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Compressive and Thermal Characterization of Syntactic Foams Containing Hollow Silicon Carbide Particles with Porous Shell

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ABSTRACT: Silicon carbide hollow particle (SiC_{HS}) reinforced vinyl ester matrix syntactic foams are prepared and characterized for compressive properties and coefficient of thermal expansion (CTE). Two types of SiC_{HS} were utilized in 60 vol % to prepare syntactic foams. These SiC_{HS} had ratio of inner to outer radius of 0.91 and 0.84 for the thin and thick walled particles. The specific compressive strength values were 33.4 and 38.8 kPa/kg/m^3 and the specific compressive modulus values were 0.8 MPa/kg/m^3 and 0.6 MPa/kg/m^3 for the thin and thick walled SiC_{HS}-filled syntactic foams, respectively. The shell of the hollow particles contained microporous voids, and the porosity was estimated as 16.6% and 24.8% in the walls of the thin and thick walled particles, respectively. The shell porosity adversely affected the specific compressive strength and the modulus of the syntactic foam. However, the SiC_{HS}-filled syntactic foams exhibited low CTE values (26.7 and 15.9 $\times$ 10^{-6}/°C). These CTE values were 65.1% and 79.3% lower than the CTE of the neat resin. Such properties can be useful for applications where syntactic foams are exposed to high temperatures and dimensional stability is important. A theoretical model is used to estimate the porosity level in the SiC shells and estimate the effective mechanical properties of the porous SiC material that forms the particle shell. Such analysis can help in using the models as predictive tools to estimate the mechanical properties of syntactic foams. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40689.

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INTRODUCTION

Syntactic foams are closed-cell composite foams synthesized by dispersing hollow filler particles in a matrix material.[1,2] Syntactic foams are finding applications in a wide range of fields such as buoyancy aids in human and remotely operated underwater vehicles, thermal insulation for under-water pipelines, and plugs assist in thermo forming machines.[3] Excellent tailorability of these materials for mechanical, thermal, and electrical properties is an important asset that is leading to such diverse applications. Hollow glass microballoons (GMB) have been commonly used as the filler for polymer matrix syntactic foams used in current industrial applications.[4–7] GMB-filled epoxy and vinyl ester matrix syntactic foams have been studied for thermal properties such as coefficient of thermal expansion (CTE),[8,9] thermal conductivity[10–12]; mechanical properties such as compressive, tensile,[13] flexural,[14] high strain rate compression[15,16]; and electrical properties such as dielectric constant and impedance.[17–19] In the case of solid particle reinforced composites, the only varying parameter is the volume fraction of the filler. The advantage with syntactic foams has been shown that the volume fraction (Φ) and the wall thickness of the filler can be varied to tailor the composite. Availability of hollow particles of desired material, diameter and wall thickness is very important for being able to design syntactic foams as per the requirements. Theoretical and experimental studies are also available to understand the failure mechanisms of hollow particles used in syntactic foams.[20,21] While most of the available literature is based on the commercially available GMBs, the present work explores a new kind of hollow silicon carbide (SiC_{HS}) particles with porous walls for potential use in syntactic foams for tailored thermal and mechanical properties.

Thermal insulation applications of syntactic foams desire tailorable CTE and to have low thermal stresses at the interface of the insulation and the substrate. The CTE of the syntactic foams has been observed to decrease with increase in the volume fraction of GMB.[8] A recent study on vinyl ester/GMB syntactic foams has shown that the CTE can be varied between 58 $\times$ 10^{-6}/°C and 30 $\times$ 10^{-6}/°C, by utilizing GMBs of densities between 220 and 460 kg/m^3 in 0.3–0.6 volume fractions.[8] In order to obtain properties beyond the limit of the commonly used GMBs, studies have used syntactic foams comprising hollow particles of carbon,[22] polymers,[23,24] and fly ash cenospheres.[25,26] Ceramic particles such as silicon carbide and alumina have high mechanical properties while possessing low CTE, which makes them a potential candidate for use as fillers in syntactic foams.

The approach of tuning the properties of syntactic foams by means of the volume fraction and the wall thickness of the hollow particles has been studied in detail.[8,17] Ascertaining the mechanical properties to the filler material is difficult due to their small size and variation from one particle to the other. However, the measured properties of syntactic foams can be used in conjunction with the theoretical models to estimate the average properties of the filler particles.[26] In the present work, SiC_{HS} reinforced vinyl ester matrix resin syntactic foams are characterized for thermal and mechanical properties. The porous nature of the walls of these hollow particles poses significant challenge in estimating the effective properties of SiC_{HS}. Such analysis can help in understanding the potential for these particles for use in syntactic foam applications.

MATERIALS AND METHODS

SiC_{HS} can be prepared using template spheres mixed with silicon powder and heating to 1300°C.[27] The hollow core is formed by calcining the particles thereby removing the excess carbon. Molten salt synthesis comprising a salt bath, carbon black template and Si has also been utilized to obtain SiC_{HS}.[28] In the present study, polyethylene core material is used as a template, on which SiC is deposited using chemical vapor deposition technique.[29] SiC_{HS} (manufactured by Deep Springs Technology, Toledo, OH) and vinyl ester resin (supplied by U.S. Composites, FL) is used to fabricate syntactic foam slabs. Methyl ethyl ketone peroxide is used as the catalyst for the resin. In the current study syntactic foams are prepared with 60% of SiC_{HS} by volume by a mechanical mixing method. The cast syntactic foam slabs are cured at room temperature for 24 h and then post cured at 70°C for 3 h in a convection oven. The detailed manufacturing procedure of syntactic foams is explained in existing literature.[13]

The hollow filler particle in syntactic foams has been characterized using the radius ratio parameter, η, which is the ratio of the inner (R_i) to the outer (R_o) radii of the hollow sphere.

$$\eta = R_i / R_o \tag{1}$$

where the radius ratio can be related to the hollow sphere wall thickness as

$$w = R_o(1-\eta) \tag{2}$$

Two types of SiC_{HS} were used in this study. The density of tapped bed of these particles was measured as 440 and 790 kg/m^3. Because of the porosity open to the surface in the walls of these particles, the direct measurement of true particle density using equipment such as pycnometer is not possible. Figure 1(a) shows the example of SiC_{HS} used in fabricating syntactic foams. Figure 1(b) shows the wall thickness of a broken SiC_{HS}. The average wall thickness and the outer diameter of the SiC_{HS} were evaluated as an average of 25 measurements taken on such micrographs of several particles and the results are shown in Table I. The average radii of the two types of particles, designated as S1 and S2, are measured as 400 and 510 μm, respectively. The average wall thickness is measured as 36.1 and 81.6 μm, respectively, for these particles. The density of SiC was used as 3200 kg/m^3 to evaluate the ideal true particle density, which is the density of hollow particles considering these measured diameter and wall thickness and fully dense walls, using[30]

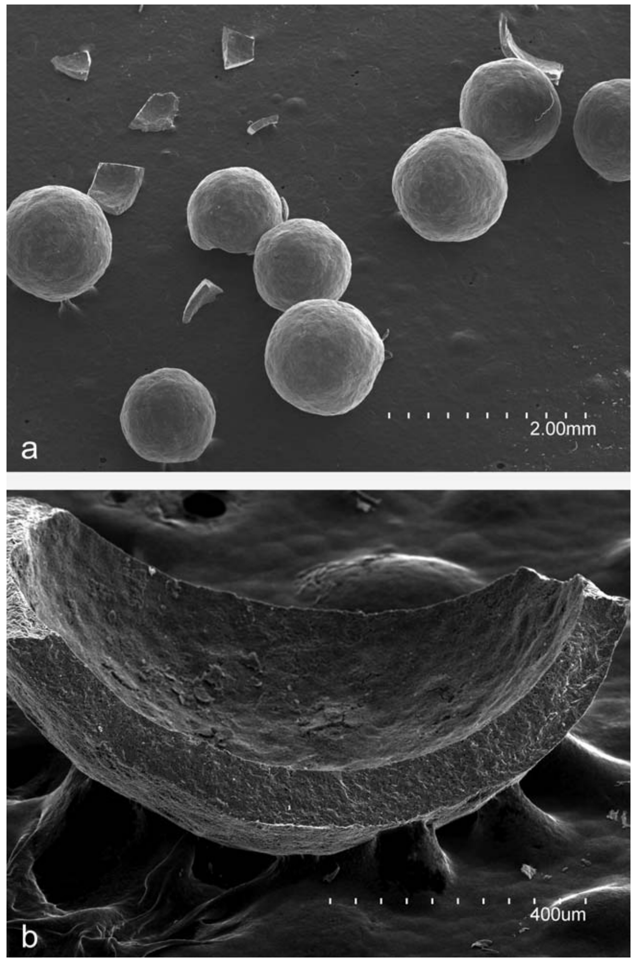

Figure 1. Scanning electron micrographs of (a) SiC_{HS} and (b) wall thickness of a broken SiC_{HS}.

$$\rho_{HS} = \rho_{SiC}\left(1-\eta^3\right) \tag{3}$$

The ideal true particle density is evaluated using eq. (3) and is found to be 787 and 1293 kg/m^3 for the S1 and S2 particles, respectively, as shown in Table I. However, the true particle density of particles is expected to be lower due to the porosity present in their walls. The experimental density of the fabricated syntactic foams containing 60 vol % SiC_{HS} was measured to be 858 ± 33 kg/m^3 and 1048 ± 44 kg/m^3 for SF1 and SF2 type syntactic foams containing S1 and S2 particles, respectively.

The quasi-static compression testing was performed on cylindrical specimens of nominal dimensions 6.5 mm diameter and 8.5 mm thickness at a constant loading rate of 1 mm/min using an electromechanical universal test system (Model 4469, Instron, Norwood, MA). The CTE study was performed on a

Table I. Average Outer Radii, Wall Thickness, and True Particle Density of the Two SiC_{HS}

Particle type	Tap density of particle bed (kg/m^3)	Average outer radius (μm)	Average wall thickness (μm)	Radius ratio η	Ideal true particle density[a] (kg/m^3)
S1	440	400 ± 30	36.1 ± 4.4	0.91	787
S2	790	510 ± 40	81.6 ± 6.8	0.84	1293

[a] SiC density is assumed to be 3200 kg/m^3.

thermomechanical analyzer (TA Instruments, New Castle, DE) using cylindrical specimens of nominal dimensions 7 mm diameter and 5 mm thickness from room temperature to 80°C at a constant heating rate of 3°C/min.

RESULTS

Compressive Properties

A representative compressive stress–strain curve of the SF1 syntactic foam is presented in Figure 3. Similar behavior has been observed for GMB/vinyl ester and GMB/epoxy syntactic foams in previous studies.[13,31,32] The deformation features of the specimen corresponding to points a, b, and c marked in the figure are shown in Figure 4(a–c), respectively. The SiC_{HS} seem largely intact in Figure 4(a), which corresponds to the end of elastic region. This point refers to the onset of particle failure, where only some weak particles start to show cracking. The weak particles may include thin-walled or defective particles. The particle fracture corresponds to the drop in stress. On further compression, crushing and compaction of particles takes place and appears as the plateau region marked by point b in Figure 3. Fracture of particles transfers the load to the surrounding matrix material. The failure of matrix appears as the shear bands in the specimen in Figure 4(b). Crushed and compacted particles along the shear band can also be observed in this figure. At the specimen failure, the cracks propagate through the entire thickness of the specimen and constitute final failure as observed in Figure 4(c). The trends of the stress–strain graph and the failure features are found to be similar for SF1 and SF2 syntactic foams.

The stress–strain graphs are used to calculate the modulus, peak strength, and plateau strength of syntactic foams presented in Table II. The higher density particles provide higher peak strength but lower plateau strength and modulus. Studies on GMB-filled syntactic foams have consistently shown higher strength and modulus for syntactic foams containing higher density particles. However, a similar trend is not visible in the present case because the particle walls are porous and the some of the pores present in the walls may be larger than the critical size to initiate failure at low stress level. It is also noted that the standard deviation in the plateau stress and compressive modulus is within $\pm 11\%$. The specific compressive strength (normalized with respect to the corresponding syntactic foam density) of SF1 and SF2 syntactic foams are 33.4 $kPa/kg/m^3$ and 38.8 $kPa/kg/m^3$, respectively. The specific compressive modulus of SF1 and SF2 syntactic foams are 0.8 $MPa/kg/m^3$ and 0.6 $MPa/kg/m^3$, respectively. These values of the SiC_{HS}/VE syntactic foams are lower in comparison to GMB/VE syntactic foams reported in a previous study.[13] These lower compressive properties can be ascribed to the micro porous voids found in the walls of the particles, as seen in Figure 2, which can lead to low effective mechanical properties and possible early failure of some particles.

Coefficient of Thermal Expansion

Thermal strain–temperature graphs are used to calculate the CTE of syntactic foams. The measured CTE of SF1 and SF2 are found to be 26.7 ± 2.7 and 15.9 ± 1.8 $\times 10^{-6}$/°C, respectively. The thicker walled SiC_{HS} resulted in lower CTE of syntactic foams. The CTE values of SiC_{HS}/VE are compared with those

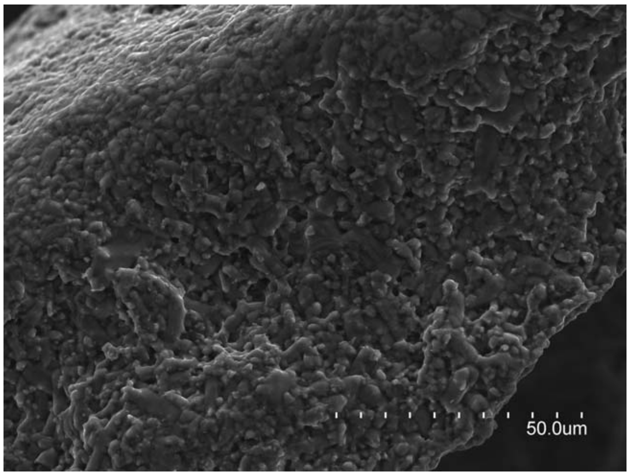

Figure 2. Scanning electron micrograph of SiC_{HS} showing micro porous voids present in the wall of the sphere.

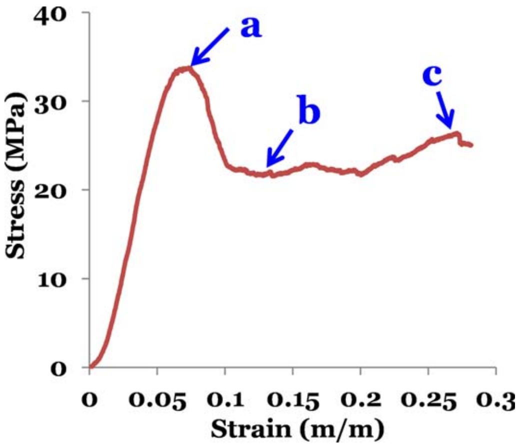

Figure 3. Quasi-static compressive stress–strain curve for SF1 type SiC_{HS}/VE syntactic foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

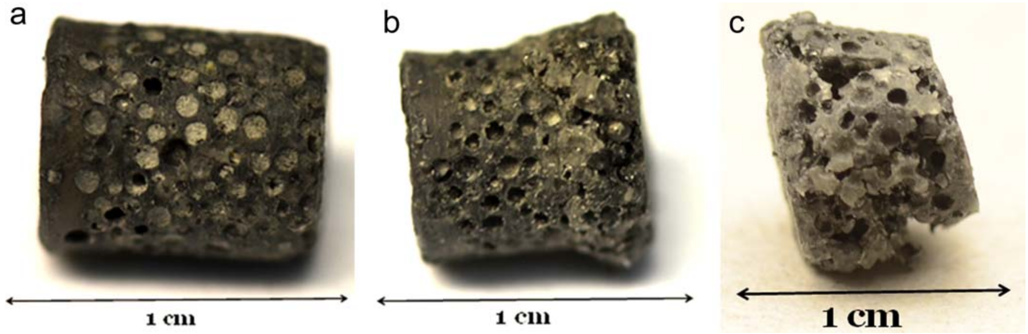

Figure 4. Failure feature of the SF1 type SiC_{HS}/VE syntactic foams subjected to quasi-static compression testing. The images (a), (b), and (c) correspond to markings a, b, and c shown in Figure 3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

obtained for GMB/VE syntactic foams in a previous study in Figure 5.[8] The GMB/VE syntactic foams contain 60 vol % of three different types of GMBs having true particle densities of 220, 320, and 460 kg/m^3. The CTE values are plotted with respect to the syntactic foam density in this figure. It is observed that the CTE of SiC_{HS}/VE is lower than the CTE values obtained for GMB/VE syntactic foams. In the case of GMB/VE syntactic foam a maximum decrease of 60.4% in CTE was observed in comparison to the neat resin. While in the case of SiC_{HS}/VE syntactic foam a decrease of 65.1% and 79.3% is observed for the SF1 and SF2 syntactic foams, respectively. The low CTE syntactic foams are useful in applications such as space mirrors and electronic packaging.[3]

Evaluation of SiC_{HS} Characteristics

To evaluate the porosity in the wall of the S1 and S2 SiC_{HS}, the density of the hollow particles was calculated from the experimentally measured density of syntactic foams using the rule of mixture. It is assumed that there is no additional porosity present in the matrix. The true particle densities evaluated by this method are 656 and 973 kg/m^3, for S1 and S2 SiC_{HS}, respectively. Using these true particle density values in Equation (3), the density of the porous SiC material is obtained as 2668 and 2408 kg/m^3 for S1 and S2 particles respectively, which is lower than the density of SiC material (3200 kg/m^3). The density difference shows that the S1 and S2 SiC_{HS} contain 16.6% and 24.8% porosity, respectively.

Theoretical models are available in recent literature to estimate the CTE of syntactic foams with respect to the volume fraction (Φ) and radius ratio (η) of hollow particles. The experimentally measured CTE is used in these models to estimate the properties of the porous SiC material of SiC_{HS}. The variation of CTE (α) of syntactic foams based on Φ and η of the filler is given by the Turner's model modified for application to syntactic foams[8]

$$\alpha=\frac{\alpha_m\Phi_m E_m\left[(1-2v_{\mathrm{SiC}})+\left(\frac{1+v_{\mathrm{SiC}}}{2}\right)\eta^3\right]+\alpha_{\mathrm{SiC}}\,\Phi_b E_{\mathrm{SiC}}\,(1-\eta^3)(1-2v_m)}{\Phi_m E_m\left[(1-2v_{\mathrm{SiC}})+\left(\frac{1+v_{\mathrm{SiC}}}{2}\right)\eta^3\right]+\Phi_b E_{\mathrm{SiC}}\,(1-\eta^3)(1-2v_m)} \tag{4}$$

where the subscript m and b represent matrix and the hollow filler material. The matrix modulus and Poisson ratio are taken as 2.82 GPa[13] and 0.35,[33] respectively. The Poisson ratio of SiC was taken as 0.14. The CTE of SiC material is taken as 4×10^{-6}/°C.[34] Using eq. (4), the modulus of hollow sphere material (porous SiC) is estimated to be 18 and 20 GPa for S1 and S2 particles, respectively. These values are significantly lower than the modulus of SiC, which is around 420 GPa, because of porosity that is present in the walls of hollow particles. This porosity adversely affects the mechanical properties but helps in achieving low thermal expansion of the syntactic foams. Innovative use of such particles can help in developing syntactic foams suitable for new applications where traditional compositions are not applicable.

Table II. Compressive Properties of the SiC_{HS}/Vinyl Ester Syntactic Foams

Specimen type	Peak strength (MPa)	Plateau strength (MPa)	Compressive modulus (MPa)
SF1	29.6 ± 4.2	20.8 ± 2.2	725.0 ± 76.0
SF2	42.0 ± 4.7	18.5 ± 1.1	692.0 ± 47.0

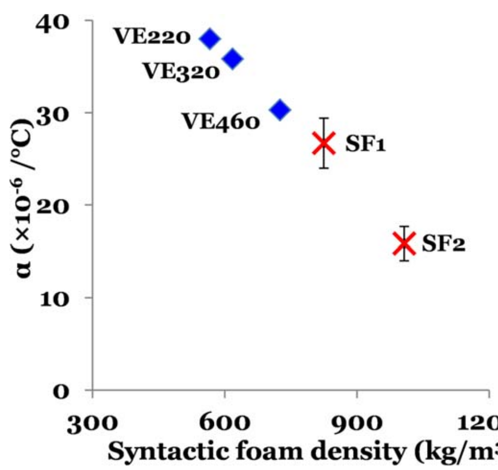

Figure 5. Variation of CTE of GMB (VE220, VE320, and VE460) and SiC (SF1 and SF2) hollow particle-filled syntactic foams with respect to the syntactic foam density. All syntactic foams contain 60 vol % hollow spheres. The CTE data for the GMB/VE syntactic foams are obtained from Ref. 8. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

SiC_{HS}/VE syntactic foams are studied for compressive properties and coefficient of thermal expansion (CTE). Two types of SiC_{HS} are used in 60 vol % quantities to fabricate two types of syntactic foams. Direct measurement of properties of SiC_{HS} is difficult because their walls are porous. Hence, the measured CTE and density values of syntactic foams are used to estimate the properties of SiC_{HS}. The ratios of inner to the outer radius of the two types of particles were measured as 0.91 and 0.84, respectively. The compressive modulus of the two syntactic foams was measured as 725 and 692 MPa, respectively. The higher density syntactic foams showed lower modulus because of the porous nature of the particles. The specific compressive strength and modulus of SiC_{HS}/VE syntactic foams was observed to be lower in comparison to GMB/VE syntactic foams. The CTE of SiC_{HS}-VE was observed to be lower than all composition of GMB/VE, indicating better thermal stability for the SiC_{HS} syntactic foams at high temperatures. A decrease of 65.1% and 79.3% in the CTE is observed for the two types of syntactic foams, in comparison to the neat resin. The modulus of the hollow sphere material predicted using the modified Turner's model were observed to be significantly lower than the Young's modulus of bulk SiC and due to the presence of porosity in the particle walls. The estimated porosities in the walls of the two types of SiC_{HS} are 16.6% and 24.8%.

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