Composites Science and Technology 72 (2011) 65–71

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

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

Novel ceramic–polymer composites synthesized by compaction of polymer-encapsulated TiO_2-nanoparticles

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ARTICLE INFO

Article history:
Received 8 March 2011
Received in revised form 25 August 2011
Accepted 5 October 2011
Available online 13 October 2011

Keywords:
A. Hybrid-composites
A. Particle-reinforced composites
A. Structural composites
B. Mechanical properties
Polymer-encapsulation

ABSTRACT

A novel processing route for producing composites from ceramic particles and a thermoplastic polymer with high ceramic content was developed. Via a radical emulsion polymerization reaction in an aqueous suspension, titanium dioxide is encapsulated by a thin layer of poly(methyl methacrylate). Subsequently, the coated particles are compacted by applying high pressure (~1 GPa) at a temperature above the glass transition temperature of the polymer (~160 °C). This technique enables producing dense, hard and stiff composites at low processing temperatures. Microstructural investigations of composites by scanning electron microscopy confirm successful coating of titanium dioxide particles by polymer. Compositions were estimated from thermogravimetric measurements. A maximum TiO_2 volume content of almost 70% was achieved. For characterizing mechanical properties, Vickers microhardness as well as flexural strength and elastic modulus were determined. With respect to pure PMMA, composites exhibit a 10-fold increase in microhardness. Furthermore, a strong increase in elastic modulus with TiO_2 contents, up to 40 GPa at 66 vol.% TiO_2 was observed. These moduli are among the highest found in literature for ceramic polymer composites. However, bending strength of the material is still low.

1. Introduction

As for many fields of research, nature serves as inspiration for creating novel advanced multifunctional materials. One example are inherently sophisticated hierarchically-structured ceramic–polymer-composites such as the hard tissues enamel, nacre, conch shells or human bone [1,2]. Besides a hierarchical structure on several length scales, those materials are primarily built up by a dominating hard ceramic phase like hydroxyapatite or aragonite and a minor soft organic phase (proteins). The content of hard phase can reach up to 95 vol.% as in nacre [2]. These intricate structured materials possess very good mechanical properties such as high stiffness, toughness and damage tolerance, which seems to be the optimum for the combination of soft and hard constituents [2,3].

Driven by the fascination for the structure and mechanical properties of these natural materials, the interest of replicating such composites using advanced ceramics and polymers has drawn much attention during the last decades [4–10]. As all natural prototypes of hard tissues consist of a high fraction of hard phase, conventional dispersion methods in materials science cannot be utilized for mimicking these composites. The most relevant drawback for the production of high filled polymer composites is the high viscosity of the material, which precludes the processing of homogeneous composites having high filler loadings via melt mixing or blending [11]. However, a high ceramic volume percentage is crucial for achieving good combinations of strength, hardness and stiffness.

To overcome this limitation, several research groups are currently working on methods for mimicking nature's concept of structuring hard and soft materials with simultaneously high ceramic content by using various innovative techniques [4–10]. However, there are different restrictions for each method applied. High ceramic contents, even up to ~95 vol.% [4], can be achieved e.g. by layer-by-layer assembly [4,6,7]. With this process, well-defined microstructures can be obtained, but slow assembly rates limit the practical use of layer-by-layer methods for other applications than for thin films [4–7]. A very high toughness and

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doi:10.1016/j.compscitech.2011.10.001

R-curve behaviour was obtained for a material produced by freeze casting with subsequent monomer infiltration [8]. A maximum ceramic content of ~75 vol.% was achieved by this method, but still a high temperature sintering process is involved and dimensions of the inorganic phase are one order of magnitude higher than found in nature [8]. Bonderer et al. [9] used a combined gel casting and hot pressing technique to achieve ceramic contents up to 70 vol.% in larger quantities. But their structures suffered from platelet misorientation and pore formation at high volume contents of ceramic. Oner Ekiz et al. [10] used a combined hot-pressing and slip-casting method to achieve high platelet filler contents in epoxy resin. The method is versatile to scale-up, but an upper limit of 60 vol.% of ceramic phase is indicated.

Common to all these structured composites is their anisotropy, as sheet-like building blocks of hard phase are being used to mimic the brick-and-mortar structure of nacre [4–10].

In this work, we focus on developing a novel isotropic polymer–ceramic composite material with high ceramic content. For achieving high ceramic contents, hard particles are coated by a thin polymer layer in a radical emulsion polymerization process and are subsequently warm pressed (Fig. 1). TiO_2 and PMMA were selected as model materials. These materials are inexpensive, easy to handle (non-toxic) and abundant. Furthermore, they are well-investigated objects for encapsulation reactions in many publications [12–15], as polymer-coated hard particles are often used to improve dispersability and compatibility of particles in polymer matrixes or paints [12–16]. For the warm pressing step in our processing route, thermoplasticity is an essential property of the applied polymer. However, the processing route is not restricted to PMMA and TiO_2 but rather thought to be applicable for various different material systems of hard (e.g. SiO_2, Al_2O_3) [13,16] and soft phases (e.g. polystyrene, polyamide), allowing for a free degree in designing and tailoring materials properties to achieve good mechanical properties.

The microstructure of composites was investigated by scanning electron microscopy. Fourier transformed infrared spectroscopy was used to qualitatively determine compositions, quantitative analysis was performed by thermogravimetric measurements. The microhardness was determined via Vickers indentation testing. Flexural strength and elastic modulus were measured. Results will be compared to other highly filled composites found in literature, with a main focus on dental restorative materials.

2. Experimental

2.1. Materials

Titanium dioxide (TiO_2) powder of rutile modification (R802) and equiaxed, quasi-spherical shape was provided by Tronox (USA). The specific surface area of the powder of (5.21 ± 0.04) m^2/g was determined by one-point BET (Quantasorb Jr., Quantachrome, USA). Methyl methacrylate (MMA) was purchased from Merck (Germany). Stabilizer was removed by filtration of MMA with alumina powder. Sodium dodecylsulfate (SDS) and potassium persulfate (KPS), both purchased from Th. Geyer (Germany), were used without further purification. For all experiments, deionized water was used.

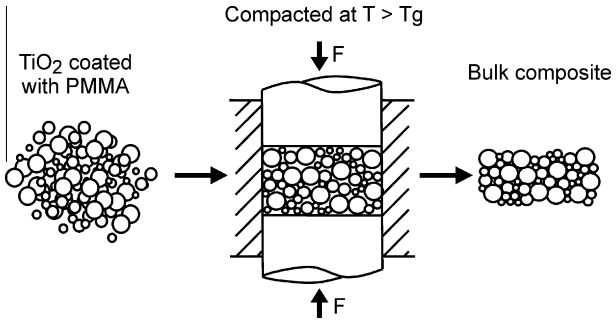

Fig. 1. Schematic of the synthesis of polymer–ceramic-composites.

2.2. Sample preparation

For deagglomeration and dispersion, TiO_2-powder was mixed with water and treated in a planetary ball mill (Type 05.202, Fritsch, Germany) at 200 rpm for 2 h using 3 mm zirconia balls. Verification of deagglomeration and measurement of the grain size distribution was performed by Ultra Small Angle Neutron Scattering (USANS). For stabilization of titania in suspension, the pH value was adjusted to ~8 with 1 N KOH. USANS was performed at the instrument DCD of the Geesthacht Neutron Facility (GeNF) in Germany. A detailed description of the measurement technique and the facility can be found elsewhere [17]. The scattering curves, measurement fit and the resulting particle size distribution are shown in Fig. 2a and b, which give a maximum of volume fraction at a radius of 100 nm.

After the milling process, appropriate amounts of water were added to adjust the TiO_2-concentration in the suspension. For suspension stabilization, but more important for localized polymer formation, SDS was added with a concentration of 2.102 g/l, as to be well below the critical micelle concentration of 8.1 mmol/l H_2O [12]. Verification of dispersion stability was performed by settling experiments.

A typical procedure for radical polymerization was conducted as follows. For coating TiO_2-particles with PMMA, the aqueous suspension with a TiO_2 concentration of 25–55 g/l and the SDS was introduced into a 2l three-necked flask (TNF), equipped with a magnetic stirrer, a thermometer, a condenser, a burette for MMA

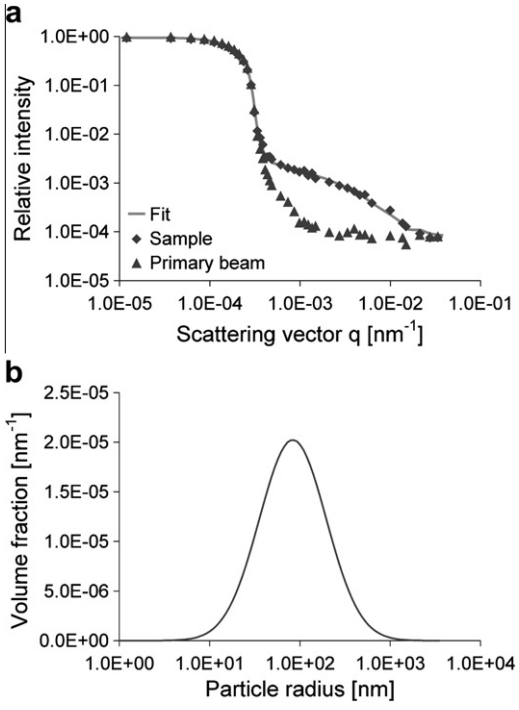

Fig. 2. Scattering curve of TiO_2 measured by USANS using a double crystal diffractometer and fitted curve (a). In (b), the particle size distribution (volume fraction) is given as determined from measured scattering curves within the framework of a two-phase model.