composites is the arrangement of large amounts of mineral platelets on the microscale, of which an example is shown in Fig. 1.2. It shows the macroscopic appearance of nacre (left) and a scanning-electron micrograph (right) of the microstructure, illustrating the presence of aligned mineral platelets. A brick-and-mortar arrangement of organic[1] and inorganic layers is important for achieving high strength and fracture toughness in these materials (Tang et al. 2003).

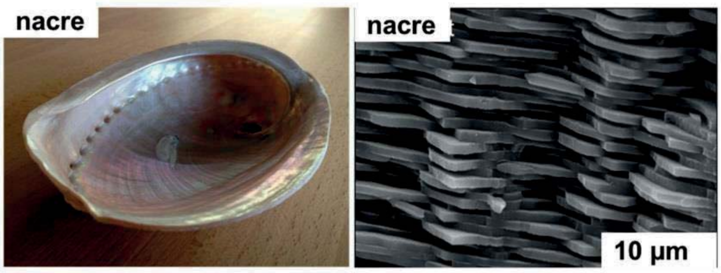

Fig. 1.2: Light-microscopic image (left) and scanning-electron micrograph (right) of nacre (adopted from SFB986 research proposal).

In order to fabricate a composite which is homogeneous on the macroscale, material phases have to be brought together and combined on the nano- and/or microscale, which requires the application of appropriate process techniques. Interestingly, a general shortcoming of process techniques can be observed for the efficient fabrication of composites which adopt design principles of biological materials. Two of the most striking aspects in this respect are the filling degree of inorganic phases in a polymer matrix and the hierarchical structuring. As is shown in this thesis, spray granulation techniques and the agglomeration of fine particle systems can play

[1] It is usually believed that the small amount of organic material in biological composites plays a crucial role for reaching the outstanding mechanical properties. Nevertheless, it would be very interesting to measure the mechanical properties of e.g. nacre after having removed the organic fraction (e.g. by thermogravimetry). However no such reports are known to the author.

an important role to improve the design of artificial composites, especially concerning the maximum amount of the hard ceramic phase in a ceramic-polymer composite. A major goal of this thesis is therefore to maximize the filling degree in particulate-reinforced polymers (cf. chapter 2).

A process which is very established in many fields due to its versatility and efficiency in treating particle systems is the fluidization of particles, and specifically the fluidized bed spray granulation. Fluidization of particles means that particles are subjected to a gas volume flow in upward direction, the drag force of which balances the gravitational force such that the particles can move freely and individually within the apparatus. The entire surface of the particles is accessible, and substances can be sprayed onto them in a fluidized or spouted bed spray granulation process (Salman et al. 2007). The main objective of this thesis is the development of process strategies based on the spouted bed spray granulation process to fabricate bulk amounts of novel composite materials. In particular, the objective is to achieve progress with regard to two design principles of biological materials which have been identified as being essential for their good macroscopic properties, namely the high filling degree and the hierarchical structure. The aim is to build materials whose inner structure exhibit certain concepts or even analogies to the structure of naturally occurring biological materials. This is done because biological materials exhibit superior properties, which include mechanical properties but go far beyond those.

In Fig. 1.3 the concept of spray granulation followed by a warm-pressing step is sketched. The warm pressing step is carried out with high pressure (~ 750 MPa) to reach maximum densification of the granules, and at a temperature between the glass transition temperature T_g and the degradation temperature of the polymer, where the glass transition temperature is the temperature at which the polymer becomes a viscous fluid (cf. section 2.1.2).

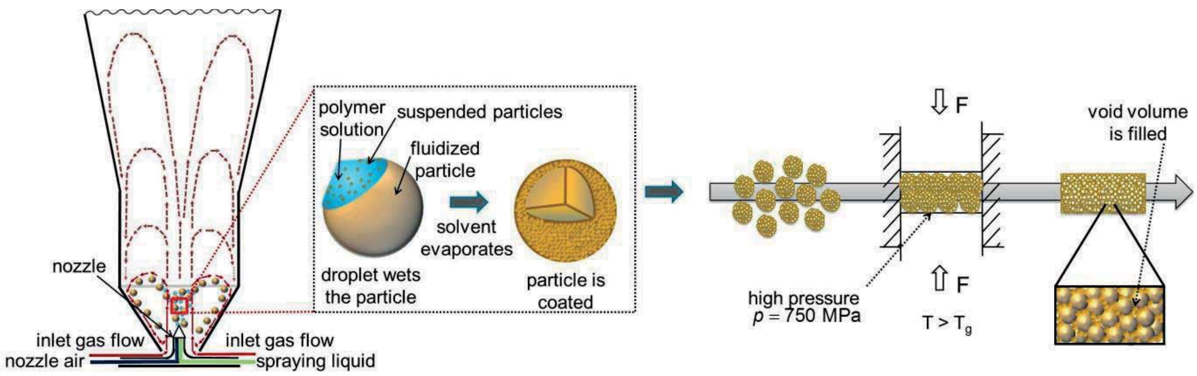

Fig. 1.3: Sketch of the spouted bed granulation process with subsequent warm-pressing.

In conventional ceramic-polymer composites that are e.g. used for artificial dentition, the polymeric phase is oftentimes hardened in order to reach sufficient hardness and modulus of elasticity of the material. By realizing very high fractions of the ceramic phase in the composite, good mechanical properties can be obtained without sintering and without hardening of the polymeric phase. Thus a pronounced fracture strain can be retained in the material, which is a very desirable property (cf. chapter 2).

The processes that are involved in the spouted bed spray granulation technology are agglomeration and granulation. The basic concept of these two processes is shown in Fig. 1.4. Both processes typically involve the formulation of granular matter by increasing the particle size. Agglomeration means the formation of a system of particles which is composed of smaller (primary) particles. The primary particles are brought into contact with each other in such a way that contact forces act between them (cf. section 3.2.2). This leads to an increase in size (cf. Fig. 1.4 a), which is always the case for any agglomeration process.

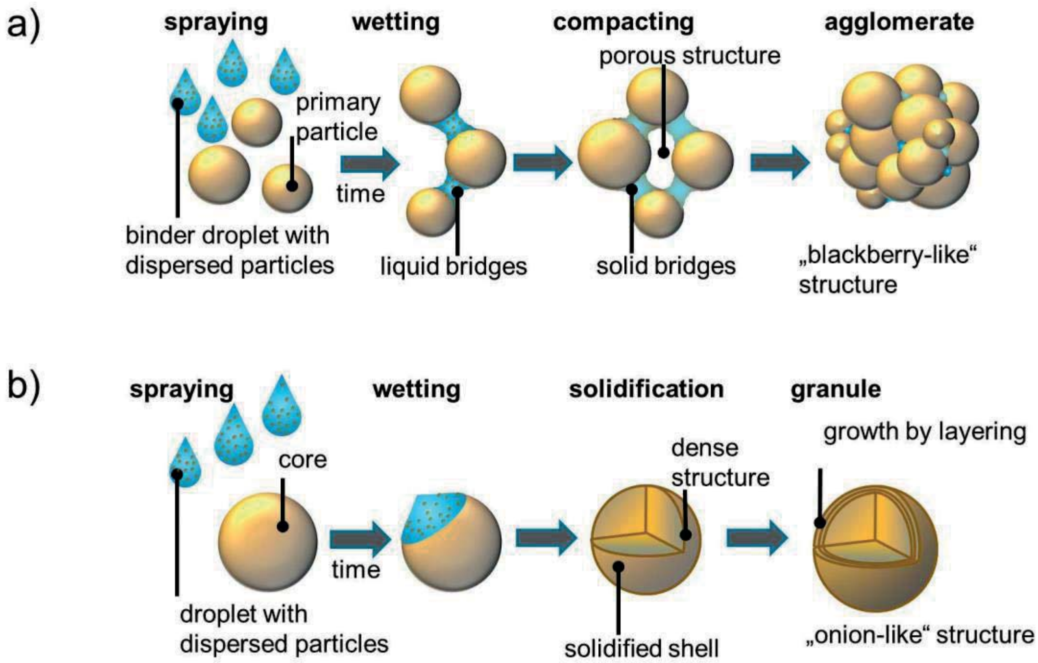

Fig. 1.4: Scheme of the (a) agglomeration and (b) granulation process (adapted from Fries 2012).

On the other hand, granulation means that matter of arbitrary form is transferred into a granular state. A granulation process is essentially any process which produces granular matter. Unlike agglomeration, this can also be a comminution process. Granular matter is basically characterized by consisting of a large number of grains of sizes between $1 \ldots 10^4$ µm. The term granulation is often specifically used for a process in which the nonvolatile part of a solution or suspension is sprayed onto small particles, thereby coating them or successively enlarging them. Such a process is shown in Fig. 1.4 b. The particles grow by successively adding layers. Therefore, the resulting structure is sometimes also called 'onion-like'. Fig. 1.4 a illustrates an agglomeration process. As several particles of the same type are merged into one agglomerate, the resulting structure is sometimes also called 'blackberry-like'.

The fabrication of bulk amounts of hierarchically structured materials is necessary to study systematically the influence of a hierarchical structure on the material properties. This would make it possible to extend the knowledge about which concepts of biological materials can and should be used in future for the fabrication of materials with properties superior to the existing ones. In general it depends on the respective application which properties of materials should be optimized. In this thesis the focus is on mechanical properties, of which the most relevant ones are shown in Fig. 1.5, along with the respective principle idea of implementation. In fact, the properties are highly interdependent in a complex way, which is explained in more detail in the following chapters.

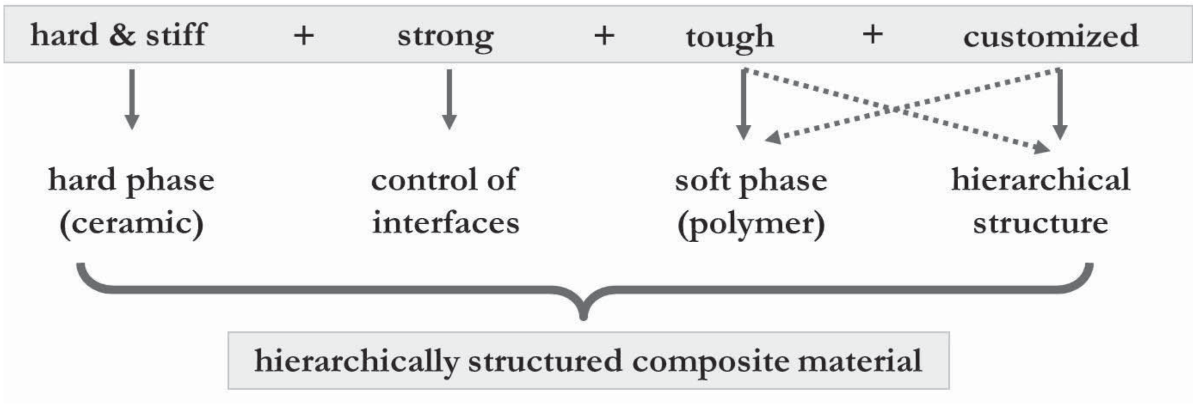

Fig. 1.5: Target material properties with the respective basic way of implementation.

Each of the mentioned properties in Fig. 1.5 is realized separately in different types of materials, but no non-metallic materials exist which combine all these properties to a satisfactory degree. As an example, composite materials which contain a polymeric phase lack sufficient hardness and stiffness for many applications. In order to improve the hardness and stiffness of such materials, the packing of particles of different sizes, as shown in Fig. 1.6, plays an important role. As will be seen, the spouted bed spray granulation process can be used to fabricate bulk amounts of composites of this kind.

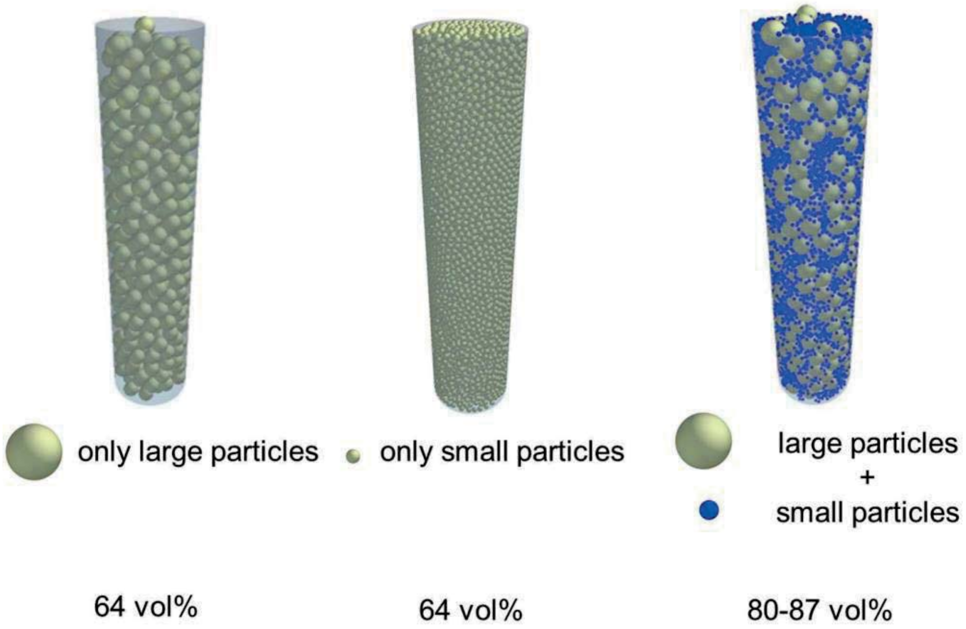

Fig. 1.6: Illustration of how the packing density is increased by combining two different particles sizes.

An important property of a set of particles is the packing structure they assume under the influence of certain forces. The packing structure, and in particular the packing density ρ_{packing} of a packing of particles depends on the distribution of particle sizes. Packing densities up to 100 % can be reached if elongated particles (cubes, platelets, fibers) are packed with perfect (or at least partial) alignment. The efficient alignment of such particles in the µm-range however is very challenging and has not been satisfactorily realized so far (cf. e.g. Bonderer et al. 2010a). Some ideas for alignment with the help of magnetic nanoparticles will be briefly discussed in chapter 8.

When spherical particles of equal size are put together in a sufficiently large box, and some mechanical agitation is performed, a packing density of roughly 0.64 is obtained (cf. Fig. 1.7). This value is independent of the particle size as long as interparticle forces on the µm- and nm scale are neglected. It is called the random-dense packing (RDP) of spheres (German 1989). When higher packing densities are aimed for, different particle sizes have to be combined such that the smaller (fine) particles fill the void volume of the larger (coarse) particles (Fig. 1.6). For an increase in packing density to occur at all, the particles have to be mixed homogeneously in the way shown in Fig. 1.6, and segregation has to be avoided.

The increase of packing density with increasing particle size ratio is shown in Fig. 1.7. For small ratios, i.e. when the two particle size fractions are similar in size, the packing density increases rapidly with increasing particle size ratio. When the size ratio reaches roughly the value of 7, the particles of the fine fraction start to fit into the voids of the coarse particles, and the increase of packing density with increasing particle size ratio slows down (cf. Fig. 1.7).

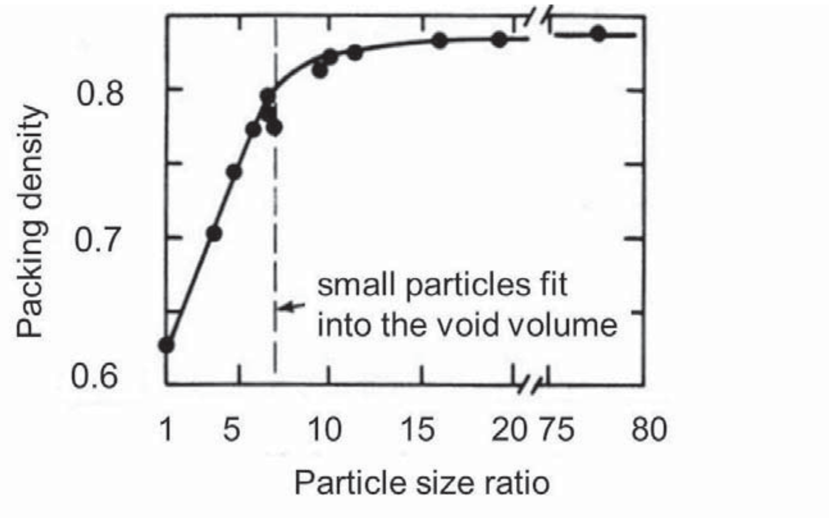

Fig. 1.7: Packing density as a function of the particle size ratio for two different monosized particle size fractions (adapted from German 1989).

The dependence of the packing density on the relative amounts of different particle size fractions is shown in Fig. 1.8. It can be seen that optimum weight fractions are roughly 60 % of the coarse particles and 40 % of the fine fraction. For very high particle size ratios, the amount of the coarse size fraction is slightly increased.

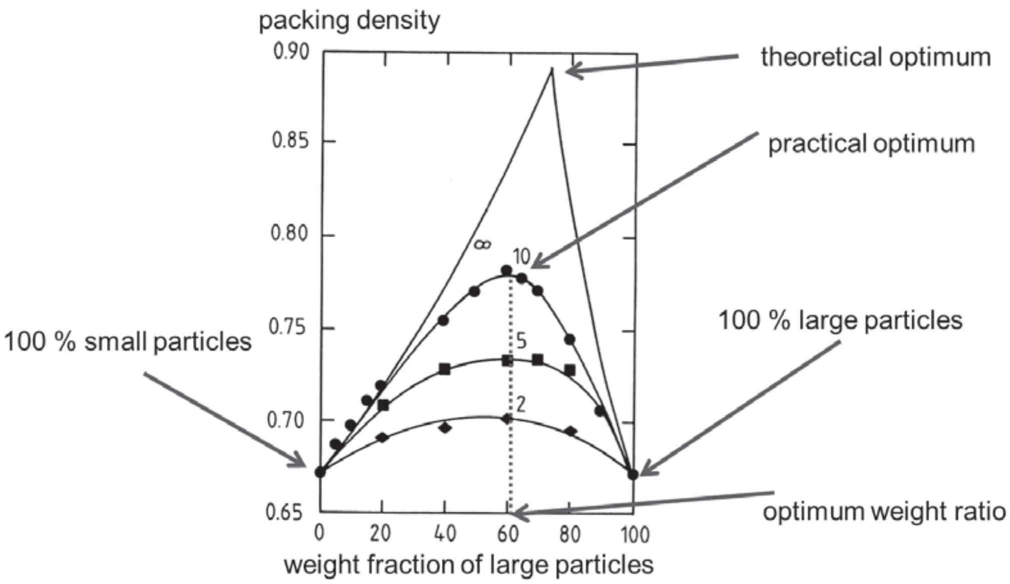

Fig. 1.8: Packing density as a function of the weight fraction of two particle sizes for different particle size ratios (adapted from German 1989).

It can also be shown that if the packing density should be further increased by a third and possibly a fourth particle size fraction, the ratio of largest to smallest particle size has to be at least 100 (3 particle size fractions) and $>10^4$ (4 particle size fractions) (Fig. 1.9). Furthermore the respective increase of packing density by an additional particle size fraction becomes smaller and smaller for increasing number of particle size fractions.

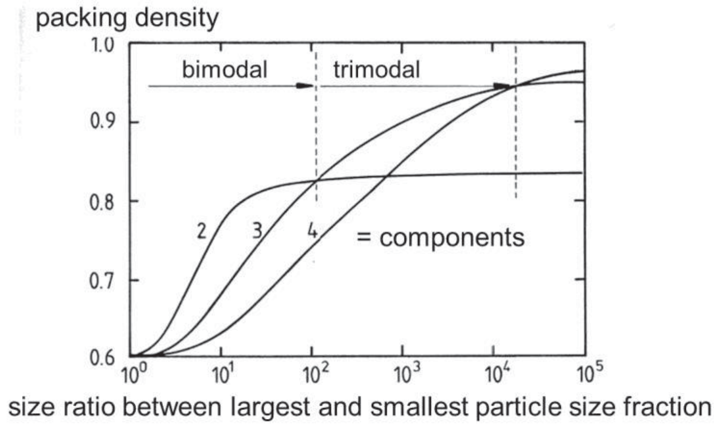

Fig. 1.9: Packing density as a function of the size ratio for different numbers of particle size fractions (adapted from German 1989).

A material which is made up of different material phases and large amounts of discrete particles is a highly complex system, for which numerical simulation tools are very useful to study the mechanical properties. In this thesis the Discrete-Element-Method (DEM) is used. This is motivated in detail in chapter 7, but Fig. 1.10 already illustrates one of the main advantages of using the DEM, namely the direct correspondence of experimental specimens and modeled structures.

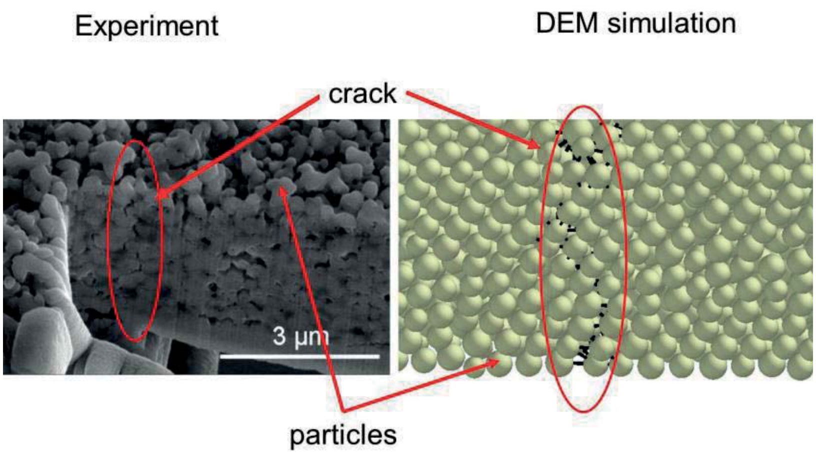

Fig. 1.10: Scanning electron micrograph (left) and simulation with the Discrete-Element-Method (right) of beams being composed of discrete particles.

In chapter 2 the properties of existing materials and composites are reviewed. In chapter 3 an overview is given over the fluidization and spouted bed technology, with focus on the spray granulation process. The experimental setup is described in chapter 4. Following this it is explained in detail in chapter 5 how the spouted bed spray granulation process can be used for the fabrication of novel composite materials, and which material properties are obtained with this approach (chapter 6). In chapter 7 the numerical modeling based on the Discrete-Element Method to simulate these properties is discussed, including the results of parameter studies for validation and comparison with experimental results from the previous chapters. The possibilities to use the developed experimental approach for various, more complex composite materials are then analyzed in chapter 8, with focus on a hierarchical structuring of the material. In the concluding chapter 9 the main results and conclusions of this work are summarized.

2 Composite materials and their properties

2.1 Building blocks of composites: Properties of ceramics, polymers, and metals

2.1.1 Properties of ceramics

Ceramics are the most abundant type material in the earth crust. Stones, sand, and in general any kind of clay minerals are examples of naturally occurring ceramics. Glass, porcelain, and bricks are examples of artificial ceramics. It is not so easy to define stringently what a ceramic material is and what it is not. Ceramic materials have in common a small structural unit of typically only several atoms (as opposed to polymers), which do not form a metallic bonding (as opposed to metals). In many relevant aspects, a ceramic is distinctly different from metals and polymers. They 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, its insulating properties, and its abundance in nature. Materials made from ceramic powders are used for applications in materials sciences and industries, ranging from sophisticated machine elements to applications in everyday life. Table 2-1 lists the most important advantages, disadvantages, and some applications of ceramic materials.

Table 2-1: List of properties of high-performance ceramics.

Advantages	Disadvantages	Applications (examples)
High stiffness and hardness	Brittleness	Insulators
High strength	Scatter of strengths	Bone replacement
Insulating (thermally, electrically)	Sintering	Artificial dentition
Wear and corrosion resistant	Processability	Crucibles
Temperature-resistant		Heat shields
Low density		Piezoelectric devices

Ceramics which can be used within the human body or for other medical purposes are often called bio-ceramics. These include e.g. alumina, zirconia, and hydroxyapatite. They have e.g. been