GLASS-MICROBUBBLE-FILLED THERMOPLASTIC COMPOSITES AS LIGHT-WEIGHT AUTOMOTIVE MATERIALS

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Abstract

Lightweighting is tremendously important to the automotive community due to fuel efficiency and reduced environmental impact. One promising lightweighting technology in plastic composite materials is the addition of glass bubbles. This technology is potentially more promising than other lightweighting technologies due to better uniformity of distribution, less processing sensitivity, and a potential for better retention of physical properties. New advances have been made in formulating and processing glass bubbles into polyolefin and nylon based composites, making improvements in lightweighting with reduced impact on physical properties.

Background and Requirements

Lightweighting has become an important consideration in the automotive industry to improve fuel economy and the environmental impact of transportation emissions. One method of lightweighting is to switch from metal to plastic components, often using glass fiber composites to retain mechanical properties in the plastic components. However, even these composites add more weight to the vehicle than is desired. Several lightweighting strategies for plastic components have been proposed. Some of these strategies include using physical and chemical blowing agents\(^1,2\), switching to lighter weight polymer binders, and adding lighter weight fibers into the composite\(^3,4\). In addition, incorporating glass bubbles into plastic components also promises to assist in lightweighting\(^5\).

Glass bubbles have potential advantages over other air entrapment technologies in that glass bubbles form more uniform dispersions and have less processing sensitivity. A study done by Fraunhofer Project Centre for Composites Research also showed that glass-bubble LFT composites potentially retain better physical properties than other air entrapment technologies\(^5\). Physical and chemical blowing agents impart gas bubbles into a polymer melt resulting in voids in the final plastic part. The size of these voids is process dependent due to the nature of the gases. Also, the gas bubbles could have a tendency to migrate to the surface of a plastic part or coalesce while the part is still in a molten state. Finally, for chemical blowing agents, the rate of gas release from the blowing agent is strongly dependent upon the conditions of the melt. All of these factors potentially make physical and chemical blowing agents less reliable as a source for lightweighting plastic parts.

Glass bubbles are not as sensitive to the temperature of processing, since they entrap the air inside them and their volume change with temperature is minimal. Also, they do not need a minimum temperature to process as do chemical blowing agents. Finally, surface modification of the glass bubbles can help in improving their dispersion and physical properties in a polymer melt, producing a more evenly distributed source of voids inside a given part. This paper gives the results of initial glass bubble testing in polypropylene and nylon composite materials, showing improved densities and good strength retention.
Experimental

The following procedures were used to investigate the incorporation of glass bubbles into polyolefin composite materials (Hyfax TYC 1168X, named "Hyfax" and Pro-fax SG702, named "PXSG") and nylon 6 materials (Ultramid B27E). The glass bubbles were first incorporated into the matrices with a twin screw extruder and strand cut into pellets. The pellets were next injection molded in a family mold into different sized parts including

- 216 mm x 12.5 mm x 3.0 mm dogbone shaped tensile bars
- 128 mm x 12.8 mm x 6.4 mm flex modulus bars
- 63.5 mm x 12.8 mm x 3.2 mm notched Izod bars

Weight reduction was measured by weighing formulated flex modulus bars and comparing them to controls. The appropriate molded bars were then tested at ambient temperatures with:

- ISO 527, 50 mm/min, for tensile strength
- ISO 178, 2 mm/min, for flex modulus
- ASTM D256 for notched Izod

Finally, glass bubble survivability for some of the masterbatches was measured using a muffle furnace and a pycnometer to measure accurate densities of the glass bubbles in the composite materials.

Glass bubbles that were incorporated into the polyolefin and nylon composite materials included unsized (3M iM16K7) and sized varieties. Coupling agents from Addcomp's PRIEX line were also included in the polyolefin formulations to couple the glass bubbles to the polyolefin binder. Coupling agents were not included in the nylon formulations. Glass bubble loadings on final parts were calculated to achieve an 11% weight reduction and incorporated at those loadings. These calculations do not account for glass bubble breakage during processing, so actual weight reduction on the final parts is decreased due to the bubble breakage.

Results and Discussion

Weight reduction, good mechanical properties and bubble survivability all define successful incorporation of glass bubbles into the polymer matrices. Weight reduction and bubble survivability show how many of the glass bubbles remained unbroken, while mechanical properties indicate the effects of unbroken bubbles and good coupling of the bubbles within the polymeric matrix. The following sections investigate these properties in the polyolefin and nylon glass bubble composites.

Glass Bubbles in Polyolefin Composites

Weight reductions on representative final polyolefin parts are shown in Table 1 below. 7% to 9% weight reduction was achieved in these parts versus the control. Some loss in weight reduction efficiency was observed compared to the 11% calculated and was possibly due to glass bubble breakage. Sized glass bubbles were used for the coupled glass bubble composites whereas unsized glass bubbles were used in the uncoupled glass bubble composites. The sized glass bubbles had a lower burst strength (around 16,000 psi) than the unsized glass bubbles (around 18,000 psi). This and/or differences in processing due to sizing and polymer interactions may account for the decrease in weight reduction seen in the coupled glass bubble composites.
Table I: Weight Reduction in Flex Modulus Bars—TPO Formulations

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Percent Weight Reduction:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyfax/Uncoupled Glass Bubbles</td>
<td>8.7%</td>
</tr>
<tr>
<td>Hyfax/Coupled Glass Bubbles</td>
<td>7.9%</td>
</tr>
<tr>
<td>PXSG/Uncoupled Glass Bubbles</td>
<td>7.7%</td>
</tr>
<tr>
<td>PXSG/Coupled Glass Bubbles</td>
<td>6.6%</td>
</tr>
</tbody>
</table>

Results from mechanical testing of the polyolefin materials are shown in Figures 1 & 2 below. Tensile strength, represented by break stress and peak stress, was maintained for the coupled glass bubble composites. Stiffness, represented by flex modulus, was slightly higher for the coupled glass bubble composites than for the control. However, loss in impact strength, represented by notched Izod impact, was observed for these materials, showing a loss in material ductility compared to the controls. This loss in ductility would be more important in exterior automotive applications than in interior or structural applications.

Figure 1: Glass Bubbles in Hyfax TYC 1168X
Some loss in mechanical properties would be expected to result from glass bubble breakage, and tests on the glass bubble masterbatches did show a small amount of breakage\textsuperscript{8} (see Table 2). Further breakage that may have occurred during injection molding of the parts is not reported in Table 2. Glass bubble survivability should be increased as processing and formulation are optimized, so better mechanical properties are expected to result in future development of these TPO and polypropylene glass bubble composites.

**Table 2: Glass Bubble Survivability in Polyolefin Masterbatches**

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Estimated Glass Bubble Survivability (Volume %):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoupled Glass Bubbles Polyolefin Masterbatch</td>
<td>95%</td>
</tr>
<tr>
<td>Coupled Glass Bubbles Polyolefin Masterbatch</td>
<td>90%</td>
</tr>
</tbody>
</table>

### Glass Bubbles in Nylon Composites

Representative glass bubble composite parts molded from nylon 6 (shown in Table 3 below) did not show as much weight reduction as the polyolefin composites. They ranged from 2\% to 5\% weight reduction and were lower due to more glass bubble breakage. Successful incorporation of the glass bubbles into the nylon matrix may have been hindered by higher processing temperatures, lower melt viscosity, and the inability of the nylon resin to effectively coat out and protect the glass bubbles during processing. In addition, it is possible to modify the screw design to reduce shear and protect the glass bubbles. Weight reduction is expected to increase with future improvements in formulation and processing.
Table 3: Weight Reduction in Flex Modulus Bars—Nylon Formulations

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Percent Weight Reduction:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6/Unsized Glass Bubbles</td>
<td>4.8%</td>
</tr>
<tr>
<td>Nylon 6/Sized Glass Bubbles</td>
<td>2.2%</td>
</tr>
<tr>
<td>Nylon 6/Sized Glass Bubbles + Impact Modifier</td>
<td>2.7%</td>
</tr>
</tbody>
</table>

Results from mechanical testing of the nylon 6 based materials are shown in Figure 3 below. Tensile strength, represented by break stress and peak stress, was higher for the sized glass bubble composites than for the control. Stiffness, represented by flex modulus, was also slightly higher for the sized glass bubble composites. Both of these results indicate effective property retention and that the coupling of the glass bubbles to the polymer matrix is occurring. Some loss in impact strength was recovered with addition of an impact modifier. However, impact strength is still lower than for the nylon resin control.

Figure 3: Glass Bubbles in Nylon 6.

Glass bubble breakage was fairly significant for the nylon 6 composites, as is shown in Table 4. This table shows only the breakage due to incorporating the glass bubbles into nylon 6 masterbatches. Any glass bubble breakage during injection molding of the parts is not included in Table 4. Improvements in formulation may include coating agents and impact modifiers to better protect the glass bubbles during processing. Changes to the twin screw extruder configuration may also help minimize breakage during the glass bubble incorporation step.
Table 4: Glass Bubble Survivability in Nylon 6 Masterbatches

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Estimated Glass Bubble Survivability (Volume %):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsized Glass Bubbles Nylon 6 Masterbatch</td>
<td>80%</td>
</tr>
<tr>
<td>Sized Glass Bubbles Nylon 6 Masterbatch Masterbatch</td>
<td>75%</td>
</tr>
</tbody>
</table>

Summary and Next Steps

- TPO glass bubble composites achieved 7% to 9% weight reduction and maintained tensile strength and stiffness.
- Nylon glass bubble composites achieved 2% to 5% weight reduction and maintained tensile strength and stiffness.
- Improvements in formulation and processing are expected to increase glass bubble survivability and thus improve weight reduction and mechanical properties further.
- Plans to incorporate glass bubbles masterbatches into glass-filled PP and PA composites to test compatibility with, and enhancements to, those systems are in progress.

Acknowledgements

Many thanks to 3M for their supply of the glass bubbles and technical support in developing composite materials.

Bibliography

7. 3M™ Glass Bubbles K Series, S Series and iM Series Product Information Sheet, 3M Company,
2013.