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Technical Paper

3M™ Glass Bubbles iM16K for Reinforced Thermoplastics

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Introduction

Additives, especially inorganic solid particulates, have greatly contributed to the growth of the polymer industry. They render polymers with improved properties (e.g. mechanical, physical, electrical, thermal), depending on their geometry and chemistry.

3M™ Glass Bubbles are finely dispersed, free-flowing powders consisting of thin-walled (0.5 – 1.5 µm) spherical soda lime borosilicate glass particles with an average diameter of 16 – 65 µm. Glass bubble technology has taken strong leaps in achieving a high "strength to density ratio," resulting in the recent development of 3M™ Glass Bubbles iM16K (Table 1) for use in demanding polymer processing operations for various plastic and rubber parts and applications.

Properties	Value
True Density	0.46 ± 0.03 g/cc
Isostatic Crush Strength (3M QCM 14.1.83M)	Min. 16,000 psi @ 90% survival
Hardness	Mohs scale 5
Softening Temp	>600°C
Typical D10 Diameter	12 µm
Typical D50 Diameter (Median)	20 µm
Typical D90 Diameter	30 µm
Packing Factor	58%

Table 1. Properties of 3M™ Glass Bubbles iM16K

Figure 1 shows the morphology of glass bubbles via scanning electron microscopy in comparison to various other fillers frequently used in plastic resin systems. A perfectly spherical shape with an aspect ratio of one makes glass bubbles efficient volume fillers because they can be incorporated at very high volume loadings (e.g. 45 vol%) without increasing the viscosity to unacceptable levels for further polymer processing and shaping operations.

Fillers with high geometrical anisotropy, on the other hand, are more efficient for reinforcing composites (i.e. increasing modulus and strength) compared to glass bubbles. This is because fibrous (e.g. glass fiber, wollastonite) and platy (e.g. talc, mica, nanoclay) fillers have large aspect ratios (20 to 50) and surface areas and tend to align preferentially in the process flow direction. These fillers also cause orientation of the polymer molecules during high shear processes such as injection molding. Preferential orientation seen in high aspect ratio fillers can introduce challenges in dimensional stability such as decreased shrinkage in the in-flow relative to the cross-flow direction, causing warpage. Glass bubbles, when used with other reinforcing fillers in an optimized formulation, can provide excellent weight reduction, performance, processing and dimensional stability characteristics.

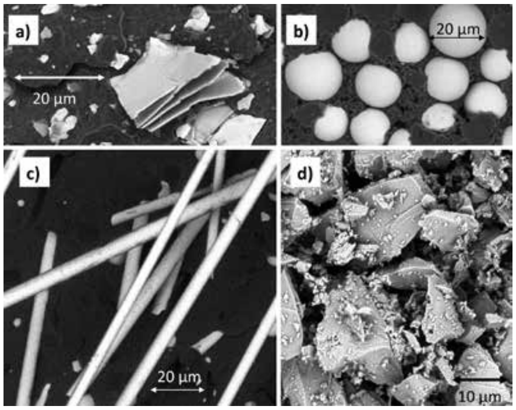

Figure 1. Scanning electron microscopy images:
a) talc; b) glass bubbles; c) glass fibers; and d) calcium carbonate.

In this paper, we provide starting formulation guidelines for glass bubbles in the presence of other fillers and demonstrate the benefits discussed above.

Materials

Two homopolymer polypropylene (PP) resins and two Nylon resins were used in this study. The polypropylene resins were manufactured by Lyondell Basell. One of the PP resins was a general purpose homopolymer PP (under the trade name Pro-fax™ 6523) with a melt flow rate of 4.0 g/10min (230°C, 2.16 kg); the other grade was a high stiffness PP (under the trade name Adstif™ HA840R) with a melt flow rate of 20.0 g/10min (230°C, 2.16 kg). Both resins had a solid density of about 0.90 g/cm^3. The Nylon 66 resin was manufactured by DuPont under the trade name Zytel® 101. The Nylon 6 used was Schulamid® 6 from A. Schulman Company; this was primarily used for the mold cycle time study and dimensional stability studies. A maleic anhydride grafted PP (MAPP) homopolymer (Polybond® 3200) was used as a compatibilizer and provided by Chemtura. Glass fibers used in this study were manufactured by PPG under the trade name ChopVantage® HP3299 for polypropylene and ChopVantage® HP3540 for Nylon resin. Jetfine® 3CC Talc was provided by Imerys. The glass bubbles used were 3M™ Glass Bubbles iM16K, with a density of 0.46 g/cc.

Note: The purpose of this paper is to provide basic information to product users for use in evaluating, processing and troubleshooting their use of 3M™ Glass Bubbles. The information provided is general or summary in nature and is offered to assist the user. The information is not intended to replace the user's careful consideration of the unique circumstances and conditions involved in their use and processing of 3M products. The user is responsible for determining whether this information is suitable and appropriate for the user's particular use and intended application.

Processing

Samples were compounded in a co-rotating intermeshing 1 inch twin screw extruder (L/D: 25) equipped with 7 heating zones (Figure 2). Polymer resin was starve-fed in zone 1 via a resin feeder and passed through a set of kneading blocks to ensure its complete melting before glass bubbles were side fed downstream in zone 4. At the point of glass bubble side feeding as well as for the rest of the downstream processing, high channel depth conveying elements (OD/ID: 1.75) were used. This is an important processing tip for attaining a high survival rate for glass bubbles. Glass fibers were introduced in zone 6 via a volumetric feeder through top feeding ports.

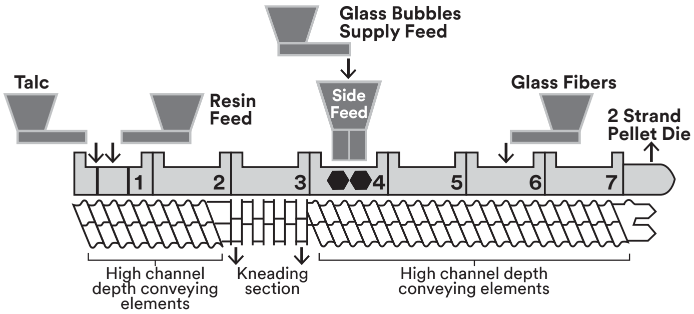

Figure 2. Compounding Set-up

Zone 1 was the hopper region and cooled with water. For Nylon (and PP) the temperatures in zones 2 to 7 were set to 250 (180), 280 (220), 280 (220), 280 (220), 280 (220), 280 (220)°C respectively. The die temperature was set to 280°C and 220°C for Nylon and PP, respectively. The screw rotation speed was set to 250 rpm in both cases. The extrudate was cooled in a water bath and pelletized.

All samples were molded using a BOY22D injection molding machine with a 28 mm general purpose barrel and screw manufactured by Boy Machines Inc. A standard ASTM mold with cavities for tensile, flex and impact bar was used for all molded parts.

Characterization

A Micromeritics AccuPyc™ 1330 Helium Gas Pycnometer was used to measure density for all samples. Mechanical properties of the injection-molded composites were measured using ASTM standard test methods listed in Table 2. An MTS frame with a 5kN load cell and tensile and 3 point bending grips were used for tensile and flexural properties, respectively. A Tinius Olsen model IT503 impact tester and its specimen notcher were used to measure room temperature Notched Izod impact strength of the molded parts. A Tinius Olsen MP200 extrusion plastometer was used for melt flow index testing on samples.

Test (Unit)	Abbr.	ASTM #
Tensile Modulus (MPa)	TM	D-638
Tensile Strength at yield (MPa)	TS	D-638
Elongation at break (%)	EL	D-638
Notched Izod Impact (J/m)	NI	D-256
Flexural Modulus (MPa)	FM	D-790
Flexural Strength at yield (MPa)	FS	D-790
Melt Index (g/10 min @ 230°C, 2.16 kg)	MI	D-1238

Table 2. Property Test Methods

Mold Cycle Time Analysis

An experimental setup with an IR camera was constructed to measure the effect of 3M™ Glass Bubbles iM16K on the cooling rate of polypropylene in injection molding. Temperature image of the molded samples were taken using a FLIR ThermaCAM™ P65 camera and analyzed by FLIR QuickReport software. Images were always taken at precisely 15 seconds; this interval included mold opening time, part ejection and placing the ejected part in front of the camera in a marked location. This ensured that all parts experienced the same cooling history before their thermal images were taken. An area average temperature was determined on each tensile bar. An average of 10 tensile bars was taken for each formulation. Since thermal imaging cameras work on the principal of thermal emissivity, it was necessary to take into account the thermal emissivity of molded parts for each formulation. This was done by adjusting the thermal emissivity parameter on the IR camera to match the temperature shown on a black material with a known thermal emissivity at 135°F. Cooling time was determined from the following equation, which is a function of melt, coolant (mold) and ejection temperatures.

$$\text{Where} \quad t_c = \frac{h^2}{\pi^2 \alpha} \, ln \left(\frac{4}{\pi} \, \frac{T_{melt} - T_{mold}}{T_{eject} - T_{mold}} \right)$$

T_c: theoretical minimum cooling time

h: thickness of the part

α: thermal diffusivity of the part

T: temperature

Dimensional Stability (Differential Shrinkage)

Dimensional stability, i.e. differential shrinkage, was evaluated by SKZ Institute (Wurzburg, Germany) in an independent study according to DIN EN ISO 294-4.

Results and Discussions

Glass Bubbles in Unfilled PP

Let us first review the effect of glass bubbles in the absence of other fillers. Mechanical properties of a low impact general purpose homopolymer PP without (Formula 1) and with glass bubbles at 20 wt% (Formulas 2 and 3) are shown in Table 3. Figure 3 shows a SEM image of PP with 20 wt% loading of glass bubbles iM16K. The difference between Formulas 2 and 3 is the presence of a compatibilizer (MAPP) in Formula 3.

Property	Formula 1 PP		Formula 2 PP-GB		Formula 3 PP-GB-MA	
	wt%	vol%	wt %	vol%	wt%	vol%
PP-General Purpose	100	100	80	69	76	65.8
Glass Bubbles	–	–	20	31	20	30.8
MAPP	–	–	–	–	4	3.4
Density (g/cc)	0.9		0.785		0.785	
TS @ RT	30		16.1		28.7	
TS @ 90°C	10.1		7.7		13.5	
TM @RT	1195		1974		1830	
TM @ 90°C	162		340		300	
FS @RT	37.9		32.5		49.2	
FM @1 % secant	1063		1585		1740	
NI @ RT	38.5		20.9		30.3	
MI	5.8		2.6		2.6	

Table 3. Properties of General Purpose Homopolymer PP-Glass Bubble Composite

The density of polypropylene is reduced from 0.9 g/cc to 0.785 g/cc at 20 wt% (~30 vol%) glass bubble loading while increasing its modulus ~60% (Formula 2). The absence of filler and polymer chain orientation combined with polar glass bubble to nonpolar PP incompatibility results in a decrease of tensile and flexural strength (at yield), as seen in Formula 2. Fortunately, compatibilizers such as maleated PP can increase adhesion between the polar glass and nonpolar PP, similar to that seen in glass fibers, recovering the loss in tensile and flex strength and even exceeding the original values for flexural strength, as seen in Formula 3. Compatibilizers also help recover the decrease in impact strength for low impact homopolymer PP. In high impact copolymer PP, the reduction in impact strength with glass bubbles can be compensated for via the use of various impact modifiers, preferably maleated alpha-olefin copolymers.

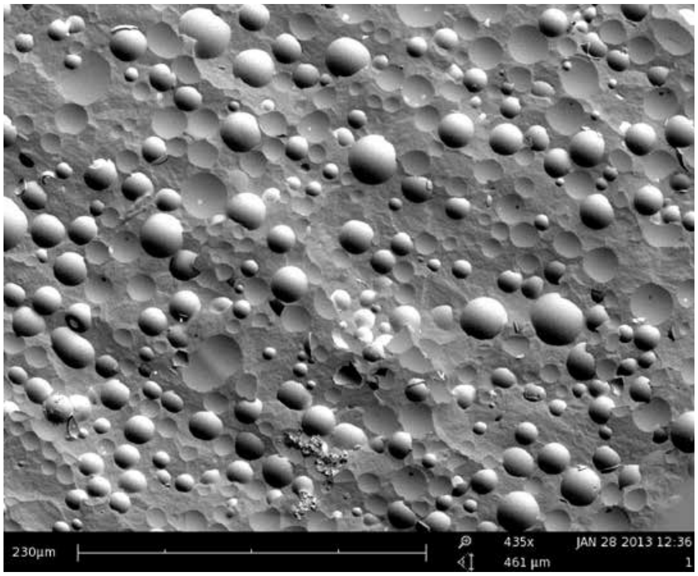

Figure 3. SEM image of PP with 10 wt% talcand 4 wt% 3M™ Glass Bubbles iM16K

Glass Bubbles in Glass Fiber Reinforced PP and Nylon

The combination of glass fibers and glass bubbles is an excellent solution for highly reinforced plastics with good dimensional stability. However, formula optimization is crucial to attaining acceptable mechanical properties. Tables 4 and 5 show optimized formulation with glass bubbles in glass fiber-reinforced high crystallinity polypropylene (HC-PP) and Nylon 66, respectively. The density was reduced from 1.046 g/cc to 0.927 g/cc in HC-PP while maintaining most of the mechanical properties (Table 4). The flexural modulus was increased 15%. Figure 4 shows an SEM image of this sample.

Table 5 shows 30 wt% glass fiber-reinforced Nylon 66 reformulated with glass bubbles iM16K. It is important to note that glass fiber content is not substantially reduced in the glass bubble-containing formulas in Tables 4 and 5. This is because glass fibers are efficient reinforcers of polymers, i.e. they increase tensile and flex strength more effectively compared to glass bubbles. In addition, in low impact polymers such as homopolymer PP or high crystallinity PP, glass fibers improve the impact strength of the composite since process oriented fibers form a barrier to crack propagation.

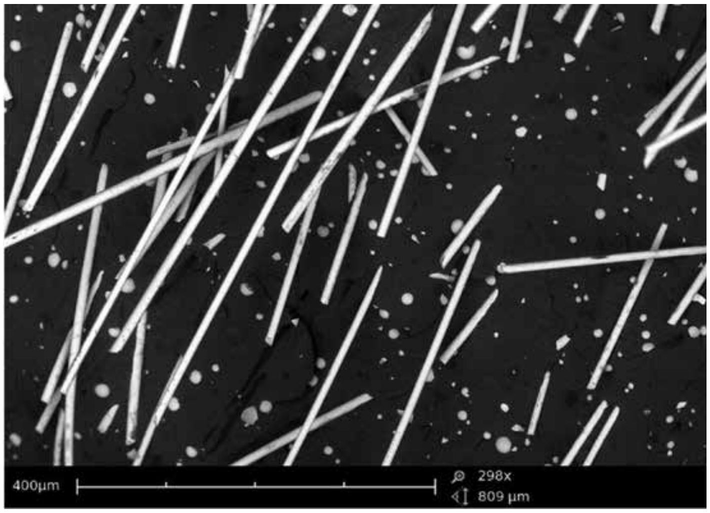

Figure 3. SEM image of 19 wt% glass fiber, 10 wt% glass bubbles iM16K in PP

Property	Formula 1		Formula 2	
	wt%	vol%	wt %	vol%
HC- PP	78	91	68.36	70.14
Glass Fiber	22	9	19	7.12
Glass Bubbles	–	–	10	20.06
MAPP	–	–	2.64	2.68
Density	1.046		0.927	
TM @ RT	4050		3960	
FS @ RT	100		94	
FM @ 1% secant	2606		3020	
NI (J/m)	54.5		51.8	

Table 4. Properties of High Crystallinity PP-Glass tFiber-Glass Bubble Composite

Property	Formula 1		Formula 2		Formula 3	
	wt%	vol%	wt %	vol%	wt%	vol%
Nylon 66	70	83.9	65	71.4	60	60.8
Glass Fiber	30	16.1	30	14.7	30	13.6
Glass Bubbles	–	–	5	13.9	10	25.6
Volume % Glass	16.1		28.6		39.2	
Density (g/cc)	1.37		1.253		1.152	
FM @ RT	7370		7660		8125	
FS@ RT	266		250		235	
NI at RT	90		87.5		78.5	

Table 5. Properties of Nylon 66 Composite with 30 wt% Glass Fiber and Glass Bubbles

Glass Bubbles in Talc Reinforced PP

When formulating in polymers containing talc, it is recommended that glass bubbles partially replace talc while maintaining the original volume loading of the resin. Table 6 shows well-balanced mechanical properties when used along with talc.

Component	Formula 1 PP-T20		Formula 2 PP-T10 GB4		Formula 3 PP-T10 GB4-M	
	wt%	vol%	wt %	vol%	wt%	vol%
PP-Homo	80	92.5	86	88.6	83	85.5
Glass Bubbles	–		4	8	4	8
Talc	20	7.5	10	3.4	10	3.4
MAPP	–	–	–	–	3	3.1
Density	1.046		0.942		0.943	
TS @ RT	31.7		27		32.7	
EL (%)	10		40		12	
TM@ RT	2110		1900		1835	
FS @ RT	49		45		50	
FM @1 % secant	1650		1620		1620	
NI	32		28		39	

Table 6. Properties of General Purpose Homopolymer PP-Glass Bubble-Talc Composite

Figure 5 shows a magnified SEM image of PP with 10 wt% talc and 4 wt% glass bubbles. One can clearly see talc platelet edges oriented in the flow direction.

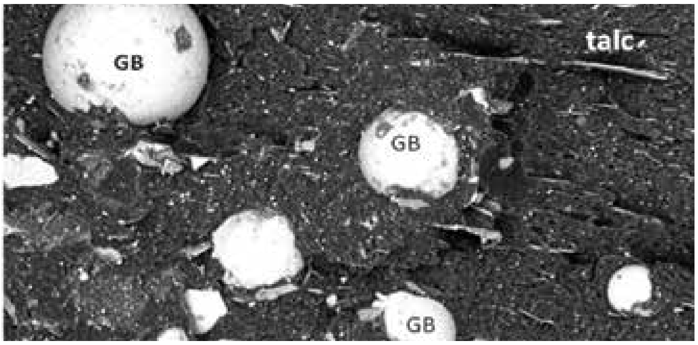

Figure 5. SEM image of PP with 10 wt% talc and 4 wt% glass bubbles

Improved productivity through faster cooling

Cooling of injection molded parts is very important to the economics and operation of the molding process. Long cooling times incur additional manufacturing costs and can limit production capacity. Glass bubbles can decrease mold cycle times by causing the parts to cool faster in the mold. Figure 6 shows thermal images of molded PP parts containing various loadings of 3M™ Glass Bubbles iM16K taken 15 seconds after part ejection. The temperature of the ejected part is reduced from 90°C to 68°C when the glass bubble loading is increased from 0 to 20 wt%, demonstrating that the parts cool faster with glass bubbles. Reduction in temperature is roughly 1.1°C per each wt% of glass bubbles added into the formulation. Table 7 shows calculated cooling time to reach an eject temperature of 90°C as a function of glass bubble loading. We can see in Table 7 that cooling time could be reduced up to 37% by the addition of glass bubbles.

This increased cooling observed in formulations containing glass bubbles can be explained by their effect on the thermal diffusivity of the part. An increased glass bubble weight fraction decreases composite density and composite specific heat capacity, which in turn increases thermal diffusivity and hence cooling rates. Composite density decreases because glass bubbles are lower in density than polymers. Composite specific heat capacity decreases because the specific heat capacity of glass (~750 J/kg K) is lower than that of most thermoplastic materials (1500 to 3500 J/kg K).

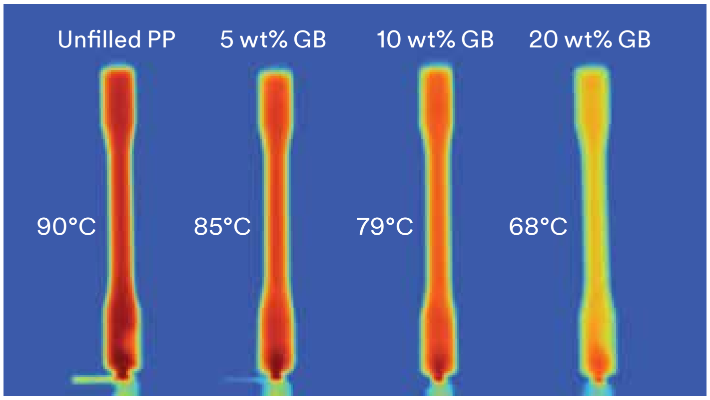

Figure 6. Thermal images of molded PP parts containing various loadings of 3M™ Glass Bubbles iM16K. Images taken 15 seconds after part ejection.

Material	GB Loading	Other Fillers	Cycle Time (sec)	Cycle Time Reduction (%)
Unfilled PP	0	–	16	–
	5 wt%	–	14.7	8.2
	10 wt%	–	13.1	18
	20 wt%	–	10	37
Glass Fiber-Filled PP	0	15 wt%	16	–
	5 wt%	15 wt%	13.5	15.3
	7 wt%	18 wt%	12.1	24
Talc-Filled PP	0	20 wt%	16	–
	4 wt%	10 wt%	15	6

Table 7. Effect of 3M™ Glass Bubbles iM16K loading on cycle time in various polymer systems

In injection molding, shrinkage and warpage constitute major challenges and can result in decreased productivity. Glass bubbles decrease the degree of shrinkage and warpage observed in parts where high aspect ratio fillers are used. An example is shown in Figure 7 for glass fiber-filled Nylon 6. Due to their isotropic geometry, glass bubbles do not orient in a certain direction and help prevent warpage due to orientation. As shown in Figure 7, Nylon 6 formulated with glass bubbles has the lowest differential shrinkage, followed by the glass bubbles-glass fiber hybrid composite. The highest differential shrinkage was observed in Nylon 6 composite containing 30 wt% glass fiber. Glass bubbles also allow the material to cool homogeneously, preventing differential shrinkage due to uneven solidification of the part.

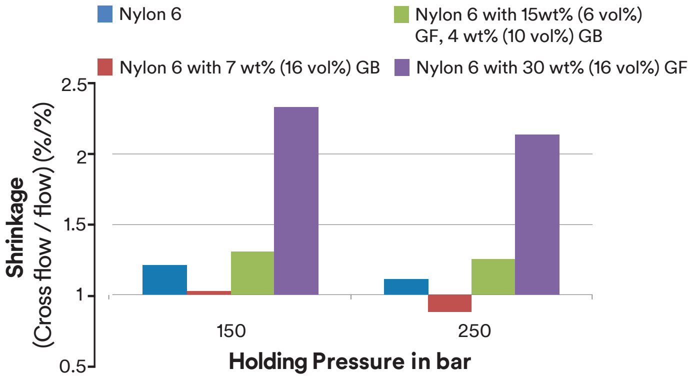

Figure 7. Differential Mold Shrinkage

Conclusions

3M™ Glass Bubbles render polymers with lower density, which is crucial in weight sensitive industries such as transportation and aerospace. In addition to weight reduction, glass bubbles reduce shrinkage by offsetting some volume of the molded plastics. Glass bubbles also contribute to faster cooling from the melt by reducing density and hence the overall volumetric heat capacity of the part. This can result in shorter injection mold cycle times or increased extrusion throughput. In this paper we have shown some of these benefits gained by using 3M glass bubbles, along with compounding suggestions.

Some of the other attributes that can be attained via the use of glass bubbles in polymers include reductions in coefficient of thermal expansion (CLTE) and thermal conductivity, along with increases in bulk modulus, hardness, scratch resistance, and heat distortion temperature. These attributes are affected by the formulation, which is essential to maintaining an acceptable balance of weight, performance and processing characteristics – especially in filled polymers.

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