Processing of Hollow Glass Sphere/Polyester/Glass Fiber Sheet Molding Composites

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ABSTRACT

The development of lightweight polymer-glass fiber (GF) composites is a major step towards more environmentally sustainable automobiles. By altering the commonly used industry polymer Unsaturated Polyester Resin (UPR) with hollow glass spheres (HGS) of various characteristics, one can create a novel resin matrix for glass fiber composites. The different glass bubbles, with their low densities ranging from 0.28–0.46 g/cm$^3$, allow for an increase in glass fiber loading while still decreasing the weight of the final composite produced using sheet molding compounds (SMC). Thorough calibration of the SMC line’s glass fiber and resin mass flow rate settings is a crucial step in achieving the desired glass fiber loading and composite density. Once completed, any changes in density of the composite can be solely attributed to the addition of hollow glass spheres. It is necessary to achieve proper dispersion of each of the types of glass spheres in order to minimize aggregates which may cause stress concentrations and, thus, decreased mechanical properties. Dispersion of HGS and GF is characterized with Scanning Electron Microscopy and optical imaging, while acetone dissolution is utilized to assess the GF loading of the SMC prior to compression molding.

1. INTRODUCTION

Glass fiber reinforced plastics are commonly used in automotive applications that require low weight, high formability, and good in-plane mechanical parameters [1]. Recently, there has been a strong impetus towards sustainability and fuel-efficiency in the automotive market. New emission standards as well as market demand have been the driving force of this movement [2]. A clear path to more environmentally-friendly vehicles lies in lightweighting the composites used for auto bodies. This can be achieved through the inclusion of a low density filler such as hollow
glass spheres (HGS) as a light weight filler to decrease the density of a polymer matrix composite [3].

Common thermoset matrices in polymer composites are phenolics, polyimides, vinylester, polyester, and epoxies [4, 5]. However, because Unsaturated Polyester Resin (UPR) has a relatively short cure time and low cost, it is most frequently used in Sheet Molding Compound (SMC) composites for automotive applications. Not only is the SMC machine an automated process, but it is also scalable making this research applicable in larger manufacturing operations. As a result, UPR is an ideal choice with which to investigate the capability of HGS as a lightweighting resin additive for automotive applications.

Typical SMC composites in the automotive industry have a 1.9 g/cm³ density. The combination of the high strength-to-weight properties of glass fibers (GF) and the low density HGS is expected to significantly reduced the density without compromising mechanical properties and performance. Optimization of weight percent HGS and GF as well as diameter, and density of HGS are necessary.

HGS have been used in microwave absorption composites, marine applications such as underwater pipeline insulation, and artificial bone [6, 7]. Foam structures created by the introduction of HGS are more mechanically robust than foams made with just voids, called open-cell foams, which have low compressive properties [8]. This is due to the fact that the resin core within each cell is stiffened on either side by glass walls creating many small microsandwich structures [9-11]. Common fillers used in SMC composites include clay, CaCO₃, and talc. However, HGS are of most interest for SMC research as they reduce product weight, decrease the amount of CaCO₃ required, and improve stiffness and stability of the composite [11].

As with many additives in polymer resin systems, a main challenge of using HGS is proper dispersion in the resin paste. Hollow glass spheres pose a unique challenge in this aspect due to their tendency to fracture or crush when sheared in such a way that two spheres collide. To achieve homogenous dispersion, while avoiding breakage, the mixing method must be vigorous enough to fully isolate the HGS while also mild enough to not induce rupture [12-14]. Furthermore, any change in the resin formulation could affect the viscosity, and ultimately, the material handling behavior; therefore, it is necessary to track any change in viscosity and adjust the manufacturing process parameters accordingly. And, possibly most critically, any agglomeration of the filler dispersion can result in stress concentration due to physical inhomogeneity.

In this study an approach for manufacturing novel polyester-HGS resin for use in SMC with random discontinuous GF was developed. Methods for calibrating the resin and glass fiber mass flow rate were examined for their efficacy. The effect of mixing blade on composite homogeneity was observed. Further work on other composite formulations as well as mechanical properties of the resulting composites is currently underway and will not be presented here.

2. EXPERIMENTATION

2.1 Materials

The polyester resin was supplied in two parts, Arotan 774 and Arotan 775 by Ashland. The UPR is shipped and stored in two components to avoid phase separation issues as recommended by the manufacturer. Calcium carbonate, Hubercarb W4, was supplied courtesy of Huber Engineered
Materials. Wetting agent, BYK 9010, was supplied by BYK Additives and Instruments. Tert-Butyl peroxybenzoate (TBPB), the initiator, was purchased from Sigma-Aldrich. Mold release agent, zinc stearate, was manufactured by Acros Organics. Magnesium oxide in resin was purchased from Chromaflo Technologies (AM-9033). Glass fiber rovings, Advantex P204, were provided by Owens Corning. Hollow glass spheres, iM16K, were provided by 3M.

The formulations for the two resin pastes studied are outlined in Table 1. The baseline resin paste that did not include any HGS was developed so that the resulting SMC plate would have a density of 1.9 g/cm$^3$. The samples with HGS would have an SMC plate density of 1.5 g/cm$^3$. The resin paste density for these trials was 1.75 and 1.24 g/cm$^3$ respectively, as determined by rule of mixtures.

<table>
<thead>
<tr>
<th>Component</th>
<th>1.9 Density (phr)</th>
<th>1.5 Density (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-Side</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arotran 774</td>
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</tr>
<tr>
<td>Arotran 775</td>
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<tr>
<td>BYK 9010</td>
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<td>Zinc Stearate</td>
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</tr>
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<td>Hubercarb W4</td>
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<td>105.00</td>
</tr>
<tr>
<td>iM16k</td>
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<td>24.00</td>
</tr>
<tr>
<td>B-Side</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AM 9033</td>
<td>1.90</td>
<td>2.50</td>
</tr>
</tbody>
</table>

2.2 Manufacturing of Composites

2.2.1 Dispersion

Proper dispersion of fillers within resin is important, as it has a significant effect on the resin viscosity, the material handling characteristics, and mechanical properties of the final composite plate. Generally, the paste is homogenized by a high shear mixing method. Some elements of resin formulations include the thermoset polymer, a curing or crosslinking agent, viscosity modifiers, dimensional stabilizers, mold release, low shrink additives, catalysts, inhibitors, and surface finish additives. Initially, a cement mixing blade was utilized to combine all components of the polyester resin, but it was established that this was inadequate at breaking up the CaCO$_3$ agglomerates. As a result, a high shear Cowles dispersion blade was acquired. Two different mixing speeds were used when combining the CaCO$_3$ and zinc stearate versus when dispersing the HGS. The former
was added at 2000 rpm while the latter was added at a motor speed of 1200 rpm to minimize possible fracture of HGS during processing.

2.2.2 Fabrication of SMC

SMC runs were completed using a line built by Finn & Fram inc. To begin the production of SMC, the prepared resin is poured into two separate reservoirs. Resin is then pulled underneath the doctor blade and below the cutter wheel by a moving carrier film. At this point, fibers chopped by the cutter wheel to a specific length, in this case 1”, are dropped onto the lower resin film. The lower film then combines with the upper film and undergoes compaction. The SMC is then collected onto a roll and allowed to mature at room temperature before compression molding (Figure 1).

![Figure 1. Schematic of SMC system with relevant components labelled.](image)

2.2.3 Calibration of SMC

Calibration of the mass flow rate of the six GF rovings being cut and distributed onto the SMC layer is the foremost step in controlling the fiber loading of the resulting SMC plies. A regression equation was created by setting the cutting wheel speed to four different values and weighing the amount of chopped GF that drops over 10 seconds. The four levels of cutting speeds were selected to be equally spaced across the anticipated machine setting range. This allows for the calculation of the mass flow rate of GF in mass per unit time.

Several techniques were used in progression with the aim to calibrate the SMC line for a novel resin paste system both with and without HGS. This process is necessary to ensure consistent and accurate production, especially with regard to GF content of the finished part. The viscosity of the resin paste after mixing influences the volume flow rate of the resin paste under the doctor blade. In the ideal case the volume flow rate of resin paste would be equivalent to product of the doctor blade height, the belt width, and the belt speed. Non-Newtonian characteristics of the resin paste will result in deviations of resin thickness from the doctor blade height and necessitate a calibration
Several methods were examined in order to standardize the machine setting, doctor blade height, with respect to the resin thickness.

### 2.2.4 Compression molding of SMC

As previously stated, the collected Polyester-GF SMC is allowed to mature at room temperature for 5-7 days in order for it to reach the desired viscosity before compression molding. During this time, the SMC is wrapped tightly to prevent any loss of styrene, which could adversely impact the mechanical properties of the final SMC plate. Following the maturation period, SMC plies of prespecified dimensions are then cut, layed-up and placed into an open aluminum mold. The mold and stack of plies, or charge, is then pressed at high pressures and temperatures to induce curing. Plates were hot-pressed using a Wabash 50 ton hot press, model v50-1818-2mx. At each of these steps the physical behavior of the material has a substantial impact on the processability and system efficacy.

### 2.3 Characterization Techniques

#### 2.3.1 Density Measurement

Density of pressed plates were determined by two methods. Water displacement was completed following ASTM D792-13 guidelines using samples cut by waterjet or table saw. Density of complete square plates was calculated by measuring the thickness at several locations using calipers and by weighing the plate.

#### 2.3.2 Mechanical Properties

Data on tensile, flexural, and impact properties that would indicate the effect of GF loadings and HGS dispersion are not presented here but will be obtained in the near future. For tensile testing, an Instron 5982 with a 100 kN load cell will be used in accordance with ASTM D638. Flexural strength data will be gathered by following ASTM D790-17 while using an Instron 33R 4466 with a 500 N load cell. Impact testing will be completed using Instron Pendulum Impact Tester following ASTM D4812-11 standard.

#### 2.3.3 Imaging

Optical microscopy was completed using a Leica DVM 6 Optical Microscope in reflectance. Secondary electron microscopy (SEM) was completed using a LEO 1530 FE-SEM at an accelerating voltage of 3kV. SEM samples were gold sputter coated to reduce charging.

#### 2.3.4 Acetone Dissolution

Due to the industrial application of this research, a fast turnaround time is desirable. The normal wait period of five days for maturation before hot-pressing the plies to determine the GF content is unattractive. One method to rapidly characterize the GF content is to use acetone dissolution of the resin paste to find the GF content of an unpressed SMC. In this technique, a 1” punchout was used to obtain samples of known dimensions. After the carrier film is removed the sample is weighed and then rinsed with acetone at 320 Hz for 2 minutes, 160 Hz, for two minutes, and then repeated by hand until the acetone runs clear. By washing the sample with acetone and filtering
over a sieve it is possible to isolate GF. Weighing the GF and comparing it to the initial sample weight gives the GF content in wt%.

3. RESULTS

Representative results are shown below.

3.1 Dispersion

Calcium carbonate (CaCO$_3$) in the 1.9 g/cm$^3$ density trial is 195 phr of the entire resin paste, making it a primary component. Thus, improper mixing can be seen as white agglomerates with optical microscopy of the plate cross-section (Figure 2.a). Better dispersion of CaCO$_3$ within the matrix material should lead to a higher viscosity due to more surface area interactions between the particles and the polymer. The trailing and leading edge of the teeth around the outside create “rolling donuts”, effectively pulling the additives down into the resin mixture (Figure 2.b insert). The higher shear is what allowed for the break-up of the clumps of powder. After switching mixing blades, a more homogenous cross section of the final pressed part was observed (Figure 2).

![Figure 2. Optical image cross sections of SMC composite plates. a) Sample prepared by cement mixing blade. b) Sample prepared by high shear mixing. Respective mixing blades are shown in inserts. Arrows indicate regions of resin inhomogeneity. Circle indicates fully impregnated glass fiber tow.](image)

The quality of dispersion of the components was qualitatively assessed with various methodologies, including SEM and Optical Microscopy. No individual or agglomerated HGS could be resolved on the optical images of the 1.5 g/cm$^3$ density formulation with iM16K glass spheres. Scanning Electron Microscopy (SEM) was utilized to assess the degree of fracture of HGS within the composite and whether it occurred during material processing, hot-pressing, or during sample preparation via circular saw. When a broken HGS is penetrated by resin, it indicates that the spheres were broken during the processing of the composite, before the sample was cured. Such an observation would mean that either the shear mixing was too high, resulting in HGS fracture, or the increased pressure during hot-pressing broke the spheres. Based on the SEM imaging there was little to no HGS broken during the SMC processing, and any observed fractures were likely a result of sample preparation (Figure 3).
3.2 Calibration

3.2.1 Cutting Speed Calibration

To obtain an equation relating the cutting speed setting to the GF mass flow rate, four runs were completed for each cutting wheel speed setting and a best fit line was plotted. The resulting regression equation was then plugged into a spreadsheet tool that calculated the necessary belt speed based on a particular fiber flow rate and vice versa. The resulting regression line was linear. This was not a parameter that was changed by the team when attempting to fine-tune the GF loading of the SMC, though, because the wheel was running at the minimum torque the machine allows. Consequently, the cutting speed could not be decreased in the pursuit of a lower GF content.

3.2.2 Resin Flow Calibration

In order to calibrate the resin flow rate two main approaches were used with the following results. A series of SMC machine runs with resin paste and no GF at various doctor blade heights were completed. No GF were used in these calibration runs to isolate the influence of the doctor blade parameter. Two methods were used to identify the volume flow rate of resin from the calibration run SMC sheets. First, a series of 4x4 in² squares were cut from the center of the sheet. The thickness of these samples was calculated using the sample mass, resin density, and length and width of the square. The results of this are plotted in Figure 4. Error may be introduced into this data because of local variations in the composite ply as well as the squeeze-out of UPR on the edges of the ply in the compaction zone.

To mitigate the effect of these errors on the calibration results, a second method was explored. Widthwise strips of SMC were excised and weighed. Because the strip spanned the width of the SMC the effects of squeeze-out on sample mass would be reduced. Resin flow rate was calculated similarly to before and averaged across several strip samples. The regression line of three different doctor blade heights used with this calibration procedure was plotted and incorporated into the calculation spreadsheet. When this regression equation was used to produce a 29 wt% 1.9 g/cm³ density sample, the final hot-pressed plate had approximately a 46 wt% fiber loading. This
deviation may be due to voids in the uncured SMC sheet, or the fact that GF changes the behavior of the resin paste in the compaction zone.

Although the attempts at calibration were not successful in producing a plate with the target density, the data produced was useful in reaching near the target density. Using the data from previous trials, the doctor blade height was estimated from earlier studies. Mass flow rate balances were used to determine the relationship between resin flow rate \(Q_r\), resin density \(\rho_r\), fiber mass flow rate \(m_f\), and glass fiber content \(w_f\), (equation [1]). As stated earlier resin flow rate is directly related to the doctor blade height. This principle was used to approximate the doctor blade height needed to reach the desired weight fraction of GF.

\[
\frac{Q_r \cdot \rho_r}{m_f} = \frac{1 - w_f}{w_f}
\]  

[1]

Furthermore, new mixing procedures were implemented to achieve better resin paste homogeneity. High shear mixing blades were employed and may have had an effect on the resin viscosity. The resulting runs produced samples with plate densities that fall within experimental error and sample to sample variation. The density of these samples as determined by water displacement measurement was 1.91 g/cm\(^3\), equivalent to 25 wt% GF. It should be noted that due to the inverse relationship between composite density and GF wt%, any small change in composite density will result in much larger shifts in GF wt% (Figure 5). Here the resin paste density is assumed to be 1.75 and 1.24 g/cm\(^3\) for the 1.9 and 1.5 g/cm\(^3\) density plates respectively. As a result, variation up to 5 wt% GF is acceptable. Subsequent SMC trials will be explored by varying material flow rate and measuring density or GF content of the resulting composite part.
Figure 5. The relationship between composite density ($\rho_c$) and glass fiber wt% with different resin contents ($\rho_r$) using a simple rule of mixtures calculation.

### 3.3 Acetone Dissolution

A comparison of Table 2 shows that there is slight disparity in GF loading between a sample cut from the center and the edge of the SMC sheet. This could be due to local variance in how the fibers randomly fall on the ply or could be a result of minor asymmetry in the roving cutting distribution. As a result, in the future samples will be cut from the center to be consistent and representative of where squares of plies are cut when creating the charge for hot-pressing. One possible source of error with this method is small pieces of GF which are cut off at the edge of the punch could pass through the sieve. This would most likely result in an underestimate of the GF loading compared to the weight percent GF calculated from density measurements.

Table 2. Comparison of glass fiber loading (wt%) between acetone dissolution, density via mass-micrometer measurements, and water displacement density.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acetone (GF wt%)</th>
<th>Mass/Micrometer Density (g/cm$^3$)</th>
<th>Mass/Micrometer (GF wt%)</th>
<th>Water Displacement Density (g/cm$^3$)</th>
<th>Water Displacement (GF wt%)</th>
<th>Target (GF wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10-Edge</td>
<td>18.8</td>
<td>1.89</td>
<td>22</td>
<td>1.91</td>
<td>25</td>
<td>29</td>
</tr>
<tr>
<td>S10-Center</td>
<td>24.6</td>
<td>1.89</td>
<td>22</td>
<td>1.91</td>
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<td>29</td>
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</table>
4. CONCLUSIONS

The material processing and manufacturing parameters of SMC sheets have a substantial effect on the glass fiber loading of a UPR-GF and UPR-HGS-GF composites. With a multitude of factors influencing the production of composite plates, the most important parameters that this research focused on were the dispersion blade use and its consequence on the homogeneity of the resulting resin system as well as the effect of the doctor blade height on resulting density and GF content of the SMC plate. Adjustments to the mixing process for 1.5 g/cm\(^3\) density formulations were needed to accommodate the inclusion of HGS while also properly dispersing the CaCO\(_3\). Furthermore, with a novel resin paste, multiple calibration practices were tested to move the glass fiber content closer to the target value. Acetone dissolution is a promising procedure to gain rapid feedback on the GF content produced by the SMC settings, allowing for a faster response time when altering the parameters for different density formulations. Further studies will examine varied loading and type of HGS in this system as well as the mechanical properties of all formulations.

5. REFERENCES


