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Technical Paper

Using Hollow Glass Microsphere Masterbatches to Optimize Formulations at the Injection Molding Press

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Abstract

Hollow Glass Microspheres or Glass Bubbles are now an accepted lightweighting technology for injection molded plastics used in transportation applications. The benefits of using hollow microspheres go beyond lightweighting and include dimensional stability, cycle time reduction and reduced sink and warpage. Often times there is a need to balance weight reduction with changes in physical properties. Using a high concentration masterbatch of these materials, at the press, can speed the optimization of a light weight resin formulation.

Background and Requirements

Low density glass microspheres have been available as plastics additives for years. Application of hollow microspheres had been limited to those of low shear or compressive force processes - most notably RTM, plastisols, potting compounds and SMC/BMC[1]. This was the case until the advent of high strength glass bubbles from 3M. These ultra-high strength glass bubbles are robust to many different extrusion and injection molding conditions[2]. Table 1 shows the 3M™ Glass Bubble product range available for high shear applications like extrusion and injection molding[2].

Often resin producers, compounders, tier one suppliers and OEMs want to do a trial of glass bubbles on existing tooling in order to optimize a formulation with respect to physical properties. There are two main ways to introduce the technology – directly compounded into the base resin at the let-down formulation or via a masterbatch. There are pros and cons of each method when running an optimization trial as shown in Table 2. Using a directly compounded material is arguably the simplest from a molding operation point of view. Put it in the hopper and shoot parts just as you would with the existing resin. With a masterbatch, one needs to have auxiliary equipment for blending or feeding at the hopper. This can also lead to potential mis-formulation issues and inhomogeneity in the final part.

Grade	Density (g/cc)	Strength (psi)	Particle Size (microns)			
			10%	50%	90%	TOP
S38HS	0.38	5500	17	45	66	83
K42HS	0.42	7500	11	22	37	42
iM16K	0.46	16000	13	20	31	37
S60HS	0.60	18000	11	30	50	60
iM30K	0.60	27000	9	16	25	29

Table 1. High-Strength Product Range of 3M™ Glass Bubbles

Direct Compounding	Masterbatch
Pre-trial Assay of Homogeneity	Flexibility to Change Formulation
No 2nd (Carrier) Resin	Ability to Utilize a “Functional” Carrier Resin
No 2nd Feeder/Blender	→ Potential Con Additional Feeder or Salt and Pepper Blend Required
No Chance for Formulation Error	→ Potential Con Assay after Molding Recommended to Affirm Concentration and Microsphere Survival

Table 2. Pros (and Cons) of Addition Methods

One of the most significant issues with a masterbatch trial is the potential introduction of a second resin to the formulation – the carrier resin for the masterbatch. This issue can be minimized if the carrier resin is similar to, or the same as, the host resin. Often though, it’s not feasible to obtain a similar/same resin to make the masterbatch. Then, there is the potential to significantly change the physical properties of the resulting part. This changes the exact properties of interest for optimization.

A different carrier resin may not be a significant issue when the additive in question is dense or added at a low concentration from a high concentration masterbatch (for example, 1 or 2 wt. % of TiO_2 added from a 70 wt. % masterbatch). A low density additive added at percentage levels is a very different story –

high weight percentages of carrier resin are incorporated and the volume percent of components can change significantly. A pictorial view of this for 5 and 10 wt. % addition of a 0.46 g/cc 3M™ Glass Bubble is shown in Figures 1 and 2.

The carrier resin concentration in both cases is in the double-digits. If this carrier resin has a similar melt flow rate (MFR) or intrinsic viscosity (IV), molecular weight, and random or homopolymer construction, the properties may not change significantly. Several experiments to evaluate effects of different carrier resins have been done in an injection molding grade of polypropylene (PP).

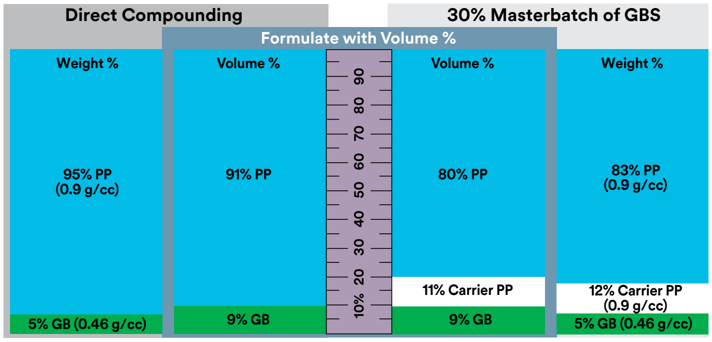

Figure 1. Directly Compounded 5% 3M™ Glass Bubbles vs. Masterbatch Addition of 3M™ Glass Bubbles – Carrier Resin wt. and Vol. % Implications.

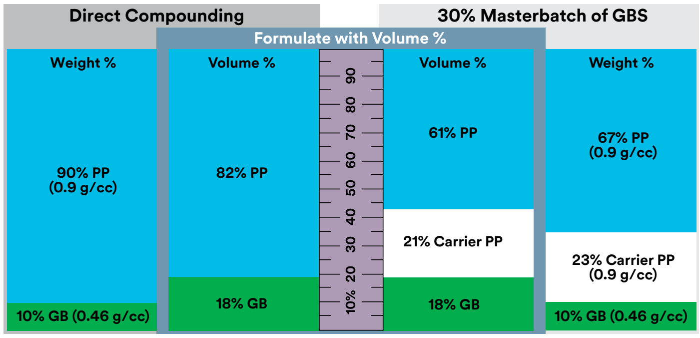

Figure 2. Directly Compounded 10% 3M™ Glass Bubbles vs. Masterbatch Addition of 3M™ Glass Bubbles – Carrier Resin wt. and Vol. % Implications.

Experimental, Results and Discussion

A series of compounds containing 5 and 10 wt. % glass bubbles (3M™ Glass Bubbles iM16K) were made using a 35 MFR high impact co-polymer PP as the host resin. Since heat history can change physical properties of PP, the "Control" was the host resin (high impact co-polymer PP) pellets, as received (without glass bubbles), extruded at the same conditions as the "Directly Compounded" (with bubbles) experimental formulation. Glass bubbles were added neat, via a side stuffer, and directly compounded into the host resin or into the masterbatch carrier resin. The masterbatch carrier resins were either the same or different MFR and different type (homo- vs. co- polymer) 3M glass bubbles as the host resin, or were altogether different in composition (polyethylene, elastomeric) to provide a functional benefit (impact modification) to the final compound. These materials are described in Table 4. The compounds were tested for physical properties as listed in Table 5.

Name in Graphs	Host Resin (wt. %)	MB (wt. %)	GB (wt. %)	Carrier Resin	Carrier Resin (wt. %)
Control	100	–	–	–	–
100 MFR PP MB	83.3	16.7	5.0	100 MFR PP	12.0
100 MFR PP MB	66.7	33.3	10.0	100 MFR PP	23.0
35 MFR PP MB	83.3	16.7	5.0	35 MFR PP	12.0
35 MFR PP MB	66.7	33.3	10.0	35 MFR PP	23.0
5 MFR PP MB	83.3	16.7	5.0	5 MFR PP	12.0
5 MFR PP MB	66.7	33.3	10.0	5 MFR PP	23.0
IM#1 MB	83.3	16.7	5.0	Impact Modifier #1	12.0
IM#1 MB	66.7	33.3	10.0	Impact Modifier #1	23.0
IM#2 MB	83.3	16.7	5.0	Impact Modifier #2	12.0
IM#2 MB	66.7	33.3	10.0	Impact Modifier #2	23.0

Table 3. Experimental Formulations

Carrier ID	Description	Functional Benefit
100 MFR PP MB	High Flow Impact Copolymer PP	Ease of Dispersing GB
35 MFR PP MB	High Impact Copolymer PP	Same as Host
5 MFR PP MB	General Purpose Homopolymer PP Pro-Fax™* 6523	Improve MW Related Physical Properties
IM#1 MB	Polyolefin Elastomer Engage™** 8137	Improve Impact Strength
IM#2 MB	Proprietary 3M Polymer	Improve Impact Strength

* Pro-Fax resins are produced by LyondellBasell Industrial Holdings B.V.
** Engage is a registered trademark of Dow Chemical Company.

Table 4. Experimental Formulations

Physical Property	ASTM Test Method
Flexular Strength and Modulus	D790
Notched Izod Impact	D252
Tensile Properties	D638
MFR	D1238-10

Table 5. Physical Property Testing was Done in Accordance with ASTM

A Prism 24 mm twin-screw extruder was used for compounding the 3M™ Glass Bubbles into the resins. The glass bubbles were added downstream using a side stuffer. The feedthroat was water cooled and the 6 zone extruder was controlled at a flat temperature profile of 210°C. A general-purpose injection molding machine (Boy 22M) with a three-zone screw (feed, compression and metering) was used to injection mold ASTM test specimens for physical property measurements.

Talc or other reinforcing fillers are often added to PP to boost physical properties. To see the effect of the masterbatch carrier resin, without confounding the data with changes in volume % of the reinforcing filler, the control used was the 35 MFR impact co-polymer PP without talc. Optimized formulations for the glass bubbles with talc, glass fiber, impact modifier, compatibilizers and coupling agents have been previously reported [3, 4, 5].

Figure 3 shows the effect of the different carrier resins on tensile strength. The 100 and 35 MFR PPs were essentially the same as the "Direct Compounding" tensile strength of 16 and 15 MPa for 5 and 10 wt. % of glass bubble respectively. The effect of higher MW can be seen for the 5 MFR PP. The tensile increased roughly 15% at both concentrations. As expected, the softer, more elastic impact modifiers IM#1 and IM#2 had significant reductions in tensile strength, especially when high volume % of carrier resin was brought in with the 10% glass bubble concentration (loss of up to 50%). The addition of the glass bubble inorganic particulate does reduce tensile strength but this can be overcome with optimized formulations as discussed in other articles [3, 4, 5].

Figure 4 shows the effect on elongation for the different carrier resins. In this high impact 35 MFR host resin, there's actually a slight improvement in elongation when directly compounding in glass bubbles at 5 wt. %. Note the fall-off however at the 10 wt. % level due to removal of a significant vol. % of resin. There is also a major improvement in elongation when the higher MW 5 MFR carrier resin is used (4 and 6.5X respectively for 5 and 10 wt. % loadings). As expected the more elastic impact modifier carrier resins significantly improve elongation as well. Note this testing deviates from the ASTM methodology and uses the crosshead travel distance to calculate the % elongation. Slippage effects may play a role but the control matches the resin's technical datasheet exactly.

The effect on flexural and tensile modulus, or stiffness, is as expected with the addition of significant vol. % loadings of stiff glass bubbles and/or elastic carrier resins. Figures 5 and 6 show the tensile and flexural modulus data respectively. There is little difference for this property at the 5 wt. % glass bubble loading within the different MFR PP systems. Interestingly, there is a significant difference to the 35 MFR host system for both higher (100 MFR) and lower (5 MFR) carrier resins at the

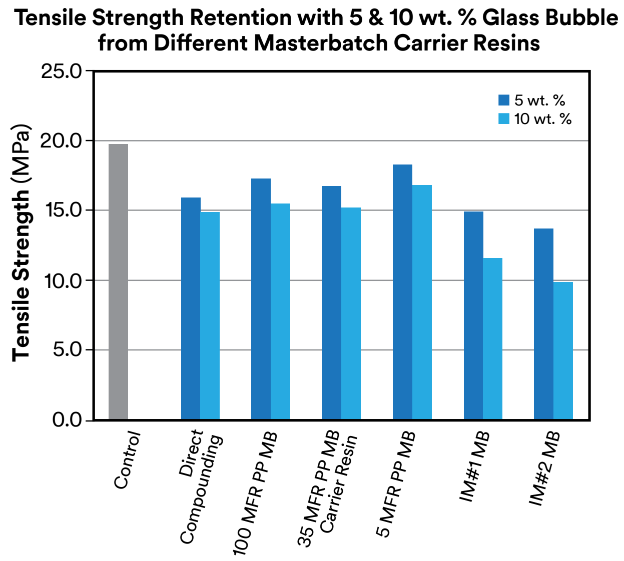

Figure 3. Tensile Strength Retention with Different Masterbatch Carrier Resins

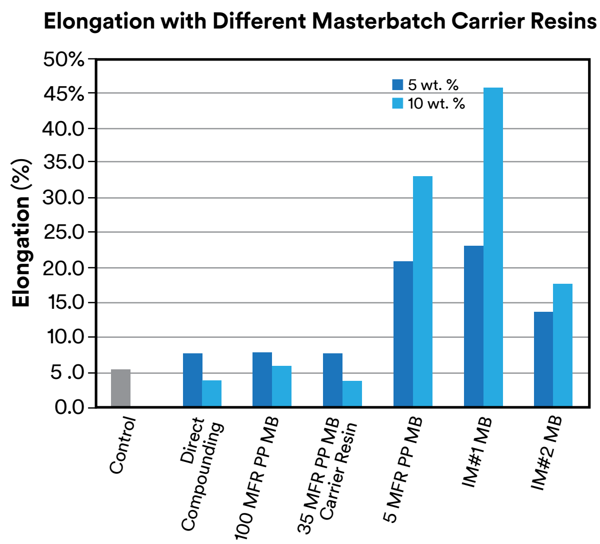

Figure 4. Tensile Strength Retention with Different Masterbatch Carrier Resins

10 wt. % glass bubble loading. This is seen in both tensile and flex modulus. The soft, elastic impact modifiers significantly reduce modulus, as expected, especially with high vol. % loading when adding 10 wt. % glass bubble.

Impact properties were modified significantly with both glass bubble addition and carrier resins. Figure 7 shows room temperature Izod impact properties. Within the different MFR PP carrier resins there was one significant deviation from the "Direct Compounding" value - the 100 MFR carrier adding 5 wt. % glass bubble. Otherwise all of the other values were within error of each other. The Engage™ 8137 worked extremely well and produced an impact result that was significantly higher than the "Control" especially with 10 wt. % glass bubble loading bringing in 23 vol. % of impact modifier. Usually, when formulating with glass bubbles, this impact modifier is added at around 5 wt. % to bring properties back to the level of the control. As a product concept – an impact modifier carrier resin for glass bubble addition at the press – this is probably over engineered and costly. The proprietary 3M impact modifier also boosted room temperature impact but not to the level of the Engage™ 8137 material.

Cold temperature (-30°C) impact, shown in Figure 8, showed similar results with respect to the different MFR PPs as the room temperature data. Interestingly, the impact modifiers switched with respect to performance at -30°C. The proprietary 3M impact modifier was significantly better than Engage and almost brought the impact back to the level of the "Control".

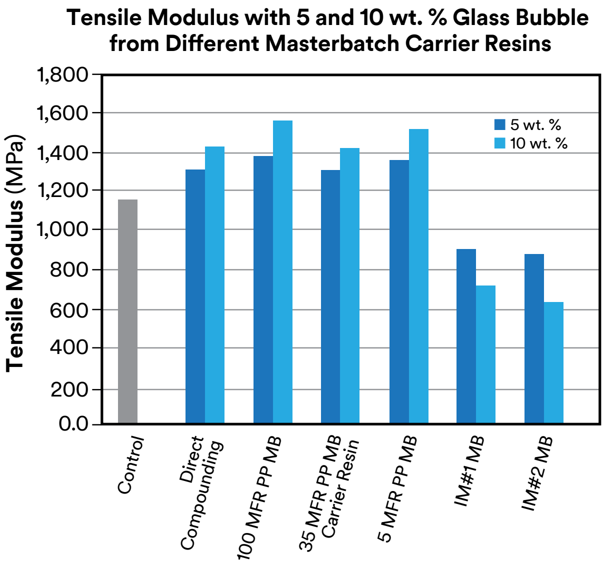

Figure 5. Tensile Modulus Changes with Different Masterbatch Carrier Resins

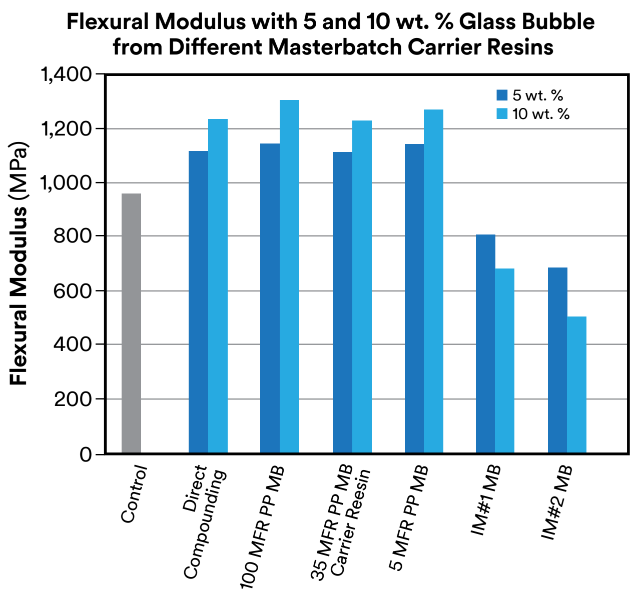

Figure 6. Tensile Strength Retention with Different Masterbatch Carrier Resins

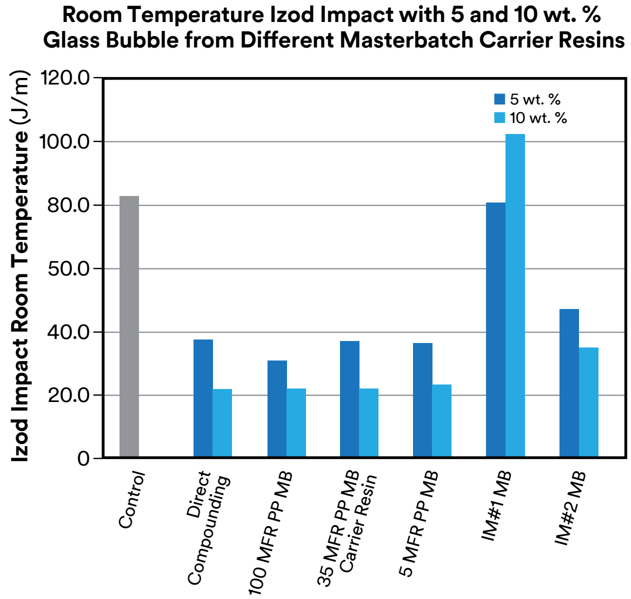

Figure 7. Room Temperature Izod Impact Changes with Different Masterbatch Carrier Resins

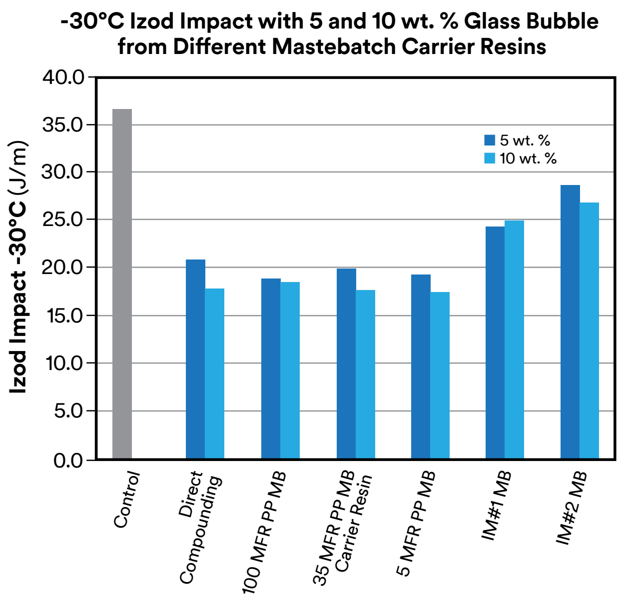

Figure 8. -30°C Izod Impact Changes with Different Masterbatch Carrier Resins

Conclusions

3M™ Glass Bubbles can be added at the press using a high concentration masterbatch without significant differences compared to direct compounding. The choice of masterbatch carrier resin is important. Using a carrier that is similar in MW/MFR to the host resin will bring the closest match to direct compounding properties.

There is an opportunity to use the carrier resin as a functional component of the compound. In this series of experiments, the use of an impact modifier as a functional carrier did exactly what it was prescribed to do – improve impact – but had higher fall off in properties in expected areas such as strength and stiffness.

Acknowledgement

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