



Reinforced and hardened three-phase-foams



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ABSTRACT

Currently and in the past several lightweight materials were evolved focusing on different applications. Many developments are based on biomimetic approaches to reach material and cost savings with a simultaneous combination of thermal insulation and sustainability, for example. The desire of needed high porosity and lower density lead to less strength of the materials. Thus, applications are limited. One way to solve this problem is the creation of foams based on three phases. A new approach is the implementation of nanotubes and further chemical treatment of the inorganic foams to avoid further energy consuming thermal treatment for strengthening. Three-phase-foams consist of pozzolanic active nanomaterials as a third phase, which can be varied and surface treated. The resulting materials can be combined with other binders to further improve their properties or used as self-contained materials.

Aided by chemical treatment a hardening of the foams has been achieved. Implementation of pre-fabricated and synthesized nanotubes as a nanoreinforcement were successfully done and properties of the foams investigated. Results based on studies of the microstructure and phase formation will be illustrated and discussed.

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1. Introduction

1.1. State of knowledge

Nowadays, in food, cosmetic or construction industries foams are commonly used for further implementation or as self-contained materials [1,2]. Hereby, biomimetic approaches enable to develop new materials [3]. Following the definition of Bikerman in 1973 foams are colloidal systems and based on aggregation of two-phases. Commonly, foams are classified as gases dispersed in liquids but also gases dispersed in solids known as solid foams [4]. The former are wet foams and normally used for implementation in other binders to observe certain porosity [1]. Foams are unstable due to high surface energy resulting from the gas-liquid (disperse-continuous) interface. Caused by the large total area, interfacial properties like surface tension and elasticity influencing foam stability [5,6]. Surface tension is defined as the ratio of work required to increase the interface and the related change of interfacial area. For lowering the surface tension and free energy of the system, surfactants are used which adsorb at the gas-liquid interface. Surface tension decreases with increasing surfactant

concentration until critical micelle concentration is reached. At this point surface tension is no longer reduced and with further increase more and more micelles are formed. Nevertheless, the metastable foam system collapses after a certain time through its effort to lower surface energy. Destabilizing effects like drainage, coalescence and Ostwald-ripening result in complete separation of disperse and continuous phase [6–10]. Furthermore, also colloidal particles can be introduced in the disperse-continuous interface which is dependent on the wetting property of the particle surface [11–16]. Pickering emulsion is hereby one of the oldest and well-known approaches of foam stabilization through particles which can be wetted by both disperse and continuous phase [11]. These partially hydrophobized particles are also observed by adsorption of surfactant molecules at solid-liquid-interfaces. Surface properties as surface tension and contact angle were determined through chemical composition of the three phases and temperature. Adsorption mechanisms are related to both the interaction between surfactant and particle and between surfactant molecules among themselves [12,17]. Several approaches of using long-chain surfactants or hydrophobic silanes were described to change particle surface properties. Gonzenbach et al. were the first group which showed high-volume particle stabilized foams which prevent drainage and fewer further destabilizing effects [18]. Due to the high content of modified particles in the liquid medium, high amounts of disperse-continuous interfacial area are stabilized.

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Thus, integration of particles in the gas-liquid (disperse-continuous) interface is enabled by electrostatic forces between the particles and surface-active agents which lead to a sorption on the particle surface. Resulting partially hydrophobized particles can also dip into the disperse phase and lead to high stability, along with a low density, even after complete water diffusion or drying of the foams [18–20].

1.2. Carbon and titanate nanotubes

In this study different nanotubes were used to improve foam performance and add their desired properties. First nanotubes synthesized were carbon nanotubes (CNTs) in 1951 by Radushkevich et al. [21]. Since Iijima et al. who published further investigations on their properties, nanotubes became an even greater focus of attention [22].

CNTs have good thermal conductivity of theoretically 6000 W/mK at room temperature. Measurements show 3500 W/mK in axial directions which is the ninefold value of copper [23]. Also, high thermal stability up to 750°C in air and 2800°C in vacuum, good electrical conductivity, low density of 1.33–1.40 g/cm³ including the cavity volume and tensile strength of 11–150 GPa are advantageous properties of CNTs [24–26]. The structure of CNTs is equal to coiled graphite layers. Thus, carbon is sp² hybridized in an aromatic ring structure and can be single-walled or multi-walled. Single-walled CNTs have diameters of 1–2 nm and three types of nanotubes are distinguished: armchair, zigzag, and chiral which have an influence on the electrical properties. There are mainly three different ways used to synthesize CNTs: arc-discharge method, laser ablation technique and chemical vapor deposition (CVD). Used prefabricated CNTs were produced by catalytic chemical vapor deposition (CCVD) a variation of CVD [22,27,28]. Due to the oxidation processes functionalities like carboxyl, carbonyl and hydroxyl groups are formed which are depending on the process and oxidant strength. Further on, CNTs can be coated by SiO₂ to improve the interaction with and thus implementation in other materials. Coating of CNTs is done in layers by adsorption of organic silicic acid ester like tetraethyl orthosilicate (TEOS) in addition with thermal decomposition or sol-gel method. SiO₂ layer thickness varies between 1 nm to several nanometers [29–33].

Compared to CNTs, titanate nanotubes (TiNTs) show differences in their structure and properties. TiNTs have a hydrophilic surface without any further treatment and consist in every case of several layers which are based on one coiled plane. Depending on the used synthesis and resulting structure different inner and outer diameters around 5.3 nm or 9.0 nm and 0.75–0.92 nm for the distance of the layers were published [34,35]. High resistance to alkaline conditions is one of the advantageous property. The stability to acidic environments is limited due to the conversion to rutile nanoparticles in strong acids [36]. In addition, TiNTs enable good ion exchange capability. Relating to the structural properties different descriptions can be found in the literature. Researchers found that the structure is similar to anatase [37–39] but also composition of TiO_x similar to rutile or anatase [34]. Also, structures related to sodium titanate or trititanic acid and their hydrated forms were postulated [35,40–44]. Nowadays, three different ways to synthesize TiNTs are used: template synthesis, anodic process and hydrothermal synthesis [45,46]. In our study, modified hydrothermal synthesis is used. Herefore, anatase is thermally treated in alkaline solution [37,47].

1.3. Hardening and nanoreinforcement

Following the approach of *Gonzenbach* et al. investigations on foams based on nanosilica (NS) as a third phase were done. Due to

this, the resulting three-phase-foams can also be hardened by chemical treatment for certain applications to avoid energy consuming thermal treatment. After storage in Ca(OH)₂ solution, pozzolanic reaction of nanosilica particles to form strength improving calcium-silicate-hydrates (C-S-H), reach denser microstructure or packing in the borders/lamellae and healing of shrinkage cracks is enabled [20,48].

In our study, we show an approach to implement different nanotubes in the microstructure of three-phase-foams. This nanoreinforcement is combined with the hardening process in solution to further stabilize the foam structure and improve foam performance. Thus, three-phase-foams consist not only of an additional third solid phase of pozzolanic active nanoparticles but also nanotubes which can influence pozzolanic activity. This research is a continuation of foregone investigations on the improvement of foam performance in Refs. [20,49,50]. Nanotubes used are oxidized/SiO₂-coated carbon nanotubes and titanate nanotubes which are synthesized. Beside the goal to successfully implement these nanotubes in the foam structure, differences in the influence of nanotubes on microstructural properties, phase development and especially pozzolanic reactivity related to the surfactant should be elucidated. Thus, our experimental results enable the understanding and knowledge for further adaption as well as improvement of inorganic foams.

It is of importance for building and material chemistry because of the opportunity to reduce the content of inorganic binders. The research we present enables research scientists to produce stable inorganic foams with low densities of 60–90 kg/m³ and a method for production of lightweight materials which are low cost energy saving materials due to material reduction. Also, the implemented nanotubes could provide additional electrical, thermal and photocatalytic properties to the foams. Moreover, these foams can also be used for foam concrete production and lead to enhanced materials properties as shown in Refs. [1,50,53,54].

2. Experimental section

2.1. Materials

2.1.1. Nanomaterials

The nanoparticles used were AEROSIL® 90 (Evonik). Prefabricated multi-walled CNTs (Bayer) were chemically treated to enhance the amount of functional groups like –COOH and –OH. Through a sol-gel process these oxidized CNTs (oxCNTs) were coated with SiO₂ (coatCNTs) and current TiNTs produced by modified hydrothermal synthesis (See 2.2 Specimen preparation).

The outer diameter of the used nanomaterials was measured by scanning electron microscopy (SEM) and with the help of gas adsorption the BET-surface (following Brunauer-Emmert-Teller) was determined. A negative zeta potential was measured at pH 7 to 12 for all nanomaterials by electrophoretic light scattering. Zeta potentials are given at pH 10 which is the pH value of the dispersions used for foam preparation (Table 1).

2.1.2. Surface active agents

As surfactant TEGO Betain F 50 (Evonik) was used. According to

Table 1
Properties of the different nanomaterials.

	NS	oxCNTs	coatCNTs	TiNTs
BET-surface (m ² /g)	104 ± 10	219 ± 1	44 ± 1	149 ± 1
Diameter _{outer} (nm)	~20	~10–20	~100–150	~10–30
Zetapotential _{pH 10} (mV)	–48	–39	–50	–34

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