Chapter 2
Fillers and Reinforcements

Abstract Syntactic foams are two component materials consisting of matrix resin and hollow particles. Reinforced syntactic foams contain an additional reinforcing material. The density of syntactic foams can be tailored based on the appropriate selection of hollow particle density and volume fraction. Glass hollow particles have been a widely used filler material because their low thermal expansion coefficient provides syntactic foams with high dimensional stability. Hollow fly ash particles, called cenospheres, have also been used as filler material. Fly ash cenospheres are inexpensive and help in developing low cost syntactic foams. However, usually defects are present in the walls of cenospheres and the mechanical properties of cenosphere-filled syntactic foams are not as high as those filled with glass hollow particles at the same density level. Enhancement of mechanical properties of syntactic foams beyond those obtained by tailoring the matrix and hollow particles can be obtained by micro- and nano-scale reinforcement of the matrix material. This chapter discusses hollow particle parameters such as wall thickness and density. Structure and properties of various reinforcements including glass fibers, nanoclay, carbon nanofibers (CNFs), carbon nanotubes (CNTs), and rubber particles are also discussed.

Keywords Syntactic foam • Porosity • Hollow particle • Silicon carbide hollow particle • Alumina hollow particle • Microballoon • Microsphere • Carbon nanofiber • Carbon nanotube • Crumb rubber • Nanoclay • Reinforced foam • Glass fiber • Carbon fiber

2.1 Type of Particles

Information about several types of ceramic hollow particles can be found in a review article [10]. Engineered hollow particles of glass, carbon, and phenolic resin have been used in fabricating syntactic foams [4, 11, 12]. The most widely used hollow

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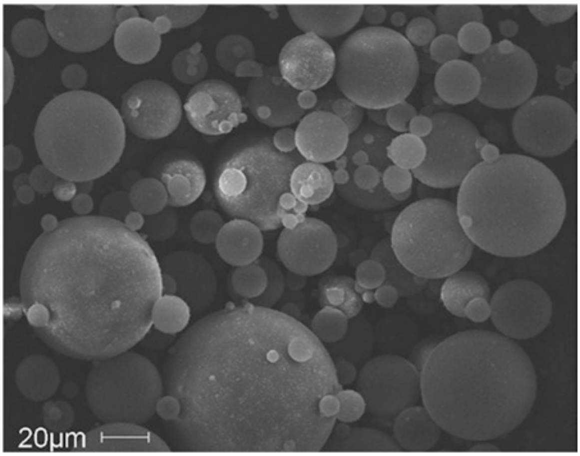


Fig. 2.1 Engineered spherical hollow particles of glass

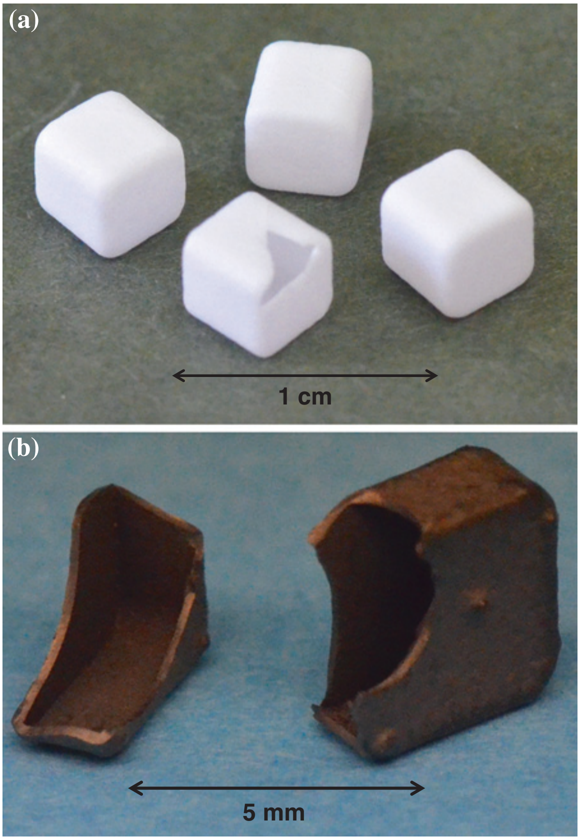


Fig. 2.2 Engineered hollow particles: **a** *cubic-shaped* particles of alumina and **b** *cuboid-shaped* particles of silicon carbide. Particles for imaging are provided by Mr. Oliver M. Strbik III of Deep Springs Technologies, OH

particles have spherical shape with diameter and density in the ranges 10–250 μm and 150–500 kg/m^3, respectively. These low density particles lead to lightweight composites because polymers used as the matrix have densities around 1,100 kg/m^3. A representative sample of 3 M Scotchlite glass hollow particles is shown in Fig. 2.1. These particles are spherical in shape and the particle size can vary over almost two orders of magnitude as observed in this figure. Now engineered hollow particles of almost any shape such as cuboidal or cylinder are available. However, such particles have not been found used in existing syntactic foams. The examples of cubic and cuboid shaped particles of alumina and silicon carbide, respectively, are shown in Fig. 2.2. Specialized applications can use such particles in syntactic foams.

Hollow fly ash particles, called cenospheres, are also used in several studies [2, 13, 14]. Cenospheres are obtained as a byproduct of coal firing in thermal power plants and have a predominantly alumino-silicate composition, along with a large number of impurities and trace elements [15, 16]. Cenospheres are recovered from waste byproducts and show a wide variation in their structure and properties depending on the composition of coal and the firing conditions. Defects such as embedded porosity in the walls can be seen in some fly ash particles in Fig. 2.3. Such defects adversely affect their mechanical properties and make them prone to failure [17, 18]. Compared to cenospheres, engineered hollow particles have better mechanical properties due to their controlled and better material quality. In addition, engineered hollow particles are manufactured under controlled conditions and show better strength and fewer defects in their structure than cenospheres. A possible method to improve the structure and properties of cenospheres is to use them as templates and coat them with a controlled outer layer [19]. The coating can cover defects, make the particle surface more uniform, and improve their mechanical properties. Both cenospheres and engineered hollow particles are widely used in metal and polymer matrix syntactic foams [20–23]. This book mainly covers engineered hollow particle filled polymer matrix syntactic foams because most studies using cenospheres have not reported properties such as

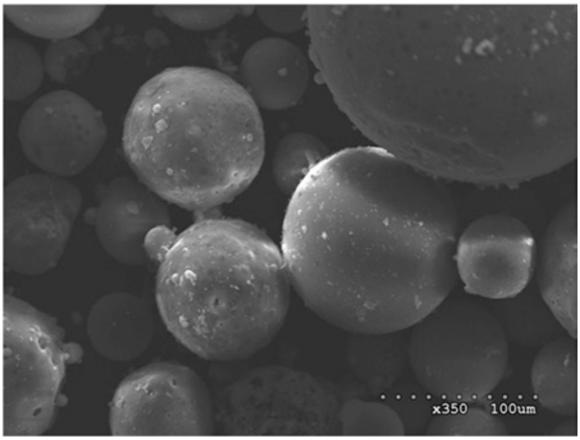


Fig. 2.3 Fly ash cenospheres

density and wall thickness of particles. In the absence of these parameters it is difficult to develop structure-property correlations and apply theoretical models.

The density of syntactic foams can be tailored by selecting the appropriate hollow particle density and volume fraction. In order to obtain properties of syntactic foams beyond those possible by tailoring the matrix and hollow particles, micro and nanosized reinforcements have been used. Carbon nanofibers (CNFs), carbon nanotubes (CNTs), and nanoclay are now widely used to enhance the mechanical properties of polymers [24–29]. Use of such reinforced polymers as matrix can provide syntactic foams with improved mechanical properties. The advantages, processing difficulties, and challenges in attaining the desired properties in reinforced syntactic foams are discussed in detail in the following sections.

2.2 Hollow Particle Parameters

The size and material density are the two main parameters in spherical solid particles. However, analysis of hollow particles requires additional parameters. Figure 2.3 shows that the diameter of hollow particles within a sample can vary over a large range, but the outer diameter does not provide any indication of the particle wall thickness. In the schematic shown in Fig. 2.4a, it can be noted that the particles of the same outer diameter can have different wall thicknesses (t). The particle wall thickness can be defined using a parameter named radius ratio [30]

$$\eta = \frac{R_i}{R_o} \tag{2.1}$$

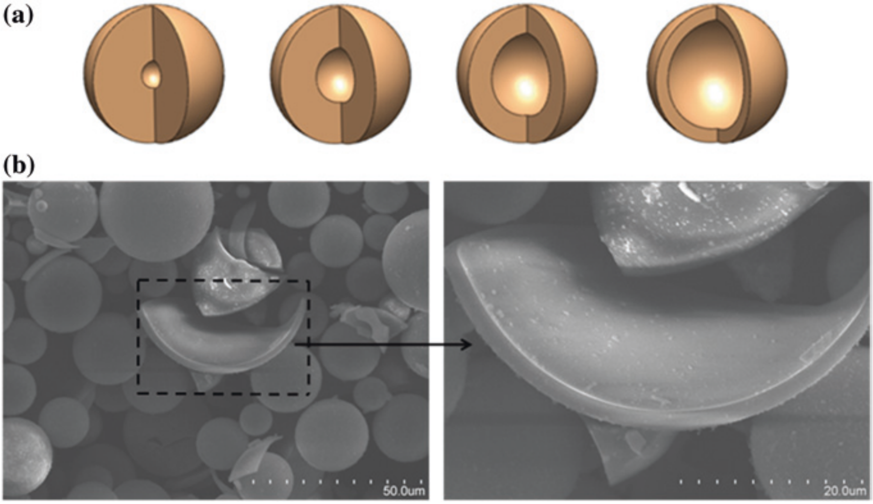


Fig. 2.4 **a** Schematic of possible variation in wall thickness of hollow particles of the same outer radius and **b** a broken hollow particle showing wall thickness

where R_i and R_o are the internal and outer radii of hollow particles, respectively. Radius ratio can be related to wall thickness by $t = R_o\,(1{-}\eta)$.

A combination of radius and wall thickness determines the properties of hollow particles. Direct measurement of wall thickness or radius ratio is usually not practical because they can be different for every particle. Average values of η and t for a batch of particles can be estimated through measurement of true particle density of hollow particles (ρ_{mb}) and the density of the particle material (ρ_g) by

$$\eta = \left(1 - \frac{\rho_{mb}}{\rho_g}\right)^{1/3} \tag{2.2}$$

where ρ_{mb} and ρ_g can be experimentally measured using a pycnometer. In general, thin-walled particles are used in fabricating syntactic foams. The commonly used glass hollow particles have true particle density in the range 150–500 kg/m^3. Considering the glass density as 2,540 kg/m^3, the radius ratios of hollow particles of densities 150 and 500 kg/m^3 are calculated as 0.93 and 0.98, respectively, which is in a narrow range. The average wall thickness for these particles can be calculated as 0.5 and 1.8 μm, respectively, for commonly used particles of 25 μm radius. Figure 2.4b shows a broken particle of about 25 μm radius having wall thickness of about 2 μm. The wall thickness to diameter ratio is less than 5 % in these particles. Although the radius ratio and wall thickness seem to be in a narrow range, this distribution is wide enough to show different trends in their mechanical properties. Within this radius ratio range, the low density hollow particles cause weakening and the high density particles cause strengthening of syntactic foams as the hollow particle volume fraction is increased [31]. Use of particles with lower radius ratio than 0.93 is not common because no additional benefit in mechanical properties with respect to the density is observed in syntactic foams. In addition, high density foams would not be useful in marine applications that require buoyancy.

It should also be noted that the wall thickness may not be constant within one particle. Locations where walls are thin become weak spots in the composite where failure can initiate. Compression testing of individual hollow particles using a nanoindenter has shown a wide range of mechanical properties in particles of the same size, which may be due to their different wall thicknesses and possible presence of defects in the walls [18].

2.3 Reinforcements

Hollow particles are an essential constituent in the syntactic foam microstructure. Therefore, any second phase material apart from hollow particles incorporated in the matrix is termed as reinforcement in this book. The purpose of incorporating reinforcement includes increase in modulus, strength, and energy absorption; modulation of electrical properties; and tailoring of thermal properties such as thermal expansion, thermal conductivity, and glass transition temperature (T_g). The following discussion presents an overview of different types of reinforcements used in syntactic foams.

2.3.1 Fibers

High aspect ratio glass, carbon and aramid fibers are used in syntactic foams as reinforcements. These fibers have diameter in the range of 8–15 μm, which is of the order of hollow particle diameter. Since the length of fibers can vary over a large range (from less than 1 mm to any desired length), they are termed as micro-scale reinforcements (or microfibers) based on their diameter measurement. Fibers can be used either in continuous or discontinuous form.

2.3.2 Nanoclay

The schematic structure of nanoclay and high-resolution TEM image of 2 wt% nanoclay dispersed in epoxy resin are shown in Figs. 2.5a and b, respectively [32]. Nanoclay has a stacked platelet structure in which platelets are bonded with each other by van der Waals forces. Intercalation and exfoliation of nanoclay clusters can expose their large surface area to bond with the matrix resin and provide improvement in mechanical properties. Functionalization of nanoclay can make it compatible with different polymers and help in obtaining exfoliation [33]. Shear mixing and ultrasonication are found effective in exfoliating nanoclay in polymeric resins [34]. A vast body of literature is now available on the processing methods for effectively dispersing nanoclay in polymers and properties of nanoclay reinforced composites [35–41].

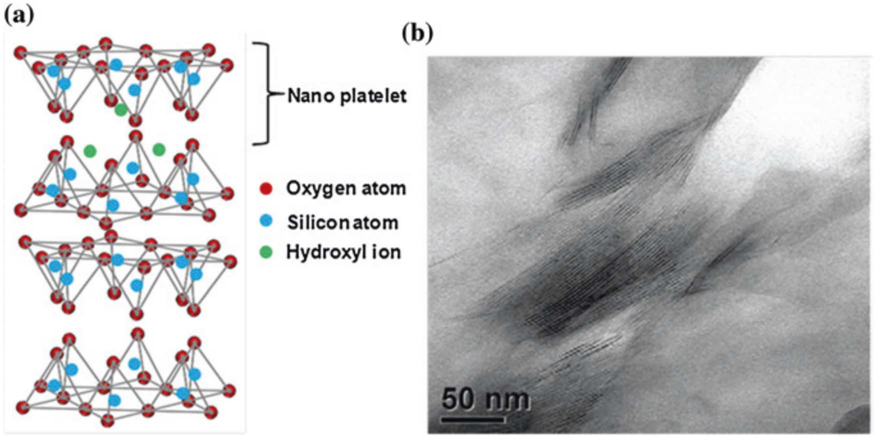


Fig. 2.5 **a** Schematic representation of nanoclay and **b** TEM image of 2 wt% nanoclay dispersed in epoxy resin [32]

2.3.3 Carbon Nanotubes and Nanofibers

CNTs and CNFs have been used as reinforcements in polymer matrix syntactic foams [42]. CNTs and CNFs are long aspect ratio fibrous materials; both contain hollow core structures, and have low density. Entanglement of such long aspect ratio reinforcements is an issue during processing. Use of excessive shear forces to disperse them can lead to their breakage. A representative structure of a CNT (single walled) and a high-resolution TEM image of CNTs suspended in a solution are shown in Figs. 2.6a and b, respectively [43]. Single and multi-wall CNTs are now commercially available. CNTs can be synthesized in desired length and chirality with the available synthesis methods. Several review articles are available about the structure, properties, and applications of CNTs [44–50]. CNT reinforced polymer matrix composites have also been widely studied in recent years and detailed information on these nanocomposites can be obtained from published review articles [51–59].

CNFs are also called stacked-cup CNTs, which refer to the stacked truncated cone structure giving them appearance of a helically coiled graphene ribbon. This kind of structure results in a hollow fiber core and graphene layers oriented at an angle from the fiber axis. The schematic of stacked-cup structure and a TEM image of a CNF sample are shown in Figs. 2.7a and b, respectively. The hollow structure of CNFs can be noticed in Fig. 2.7b. The bonding between graphene layers is important in determining the level of mechanical property improvement obtained in CNF reinforced composites. CNFs have been used for tailoring the mechanical, electrical, and thermal properties of syntactic foams [60]. Detailed discussion on the structure and properties of CNFs [48, 61] and CNF reinforced composites [62–69] can be found in recent review articles.

Theoretical estimates and experimental measurements of mechanical properties of CNTs and CNFs are available in literature. The modulus of CNTs is measured to be over 4 TPa in some studies and is routinely reported in the range 0.95–1.28 TPa [70]. However, the measured elastic modulus of CNT reinforced composites is lower than

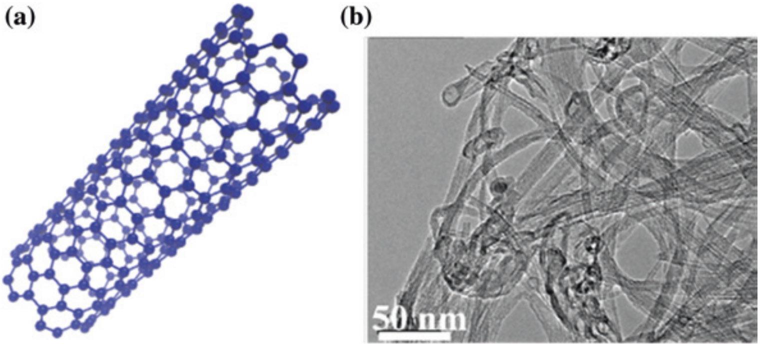


Fig. 2.6 **a** Schematic representation of an armchair carbon nanotube and **b** TEM image of single walled CNTs dispersed in a solution [43]

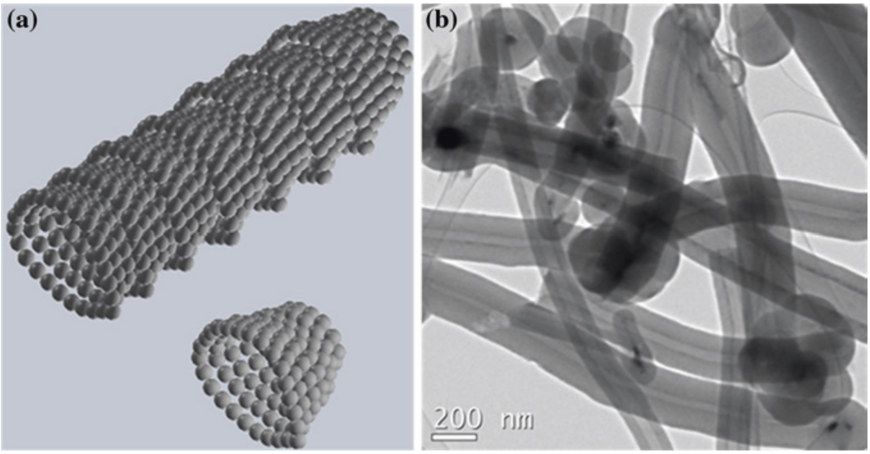
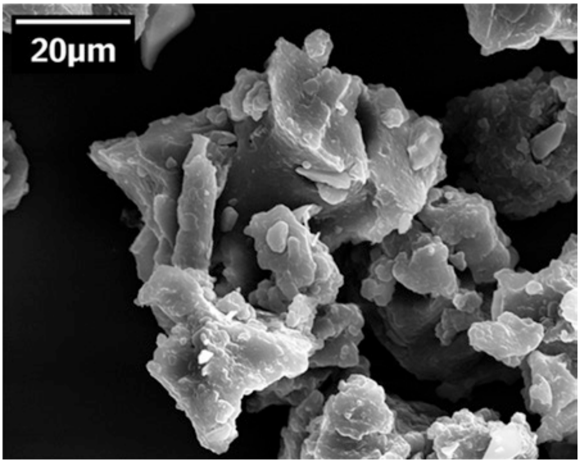


Fig. 2.7 **a** Schematic representation of stacked-cup structure and **b** TEM image of carbon nanofibers showing hollow core structure

Fig. 2.8 Scanning electron micrograph of crumb rubber particles generated by mechanical grinding process



that expected from such high values, which is attributed to factors such as curviness of CNTs leading to buckling and shearing, entanglement and poor dispersion, porosity entrapped in the composite during processing, CNT/matrix interfacial bonding issues, and defects in CNT structures.

2.3.4 Rubber Particles

Rubber particles are also used in syntactic foams as secondary particulate fillers. Crumb rubber particles obtained from waste tires are used for this purpose [71–74]. Some of these efforts are oriented toward developing useful applications of about 300 million waste tires generated each year in the United States. About 25 % scrap tires are disposed of in landfills, which are an enormous economic and environmental burden [75, 76].

Two methods are used for grinding waste tires to generate crumb rubber particles [77]. In the cryogenic method, the tires are cooled below their embrittlement temperature and then fractured either by impact or grinding. In the second method, the tires are mechanically ground at room temperature. The surface area of room temperature processed particles is higher and they show better reinforcing capabilities in composites. A sample of crumb rubber particles obtained by the mechanical grinding process is shown in Fig. 2.8. A very high surface area and irregular shape of this particle due to shearing fracture are useful in obtaining interfacial bonding and mechanical interlocking with the matrix resin.

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