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Hollow glass spheres in sheet molding compound composites: Limitations and potential

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Abstract

Sheet molding compounds (SMC) are commonly used in automotive applications as they lead to increased fuel efficiency of vehicles due to their high strength to weight ratios. This study focuses on understanding the effect of replacing calcium carbonate ($CaCO_3$) with hollow glass spheres (HGS) in an unsaturated polyester resin matrix SMC composite with the ultimate goal to further reduce density without compromising performance. The resulting glass fiber (GF)-reinforced syntactic foam laminate composites with GF content ranging from 10 to 15 vol% have densities of 1.2 and 1 g/cm^3, respectively. This is significantly lower than the industry standard SMC density of 1.9 g/cm^3. The HGS parameters of interest are primarily HGS type (S28HS and S32HS), loading level (33–44 vol%), and surface functionalization (methacrylsilane). The syntactic foam composites were characterized in terms of tensile, flexural, and impact properties, and their properties were compared to those of standard density SMC. As expected, the flexural, tensile, and impact properties were compromised with a decrease of density. However, they were higher than the corresponding properties of low- and ultra-low density composites reported in the literature, as we were able to add higher GF content in these low-density SMC formulations. It was also concluded that methacrylsilanized surface treated HGS showed promise in maintaining the mechanical properties, especially at high sphere loadings. The impact energy of the low-density formulations was relatively unaffected by HGS type or loading.

KEYWORDS

composites, fillers, mechanical properties, polyesters

1 | INTRODUCTION

Sheet molding compounds (SMC) consist of sheets of premixed glass fibers (GFs), mainly chopped, and thermoset resins that, once stacked in a mold and hot-pressed, yield composites with high strength to weight ratios.[1] SMC technology was first brought to the United States in 1965, and it is now the third most utilized polymer composite manufacturing process, after only injection molding and hand lay-up.[1] SMC autobody parts are superior to comparable steel parts because the SMC enables more complex geometries, higher strength-to-weight ratio, improved corrosion resistance, and lower tooling cost.[1] Epoxy, vinyl ester, and phenolic resins can all be used as polymer resins in an SMC. In this work, unsaturated polyester resin (UPR) was used due to its pervasiveness

in the automotive industry.[2,3] Furthermore, this low-cost matrix has a short cure time and good mechanical properties.[1] Fillers in the range of 33%–43% of the total volume, are a major portion of SMC Class-A formulations.[4] Typical fillers in polymer resin pastes are talc, mica, alumina, kaolin clays, and silica.[1,4] Inexpensive fillers, such as calcium carbonate ($CaCO_3$) which has a density of 2.71 g/cm,[3] are used to add volume to the resin paste while minimizing the cost of the final product.[1] The density of SMC composites can be reduced by replacing high-density fillers with lightweight hollow glass spheres (HGS).

Material systems with HGS are referred to as "syntactic foams." These are a class of closed-cell foams, in which the gaseous phase is completely enclosed by the glass sphere.[5] Prior syntactic foams were made from perlite spheres, phenolic spheres, and aluminum oxide ceramics.[5] They have also been produced using fly ash cenospheres, a by-product of coal production. However, the inherent material flaws in these cenospheres make them inferior to HGS created specifically for this purpose.[3,6] Syntactic foam composites are stiffer, have higher modulus and strength, and create a more robust system when compared to open-cell foams, which have an interconnected pore structure.[7,8] When reinforcements are incorporated, such as discontinuous, chopped GF, then the system is called a fiber reinforced syntactic foam, or "hybrid composite".[9,10] HGS do not behave as reinforcements in two- or three-phase syntactic foams. As a result, when creating composite formulations, it is necessary to control the GF volume fraction to maintain properties to the greatest degree possible.[4]

Most published research on syntactic foams focused on those without fiber reinforcements.[5,11–16] Studies reported on hybrid composites with densities below 1.0 g/cm^3, but these were achieved with GF loadings less than 4.51 vol%[9,10,17–22] which means the composites have low mechanical properties. Ferreira, et al. examined the flexural stiffness of nonreinforced as well as glass and carbon fiber reinforced syntactic foams. When GF between 0 and 1.2 vol% were added to the syntactic foam samples, there was a decrease in flexural stiffness as the HGS content increased from 10 to 43 vol%. As expected, the addition of such a small amount of GF does not greatly increase the properties at 43 vol% HGS.[9] Oldenbo, et al. investigated HGS/GF/UPR SMC systems with 18–22 vol% GF, a relatively high GF content which resulted in conservative decrease of density to ~1.57 g/cm. Additionally, the HGS used were not surface functionalized.[17] Industry has also incorporated HGS into commercial SMC products creating low-density composites down to 1.2 g/cm^3.[23,24]

This study is motivated by the need for more fuel-efficient vehicles that is driven by consumer demand as well as federal policies. To comply with the continuously decreasing Environmental Protection Agency (EPA) Greenhouse Gas (GHG) emissions standards,[25] automotive companies are looking for novel techniques to decrease the mass of their vehicles. One possible path forward is the creation of an SMC resin paste that utilizes HGS, with densities of 0.28 and 0.32 g/cm^3. These would act as a lightweight replacement for heavy fillers, in particular $CaCO_3$, which has a density of 2.71 g/cm^3. This study bridges the existing gaps by investigating the potential of HGS in reducing the density of SMC composites as low as 1.0 g/cm^3 while at the same time maintaining GF content between 10 and 15 vol% necessary for the preservation of the mechanical properties. In addition, the presented research explores the potential of using surface modified HGS to reduce the density while maintaining the properties. It is noted that the effect of HGS surface modification on the properties of ultra-low density fiber-reinforced syntactic foams has not been investigated before. The HGS parameters of interest are diameter (μm), density (g/cm^3), loading (vol%), and surface functionalization.

2 | MATERIALS AND PROCEDURES

2.1 | Materials

A two-part UPR system of a 1:1 vinyl ester: Unsaturated ester blend (Arotran 774) and a low profile additive polymer blend (Arotran 775) was supplied by the Ashland Inc. This resin system was specifically designed for lightweight systems and has a density of 1.07 and 1.05 g/cm^3 for the two resin components, respectively. The calcium carbonate ($CaCO_3$) filler used, Hubercarb W4, was supplied by the Huber Engineered Materials. BYK Additives provided the wetting agent, BYK 9010. The initiator, Tert-butyl peroxybenzoate (TBPB) was purchased from the Sigma-Aldrich, the magnesium oxide thickener, AM9033, was obtained from the Chromaflow Technologies and the Zinc Stearate, used as mold release agent, was produced by Acros Organics. The GF rovings, Advantex P204, with a tensile modulus of ~80 GPa, were provided courtesy of Owens Corning. The sizing of these GF was designed to be coupled with UPR used in this work. Three types of 3M HGS were utilized: S28HS, S32HS, and S32HS-MAS-1. These are referred to in this manuscript as 28, 32, and 32-MS, respectively, and their corresponding physical properties are given in Table 1.

TABLE 1 Hollow glass spheres (HGS) nomenclature. All three types of HGS had a radius ratio of 0.96 and wall thickness of 0.58 μm

Name	Density (g/cm^3)	Outer diameter (μm)	Surface functionalization
28	0.28	30	No
32	0.32	25	No
32-MS	0.32	25	Yes

TABLE 2 Sample nomenclature and their corresponding resin paste formulation. Data are given as mean +/− one SE. Theoretical densities were calculated using the measured glass fiber vol%

Sample name/ formulation	Resin paste density (g/cm^3)	Plate density (g/cm^3)	Theoretical plate density (g/cm^3)	HGS vol%	Target $CaCO_3$ vol%	Measured GF vol%
S	1.75	1.9 ± 0.00	1.94	—	35.76	21.8 ± 0.17 (22)
L28	0.86	1.1 ± 0.01	1.08	33	4.50	12.5 ± 0.33 (13)
L32	0.86	1.1 ± 0.01	1.07	35	4.50	11.9 ± 0.66 (12)
L32-MS	0.86	1.1 ± 0.02	1.12	34	4.50	14.8 ± 0.98 (15)
U28	0.69	0.9 ± 0.00	0.94	43	0	12.8 ± 0.47 (13)
U32	0.70	0.9 ± 0.01	0.89	44	0	10.1 ± 0.15 (10)
U32-MS	0.70	1.0 ± 0.01	0.98	42	0	14.6 ± 0.71 (15)

For HGS 28 and 32, they have differing densities (0.28 and 0.32 g/cm^3, respectively) and diameters (30 and 25 μm, respectively), but have the same calculated radius ratio (0.96) and similar wall thickness (0.58 μm).[5] HGS 28 and 32 are not surface treated. 32-MS is the same HGS as 32 but with a methacrylsilane (3-(trimethoxysilyl)propyl methacrylate) surface functionalization. Assessing the effect of HGS type with two simultaneously changing parameters (density and diameter) on composite mechanical properties was not possible within the scope of this research. As a result, HGS type was considered a secondary mechanism compared to the differences in either volume fraction GF, volume fraction HGS, or composite density.

Resin paste formulations, seen in Table 2, were compounded with various combinations of glass sphere types and loadings. The letters "S", "L", and "U" are used to represent SMC composites with standard density of 1.94 g/cm^3, low-density of 1.2 g/cm^3, and ultra-low density of 1.0 g/cm^3, respectively. The formulation dictates the amount of HGS needed to reach the target density. It is evident in Table 2 that $CaCO_3$ content decreases and HGS content increases as composite density declines. The standard density formulation has no HGS and only $CaCO_3$ while ultra-low density formulations have only HGS and no $CaCO_3$. In all formulations investigated, the resin was kept at approximately 45 vol% to enable sufficient wetting of all solid fillers. To provide a more direct comparison between samples, GF vol% was attempted to be held constant at approximately 20 vol%, thus any effect of GF on the mechanical properties would be normalized in the data. However, the experimentally determined true GF content proved that this target vol% was not always achieved. Small changes in polymer resin viscosity, the viscosity of the paste when HGS are added, and/or the SMC machine belt speed-among other factors-can result in significant shifts in GF vol%. In addition, as reported in Table 2, only the standard, S, and the ultradensity, U32, formulations have significantly different GF content compared to each other and compared to the other formulations, that is, ~22 vol% for the S formulation and 10 vol% for U32. In all other formulations, the GF content is in average between 12 and 15 vol% and considering the overlap of the SD, their difference is not statistically significant. Furthermore, the calibration of the SMC pilot line was challenging considering that these are complex systems and only a small amount of material for each formulation was available. As a result, the GF content in samples from this study varied from 10 to 22 vol%, with all but the S and U32 formulations having 12–15 vol% and the resin content varied from 40 to 50 vol%. The differences, although very small, in actual GF loading may contribute to discrepancies in mechanical properties between formulations. Consequently, uncertainty must be considered in the interpretation of the results, so comparisons were primarily made between formulations with equivalent or comparable GF vol%.

2.2 | Composite processing

An overview of the SMC composite manufacturing process is shown in Figure 1. Initially, the resin paste was compounded using a Cowles blade attached to an IKA Eurostar 20 mixer. The mixing blade was positioned equally from the sides and bottom of the container to create "rolling donuts" for quality dispersion of the materials. First, Arotran 774, Arotran 775, TBPB, and BYK 9010 were combined. Then, $CaCO_3$ and zinc stearate were gradually added at a speed of 2000 rpm. This mixing velocity was held for 3 min. Next, for the mid-, low-, and ultra-low density formulations, the predetermined amounts of HGS were slowly incorporated at 1200 rpm to prevent their breakage. The mixer was kept at 1200 rpm until the resin paste reached 35 C or for 10 min. Finally, AM9033 was added and mixed for 3 min at either 2000 rpm for standard density or 1200 rpm for all other formulations.

Upon completion of the compounding, the resin paste was split equally between the upper and lower reservoirs of the SMC line, built by Finn & Fram, Inc. One carrier film moves underneath each of the reservoirs carrying the resin paste under doctor blades at a set height. This deposits a resin layer of the desired thickness on each carrier film. A cutting roller chops the GF rovings into 2.54 cm fibers and continuously drops them onto the lower carrier film in a random orientation over a 25.4 cm width. The lower and upper carrier films meet, forming a sandwich of the two layers and go through a compression zone, which ensures better wetting of the GF rovings and other solids by the resin. The resulting material collected at the end of the line was in the form of a 30 cm wide sheet. These uncured SMC sheets were folded and stored in a nylon bag and wrapped in aluminum foil to prevent the volatilization of styrene, which would decrease the degree of crosslinking and mechanical properties of the final composite. The SMC sheets were kept at room temperature to mature for 7 days to improve handling and increase viscosity to required levels for hot-pressing.

For SMC composite processing, square plies with edge lengths approximately 20.5 cm were cut from the uncured SMC sheet. The carrier film was then peeled off and three or four plies were then stacked while flipping each alternating layer over the y-axis to minimize the effect of any off-axis bias along the SMC direction. Thus, each ply had randomly oriented fibers in-plane and the 2-D plies were parallel in the transverse direction. The stack of plies, or charge, was placed in a 28 cm × 28 cm aluminum mold that was coated with zinc stearate and preheated. The charge was then cured in a Wabash 50 ton hot press, model v50-1818-2tmx, under approximately 44.7 metric tons of force (5.7 MPa of pressure) at 146 C for 2 min. The final composite plate was removed from the mold and cut into mechanical testing coupons with their long axis along the SMC direction with a waterjet and then stored at room temperature until testing.

2.3 | Characterization techniques

The tensile, flexural, and impact properties of the composites were determined as a function of the HGS characteristics. ASTM D638 Standard Type I was followed to obtain tensile properties on an Instron 5982 with a 100 kN load cell. The preload for each test was 440 N/min up to 40 N. Flexural data were acquired according to ASTM D790-17 on an Instron 33R 4466 with a 500 N load cell. The sample dimensions were 117 mm × 20 mm with 5–6 mm thickness and the testing was performed at room temperature with a three-point bending fixture with a span length of 85 mm at a test rate of 4.54 mm/min. Impact properties were determined according to ASTM D4812-11 with an Charpy Instron Pendulum Impact Tester. Impact specimens of 5–6 mm thickness were cut with dimensions of 63.5 mm × 12.7 mm and tested with a 30 kg anvil at a latch angle of 136 at room temperature. A minimum of four coupons were tested for every composite formulation in every testing.

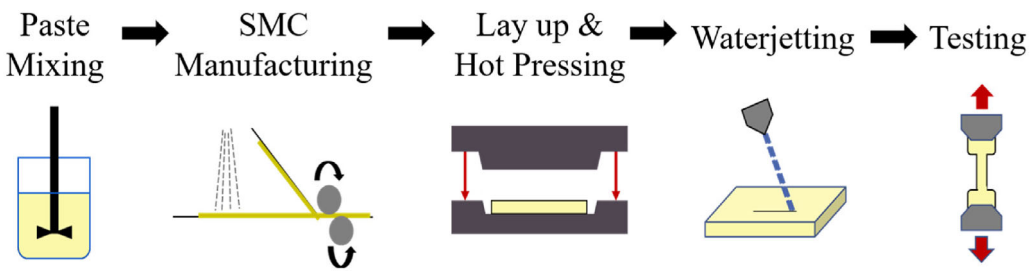

FIGURE 1 Key steps of sheet molding compounds (SMC) unsaturated polyester resin-glass fiber-hollow glass spheres composite processing [Color figure can be viewed at wileyonlinelibrary.com]

Fracture surface imaging samples were prepared by freeze fracturing tested tensile samples. As mechanical testing leads to an incomplete failure, (ie, the two ends of the specimen are still attached via exposed fibers), samples were frozen in liquid nitrogen and pulled apart manually. The specimens were then sectioned, mounted on scanning electron microscope (SEM) stubs, and sputter coated with conductive material. Samples were imaged with a Phenom ProX SEM at 10 kV.

2.3.1 | Determination of density and GF content

The density of the SMC composite plates was determined by water displacement according to ASTM D792-13. Ultra-low density formulation composites could not be submerged, so these sample densities were calculated using the mass and average measured dimensions. The density values were averaged over three samples for every formulation. The GF volume fraction, V_f, was found from the density using Equation (1), where ρ_c is the composite matrix, ρ_m is the matrix density, and ρ_f is the fiber density.

$$Vf = \frac{\rho c - \rho m}{\rho f - \rho m} \quad (1)$$

For all formulations, the maximum pressure possible, 5.7 MPa, was utilized. Representative composite samples were investigated using optical microscopy and SEM. Figure 2(A) shows adequate impregnation of the resin and HGS into the GF rovings as well as minimal void content. The hollow, fractured HGS (Figure 2(A)) also indicate that the compression molding pressure did not break the HGS, rather they were broken during water-jetting of the test coupons. Had the HGS fractured during compression molding, the broken spheres would have been filled with cured resin. As a result, it was assumed when calculating density that void content was constant and negligible throughout all samples. This assumption is shown to be correct by the comparable theoretical and measured plate densities in Table 2. Furthermore, due to the high GF vol%, the test coupons did not experience

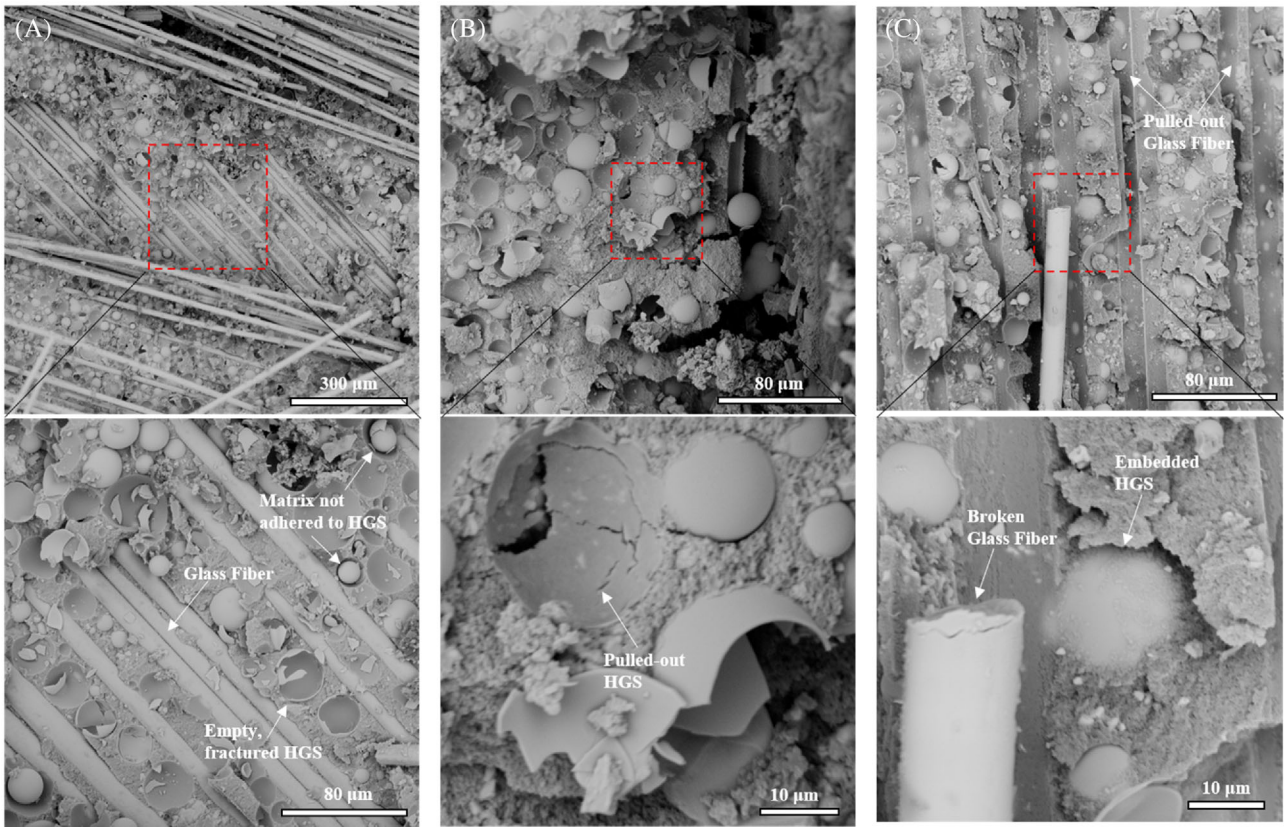

FIGURE 2 Scanning electron microscopy images of tensile fracture surface from (A) L28, showing the matrix minimally adhered to the spheres as well as hollow, fractured HGS (B) Images of L32 with spheres pulled out at fracture surface (C) L32MS fracture surface with fiber pull-out and minimal fiber breakage [Color figure can be viewed at wileyonlinelibrary.com]

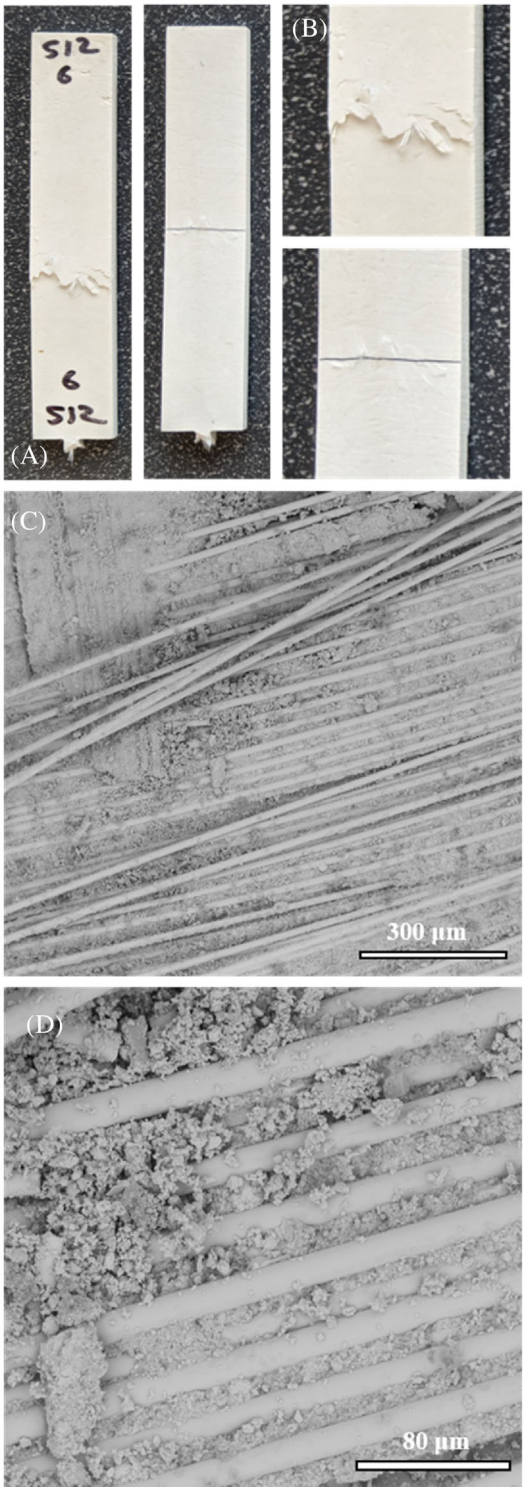

FIGURE 3 (A) The front and back of flexural samples after fracture; (B) Close-up of the fractured flexural samples; (C) Scanning electron microscopy (SEM) images of tensile fracture surface approximately 1/3 into the thickness of the composite system (D) Zoomed-in SEM image shows clean fiber surfaces indicating debonding due to a weak interface [Color figure can be viewed at wileyonlinelibrary.com]

complete fracture. The fibers partially pulled out of the matrix but maintained the connection between the two halves of the samples (Figure 3(A,B)). Figure 3(C,D) show representative fracture surfaces of standard density samples. The clean fiber surfaces and debonding indicate that the interface between the GF and the matrix was weak. This might explain why Figure 2(C) shows that fiber pull-out was more prevalent than fiber breakage at the fracture surface.

3 | RESULTS AND DISCUSSION: EFFECT OF HGS ON MECHANICAL PROPERTIES

The goal of this study was to explore the effect of HGS type, surface functionalization, and quantity (vol%) on the density and mechanical properties of hybrid composites. SMC composites with HGS and GF were compared in terms of their tensile, flexural, and impact properties to those of the typical standard density formulation (Table 3). Each, or a combination, of these HGS variables could contribute to the mechanical behavior of these complex reinforced syntactic foams although the GF is the main reinforcing phase. Ideally, to investigate the effect of the HGS characteristics, the GF content in terms of vol% should be the same in all formulations. However, due to the inherent randomness in the SMC process and the random error introduced during the determination of the GF content, there was a slight variation in the GF volume fraction which is accounted for in the discussion and interpretation of the results. In all plots, the experimentally determined GF volume content for each formulation studied is listed next to each data point. The dotted lines connecting data points indicate general trendlines not interpolation of the data. Advanced statistical analysis was not conducted on the presented data because a full- or fractional-factorial could not be completed.

TABLE 3 Standard density sheet molding compounds composite mechanical properties produced in this study with 21.84 vol% glass fiber

Property	Value
Tensile strength (MPa)	69.8 ± 2.81
Tensile modulus (GPa)	8.2 ± 0.33
Flexural strength (MPa)	114.0 ± 5.05
Flexural modulus (GPa)	7.9 ± 0.37
Impact energy (J/cm^2)	9.9 ± 0.73

3.1 | Tensile properties

The tensile strength and modulus as a function of HGS type and loading and of the GF content are shown in Figure 4(A,B), respectively. There was a drop in the tensile strength between both formulation pairs L28 and U28, and L32 and U32 that were larger than their respective SE values. Since the GF vol% was similar within these pairs, the decrease in strength was considered to be attributed to the larger volume content of HGS in the composite. Although all formulations aimed to have approximately 45 vol% resin, this may not be sufficient for complete wetting of the higher HGS content in the ultra-low density formulation. Among the low-density formulations, that is, HGS content around 34 vol%, there appears to be no difference in tensile strength due to the varying characteristics of the HGS. The effect of surface functionalization on the tensile strength may not be evident with the small HGS volume fractions found in low-density formulations. However, among the ultra-low density formulations, that is, HGS content between 42 and 44 vol%, the surface functionalized HGS 32-HS maintained the tensile strength to the greatest degree. The surface functionalization may have enhanced interfacial interactions between the polymer and the HGS filler, enabling better wetting by the polymer resin, as with the embedded HGS in Figure 2(C). This could result in stronger and/or defect free interfaces that subsequently minimize stress concentration points, which can lead to inefficient load transfer and nucleating of a crack. As reported in the literature, tensile fracture often occurs due to the debonding of the particle-matrix interface. It follows that a stronger interfacial bond due to the silane surface treatment would increase tensile strength properties.[12]

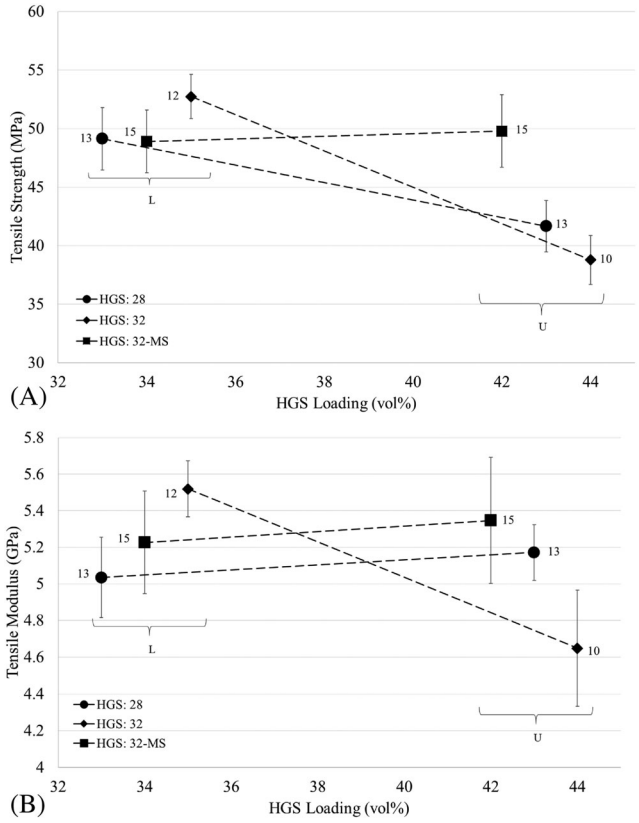

FIGURE 4 (A) Tensile strength (MPa) versus hollow glass spheres (HGS) loading (vol%) of three sphere types; (B) Tensile modulus (GPa) versus HGS loading (vol%) of three sphere types. Glass fiber vol% is listed next to each data point. Data are given as mean +/− one SE. Standard density tensile strength and modulus are 69.8 ± 2.81 MPa and 7.9 ± 0.37 GPa, respectively

When comparing the tensile moduli of these six formulations (Figure 4(B)), the low-density formulation L32 had a comparable value, that is, within experimental error, to the low-density L32-MS which contained the surface modified HGS and essentially equivalent GF content. Despite this, HGS 32-MS maintained the composite's tensile modulus at a higher HGS loading, in the case of ultra-low density composites. This might be explained by the mechanisms seen in Figure 2. In Figure 2(A), the matrix has no adhesion with some nonfunctionalized HGS, and in Figure 2(B), pulled-out HGS are visible at the fracture surface. However, regarding L32-MS, the spheres are obviously embedded into the matrix and coated with a layer of resin (Figure 2(C)). These mechanisms could be amplified at higher HGS volume fractions, leading to the greater modulus of U32-MS. This trend is also in agreement with what has been reported in the literature for polypropylene syntactic foams where the tensile modulus increases with the content of the silane treated HGS.[26]

In case of HGS 28, the tensile modulus remained constant as the HGS vol% increased from the low- to the ultra-low density formulations. For HGS 32 the modulus decreased with increasing HGS vol%, however, the ~2 vol % lower GF content may have partially contributed to this decrease. Finally, the modulus remained constant in case of surface modified HGS 32-MS as the HGS content increased from 35 to 44 vol%. There are contradicting results reported in the literature of syntactic foams, with some studies reporting that the modulus increases and others that it decreases with increasing HGS content.[15,27,28] The response is also dependent upon the HGS properties including strength and radius ratio. If the HGS replace a stiff matrix polymer, the modulus will decrease. Conversely, if HGS replace a relatively compliant polymer or filler, the syntactic foam modulus will increase.[27] In this case, HGS replaced $CaCO_3$, which may have led to compromised properties. Unfortunately, without knowing the moduli of the HGS or $CaCO_3$, no definite explanation can be provided here.

The tensile strength of the U32 formulation was found to be 26.4% lower than the strength of L32, while the tensile strength of U32-MS was actually found to be 1.8% higher than L32-MS. Likewise, the tensile moduli of U32 compared to L32 and U32-MS compared to L32-MS were found to be 15.6% lower and 2.3% higher, respectively. This is an indication that the surface functionalization of HGS is indeed contributing to the decrease of the density while compromising the properties to a lesser degree.

As expected, almost all reinforced syntactic foam samples had higher specific properties (Table 4) than the standard density composite samples. Considering the specific tensile strength, there is no change in properties between L28 and U28, but U32 is lower than L32. The specific strength of U32-MS is greater than that of L32-MS with equivalent GF loading, indicating that higher loadings of functionalized HGS improves the specific tensile strength. For specific tensile modulus, ultra-low density samples are either comparable to or slightly higher than the low-density samples.

3.2 | Flexural properties

The effects of HGS type and loading on the flexural strength and modulus are shown in Figure 5(A,B), respectively. All three low-density formulations exhibited the same flexural strength, within experimental error, no matter what type of HGS was used and with a GF content variation between 12 and 15 vol%. In the case of the ultra-low density formulations, those with HGS 28 exhibited a drop in the flexural strength. No real effect of the surface modification was observed based on the samples' SE bars. Formulations with HGS 32 and HGS 32-MS exhibited the same flexural strength for both low- and ultra-low density formulations. Comparing the L32 and L32-MS formulations, at low HGS content, it is expected that the strength in the L32-MS will be higher due to the surface modification of the HGS and the

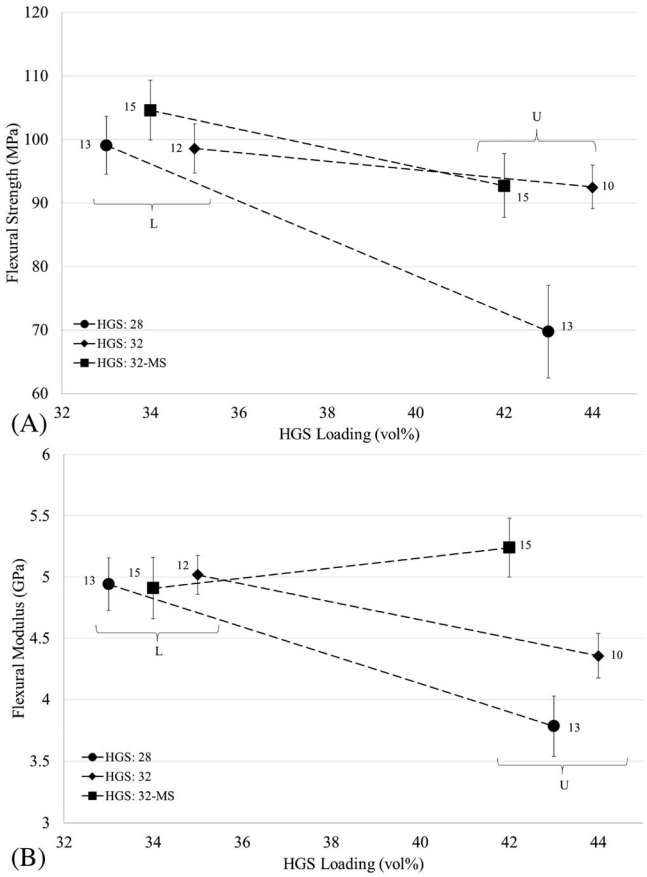

FIGURE 5 (A) Flexural strength (MPa) versus hollow glass spheres (HGS) loading (vol%) of three sphere types; (B) Flexural modulus (GPa) versus HGS loading (vol%) of three sphere types. Glass fiber content is listed next to each data point. Data are given as mean +/− one SE. Standard density flexural strength and modulus are 114.0 ± 5.05 MPa and 8.2 ± 0.33 GPa, respectively

TABLE 4 Specific properties of standard, low-, and ultra-low density formulations. Data are given as +/− one SE, calculated using propagation of uncertainty

Sample name/ formulation	Specific tensile strength (KNm/kg)	Specific tensile modulus (MNm/kg)	Specific flexural strength (KNm/kg)	Specific flexural modulus (MNm/kg)	Specific impact energy (Nm^2/kg)
S	36.0 ± 1.5	4.2 ± 0.2	58.8 ± 2.6	4.1 ± 0.2	51.0 ± 3.8
L28	45.5 ± 2.5	4.7 ± 0.20	91.8 ± 4.2	4.6 ± 0.2	61.1 ± 2.4
L32	49.3 ± 1.8	5.2 ± 0.1	92.2 ± 3.6	4.7 ± 0.1	52.9 ± 1.4
L32-MS	43.7 ± 2.4	4.7 ± 0.3	93.4 ± 4.2	4.4 ± 0.2	64.1 ± 8.3
U28	44.3 ± 2.3	5.5 ± 0.2	74.2 ± 7.8	4.0 ± 0.3	73.6 ± 5.1
U32	43.6 ± 2.3	5.2 ± 0.4	104.0 ± 3.9	4.9 ± 0.2	64.9 ± 10.4
U32-MS	50.8 ± 3.2	5.5 ± 0.4	94.6 ± 5.1	5.3 ± 0.2	72.7 ± 3.9

relatively higher GF content (15 vs. 12 vol%). However, this is not the case. The L32 with smaller GF content and nonmodified HGS exhibits the same flexural strength. This indicates that the HGS type may have stronger effect on flexural strength than the HGS surface modification for the surface modification and types of HGS considered in this study. This does not align with expectations and what has been reported in the literature regarding surface modification increasing flexural strength as it facilitates load transfer along an HGS-resin interface.[11,29] It may also prevent crack initiation, which is most likely to occur on the tensile side of the composite coupons during the three-point bending, and crack propagation.[29,30] Additionally, it was expected that functionalization may have allowed for better wetting of HGS and a more perfect interface.

Similarly, there was no difference in the flexural modulus of the low-density formulations. However, the ultra-low density formulations had greater disparity. Both U28 and U32 formulations exhibited a drop in flexural modulus compared to their low-density counterparts. It is also observed that the modulus drop was larger in the case of the U28 formulation despite the fact that the GF content is slightly higher than that in the U32 formulation. Although the U28 and U32 resin paste densities were similar, there is a 20% difference in the density of the two HGS which are 0.28 and 0.32 g/cm^3, respectively. Thus, HGS 28 is lighter than HGS 32 so they tend to float during high-shear mixing and may not be as homogeneously dispersed in the resin paste. These differences are amplified at higher volume content of HGS and could contribute to a more dramatic drop of the modulus in case of HGS 28. The reduction of flexural modulus with the addition of HGS 32 has also been reported in[11] where HGS with a density of 0.32 g/cm^3 replaced vinyl ester, in unreinforced syntactic foams. In the present study, the effect of the HGS surface functionalization is positive, in which the flexural modulus remains constant when going from low to ultra-low density formulations. This is a trend that is in agreement with results reported in the literature. For example, Yalcin, et al. has shown that UPR composites containing HGS functionalized with methacryloxypropyl trimethoxysilane had 5% greater flexural modulus than those composites containing unmodified HGS.[4] In this study, it was found that methacrylsilanated HGS (e.g., 32-MS) at low-density loadings had a 2.2% drop but at ultra-low density loadings it had a 20.2% improvement in flexural modulus over identical nontreated HGS. This clearly indicates that surface functionalization may have a greater influence on flexural modulus when there is a larger volume fraction of HGS in the formulation.

The greatest drop in flexural properties seen with HGS 28 at high loadings both in comparison with the low and other ultra-low density formulations and with the standard density formulation. The flexural strength and modulus of U28 was 38.8% and 52.2%, respectively, lower than the corresponding properties of the standard formulation (Table 3).

The specific flexural strength and modulus are also given in Table 4. The specific flexural strength of all low-density samples is comparable. However, at higher HGS loadings, all three samples behave differently—U28 is lower, U32 is higher, and U32-MS is the same—than their corresponding low-density formulations. Despite having the highest density of all ultra-low density samples, at 1.0 g/cm^3, U32-MS shows the greatest increase in specific flexural modulus.

3.3 | Impact properties

Impact energy is an indication of the ability of the composite to absorb energy at a high rate before fracture.[29] As shown in Figure 6, and in comparison with Table 3, the impact energy reduced upon addition of HGS, but remained constant for low and ultra-low density formulations, that is, it had no dependence on the HGS content. Overall, there was little difference in the resulting impact energy across HGS type, loading and surface modification. However, the apparent higher impact energy for 32-MS, as compared to 32, may be an artifact from either the surface functionalization or higher GF vol% in the 32-MS composites. The impact energy decrease of the syntactic foam composites compared to the standard density ones is expected and is reported in the literature.[30,31] It is attributed to HGS acting as stress concentration points and restricting the plastic flow of the polymer.[30] Additionally, the standard density composites typically have much higher GF vol%, which will

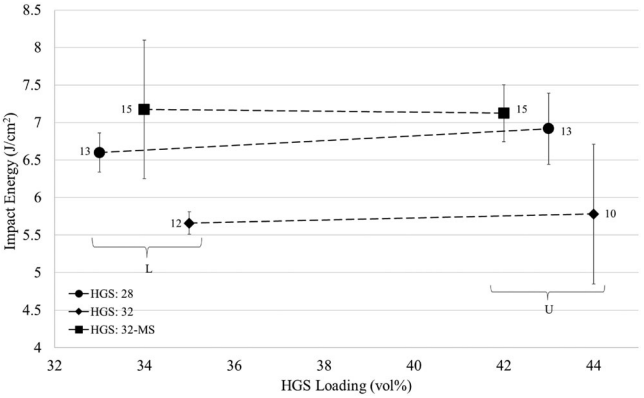

FIGURE 6 Impact energy (J/cm^2) versus hollow glass spheres (HGS) loading (vol%) of three sphere types. Data are given as mean +/− one SE. Standard density impact energy is 9.9 ± 0.73 J/cm^2

dominate the resulting impact properties. For example, in this study the standard density composites had GF ~22 vol%, and an impact energy of 9.9 J/cm^2, which is much higher than any of the HGS composites. Interestingly, considering that 32-MS had a GF content of 15 vol %, its impact energy of 7.1 J/cm^2 is not greatly compromised, especially for the ultra-low composites, where the density (0.98 g/cm^3) is much lower than that of the standard density composites (1.94 g/cm^3).

When referencing the tabulated specific impact energy results (Table 4), the large standard deviations of L32-MS and U32 create difficulty in making any conclusive observations. However, as HGS loading increases from L32 to U32, the results indicate that the specific impact energy may have increased since their standard deviations do not overlap.

3.4 | Ashby plots

Ashby plots, shown in Figure 7 and Figure 8, provide contextualization for the results of this study by benchmarking the tensile and flexural properties versus composite density against other representative polymer composite systems found in the literature. Although the comparisons are not ideal in that there are differences in various composite parameters (e.g., composite fabrication process, GF vol%, reinforcement fiber type, matrix polymer, etc.), it puts into perspective of how the mechanical properties reported in this work compare to similar formulations and the current state-of-the-art (Table 5). Ideally, data points would be in the upper-left hand corner of the plot, with very low density and high property values.

When considering the Ashby plot for tensile properties (Figure 7) the general trend of increasing tensile strength and modulus with increasing density is shown. The higher density side of the plot is the region of the standard density composites having a density of around 1.9 g/cm^3. The composites produced in the current study were comparable in density (e.g., 1.94 g/cm^3) to the SMC GF-UPR composites produced by IDI Composites[32] and Oldenbo, et al.[17] Interestingly, even with similar densities, composite processing, volume fraction GF, and

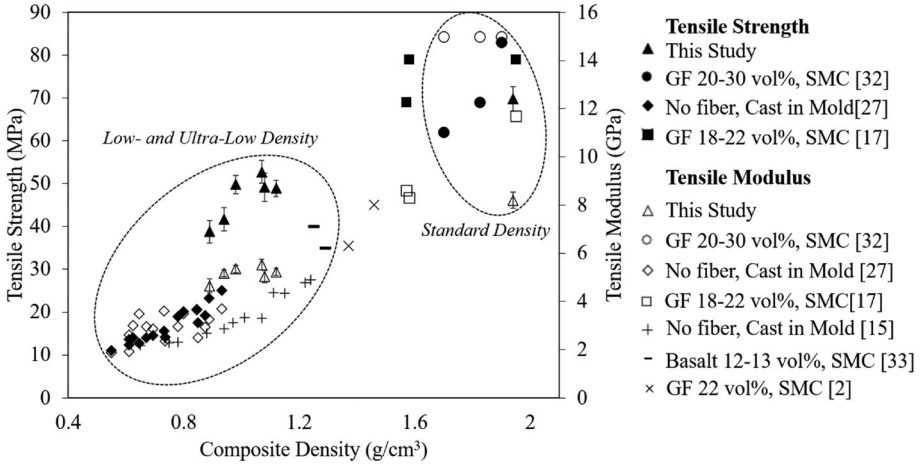

FIGURE 7 Ashby plot of tensile strength (MPa) and tensile modulus (GPa) versus composite density (g/cm^3). This plot shows that the low- and ultra-low density formulations in this study had superior properties to those found in the literature. Abbreviations: GF, glass fiber; SMC, sheet molding compounds

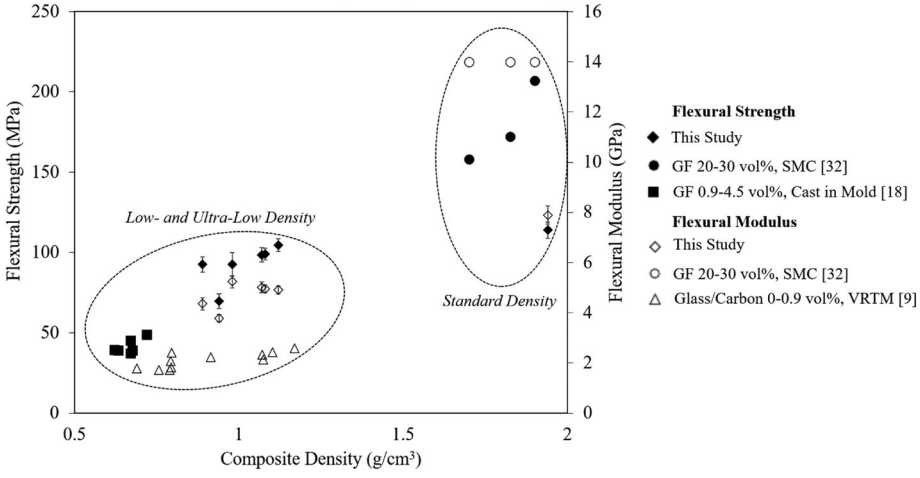

FIGURE 8 Ashby plot of flexural strength (MPa) and flexural modulus (GPa) versus composite density (g/cm^3). The low- and ultra-low density formulations from this study had higher properties than those found in the literature, while the standard density formulations are inferior to existing data. Abbreviations: GF, glass fiber; SMC, sheet molding compounds

TABLE 5 Materials and methods of existing literature for benchmarking in Ashby plots (Figures 7 and 8)

Citation	Composite fabrication method	Matrix	Syntactic foam	HGS vol%	Fiber type	GF vol%
This study	SMC	UPR	Yes	33–44	Glass	10–22
[17]	SMC	UPR	Yes	18	Glass	18–22
[32]	SMC	UPR	No	—	Glass	20–30
[33]	SMC	Epoxy	No	—	Basalt	12–13
[2]	SMC	Epoxy	No	—	Glass	22
[18]	Cast in mold	Epoxy	Yes	47–53	Glass	0.9–4.5
[9]	VRTM	Epoxy	Yes	0–43	Glass/carbon	0–0.9
[27]	Cast in mold	Epoxy	Yes	30–60	None	—
[15]	Cast in mold	UPR	Yes	0–35	None	—

Abbreviations: GF, glass fiber; HGS, hollow glass spheres; SMC, sheet molding compounds; UPR, unsaturated polyester resin.

matrix UPR resin, the tensile strengths and moduli of the composite produced in the current study were lower than what was reported by IDI Composites[32] and Oldenbo, et al.[17] This could be due to either using a lower performance resin and/or lower pressure during compression molding in this study. The pressure of 5.7 MPa used was the maximum possible given the available hot-press but is still lower than the pressure used commonly in making SMC composites. The low-density formulations of the current study had greater tensile strength properties as compared to syntactic foam composites produced by Gupta, et al.[27] However, these composites were considerably different (not SMC, different resin, and no GF reinforcement) from those of the current study, limiting the level of comparison that can be made. The tensile moduli found in this research were marginally higher than Gupta et al. and Huang, et al. for similar composite densities.[15,27] This most likely results from the fact that neither of those studies utilized fiber reinforcements. It is noteworthy that this study was able to include 10–15 vol % GF while maintaining a density, around 1.0 g/cm^3, similar to nonreinforced syntactic foams.

When considering the Ashby plot for flexural properties (Figure 8) the general trend of increasing flexural strength and modulus with increasing density is shown. For the standard density composites, this study exhibited lower flexural strength and modulus compared to that of IDI composites,[32] despite the similarities of the composites that were produced. Possible reasons for this are similar to those listed in the preceding paragraph. Adding HGS to create lightweight composites clearly compromised the flexural strength when compared to standard density IDI Composites.[32] For low-density formulations it is interesting to note that for the current study, there is a small difference in terms of strength and modulus between the low- and ultra-low density composites as compared to the standard density composites, suggesting that there may be additional defects in the standard density composites. At low densities and ultra-low densities, the current study exhibited higher density and flexural strength than those reported by Karthikeyan, et al.[18] Also, for flexural modulus, the composites reported here had equivalent density to those reported by Ferreira, et al. but superior flexural modulus.[9] This is attributed to the higher GF content of our composites, that is, 10–15 vol% compared to the composites with 1.2 vol% GF studied by Ferreira, et al.[9]

Effectively, these Ashby plots appear to show that the composites studied here behave differently compared to existing data when looking at low/ultra-low versus standard density composites. A comparison of standard formulations with density of ~1.9 g/cm^3, indicated that the standard composites of this study exhibit inferior properties with the same GF content compared to those reported in the literature. Once again, this difference in properties may likely be attributed to variation in the compression molding pressure during SMC manufacturing. For low/ultra-low formulations, the composites studied here exhibit near equivalent densities, but superior tensile and flexural properties compared to composites reported in the literature. This is most likely due to the fact that with low- and ultra-low density formulations, their properties were being assessed against non-SMC syntactic foams with no or very low fiber reinforcements. Once again, it is novel that fiber-reinforced syntactic foam composites with high fiber content, of 10–15 vol% GF, were able to be produced with densities at or below 1.0 g/cm^3.

4 | CONCLUSION

The effects of HGS type, loading, and surface functionalization on the mechanical properties of lightweight SMC GF/polyester composites were investigated. This

study was unique in that it (a) produced and tested composites of 1.2 and 1.0 g/cm^3 densities with high reinforcement loading and (b) incorporated methacrylsilane treated HGS into a GF-reinforced SMC composite at high HGS loadings. The tensile and flexural properties and impact energy of these low and ultra-low density composites were compared to those of standard density SMC composites and to similar density composites reported in the literature. Though there was no difference in tensile strength between the formulations at low loadings, 32-MS maintained this property to the greatest degree at high loadings. For both flexural strength and modulus, the HGS 28 resulted in composites with the worst properties compared to all formulations investigated. Moreover, flexural modulus is maintained with surface functionalized HGS when increasing from low- to ultra-low formulations. Finally, impact energy of fiber reinforced syntactic foams was relatively independent of HGS type and loading. While the standard density tensile and flexural properties were lower than those reported in existing literature, at low- and ultra-low densities, the samples produced in this study had improved properties compared to previous studies. The major finding of this study was that an appropriate surface modification of the HGS has been identified that can allow a decrease of the composite's density by more than 12%, that is, from an average of 1.2 g/cm^3 for the low-density formulations to 0.98 g/cm^3 for the ultra-low formulation, with only a 10 percentage point increase in HGS vol%, while maintaining the properties. Through volume percent calculations, one can determine the $CaCO_3$ and HGS contents necessary to reach a specific density goal. It is clear that a compromise of properties is unavoidable in order to significantly decrease the density. Thus, the properties reported in this study can be utilized as a reference for the range of mechanical performance for composites of various HGS type, content, and composite densities.

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REFERENCES

[1] Dumont LO, PJJ. Sheet molding compounds (SMC). **2015**, 2683. http://www.idicomposites.com/smc-bmc.php.
[2] A. Asadi, M. Miller, S. Sultana, R. J. Moon, K. Kalaitzidou, *Compos. Part A Appl. Sci. Manuf.* **2016**, *88*, 206. https://doi.org/10.1016/j.compositesa.2016.05.033.
[3] Gupta N, Pinisetty D, Shunmugasamy VC. *Reinforced Polymer Matrix Syntactic Foams: Effect of Nano and Micro-Scale Reinforcement*, Springer, Heidelberg **2013**.
[4] B. Yalcin, *Hollow Glass Microspheres in Sheet Molding Compounds*, Elsevier, Amsterdam **2015**. https://doi.org/10.1016/B978-1-4557-7443-2.00005-0.
[5] D. Pinisetty, V. C. Shunmugasamy, N. Gupta, Hollow glass microspheres in thermosets-epoxy syntactic foams. in *Hollow Glass Microspheres for Plastics, Elastomers, and Adhesives Compounds*, Elsevier, Amsterdam **2015**, p. 147. https://doi.org/10.1016/B978-1-4557-7443-2.00006-2.
[6] N. Gupta, R. Ye, M. Porfiri, *Compos. Part B Eng.* **2010**, *41*, 236. https://doi.org/10.1016/j.compositesb.2009.07.004.
[7] D. D. Luong, O. M. Strbik, V. H. Hammond, N. Gupta, K. Cho, *J. Alloys Compd.* **2013**, *550*, 412. https://doi.org/10.1016/j.jallcom.2012.10.171.
[8] L. D. L. J. G. Wegner, *Acta Mater.* **1995**, *43*, 1651.
[9] J. A. M. Ferreira, C. Capela, J. D. Costa, *Compos. Part A Appl. Sci. Manuf.* **2010**, *41*, 345. https://doi.org/10.1016/j.compositesa.2009.10.018.
[10] E. M. Wouterson, F. Y. C. Boey, X. Hu, S. C. Wong, *Polymer* **2007**, *48*, 3183. https://doi.org/10.1016/j.polymer.2007.03.069.
[11] G. Tagliavia, M. Porfiri, N. Gupta, *Compos. Part B Eng.* **2010**, *41*, 86. https://doi.org/10.1016/j.compositesb.2009.03.004.
[12] G. Hu, D. Yu, *Mater. Sci. Eng. A* **2011**, *528*, 5177. https://doi.org/10.1016/j.msea.2011.03.071.
[13] S. J. Park, F. L. Jin, C. Lee, *Mater. Sci. Eng. A* **2005**, *402*, 335. https://doi.org/10.1016/j.msea.2005.05.015.
[14] Huang C, Huang Z, Lv X, Zhang G, Wang Q, Wang B. Surface modification of hollow glass microsphere with different coupling agents for potential applications in phenolic syntactic foams. **2017**, *44415*. https://doi.org/10.1002/app.44415.
[15] J. S. Huang, L. J. Gibson, *J. Mech. Phys. Solids* **1993**, *41*, 55. https://doi.org/10.1016/0022-5096(93)90063-L.
[16] E. M. Wouterson, F. Y. C. Boey, X. Hu, S. C. Wong, *Compos. Sci. Technol.* **2005**, *65*, 1840. https://doi.org/10.1016/j.compscitech.2005.03.012.
[17] M. Oldenbo, S. P. Fernberg, L. A. Berglund, *Compos. Part A Appl. Sci. Manuf.* **2003**, *34*, 875. https://doi.org/10.1016/S1359-835X(03)00155-6.
[18] C. S. Karthikeyan, K. Sankaran S, *Macromol. Mater. Eng.* **2005**, *290*, 60. https://doi.org/10.1002/mame.200400177.
[19] L. Wang, J. Zhang, X. Yang, C. Zhang, W. Gong, J. Yu, *Mater. Des.* **2014**, *55*, 929. https://doi.org/10.1016/j.matdes.2013.10.065.
[20] C. S. Karthikeyan, K. Sankaran S, *Mater. Lett.* **2004**, *58*, 995. https://doi.org/10.1016/j.matlet.2003.08.012.
[21] J. A. M. Ferreira, K. Salviano, J. D. Costa, C. Capela, *J. Mater. Sci.* **2010**, *45*, 3547. https://doi.org/10.1007/s10853-010-4397-4.

[22] C. S. Karthikeyan, S. Sankaran, M. N. J. Kumar, *Polymer* **2001**, *81*, 405.
[23] IDI Composites International. S80 Series SMC datasheet. **2016**.
[24] A. Hamarneh, *Reinf. Plast.* **2014**, *58*, 19. https://doi.org/10.1016/S0034-3617(14)70134-1.
[25] Emissions GG, Economy F. The EPA automotive trends report. March **2020**.
[26] J. Z. Liang, R. K. Y. Li, *Polym. Compos.* **1998**, *19*, 698. https://doi.org/10.1002/pc.10142.
[27] N. Gupta, R. Nagorny, *J. Appl. Polym. Sci.* **2006**, *102*, 1254. https://doi.org/10.1002/app.23548.
[28] S. He, D. Carolan, A. Fergusson, A. C. Taylor, *Mater. Des.* **2019**, *169*, 107654. https://doi.org/10.1016/j.matdes.2019.107654.
[29] S. Mishra, A. K. Mohanty, L. T. Drzal, M. Misra, S. Parija, S. K. Nayak, S. S. Tripathy, *Compos. Sci. Technol.* **2003**, *63*, 1377. https://doi.org/10.1016/S0266-3538(03)00084-8.
[30] E. M. Wouterson, F. Y. C. Boey, X. Hu, S. C. Wong, *J. Cell Plast.* **2004**, *40*, 145. https://doi.org/10.1177/0021955X04041960.
[31] H. S. Kim, C. Mitchell, *J. Appl. Polym. Sci.* **2003**, *89*, 2306. https://doi.org/10.1002/app.12470.
[32] IDI Composites International. IDI Composites. **2013**.
[33] A. Asadi, F. Baaij, H. Mainka, M. Rademacher, J. Thompson, K. Kalaitzidou, *Compos. Part B Eng.* **2017**, *123*, 210. https://doi.org/10.1016/j.compositesb.2017.05.017.

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