

‘Plug-and-Play’ Weight Reduction Solution by Hollow Glass Microspheres

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Introduction

Fillers have been in use since the early days of plastics. Today’s enormous growth of the polymer industry is due to the unique properties that fillers impart to polymers. Glass bubbles (low density hollow glass microspheres) as fillers have been incorporated into thermoset polymers for decades. They are tiny hollow spheres and are virtually inert. These glass bubbles (GB) are compatible with most polymers. Until recently, their use with thermoplastic polymers has been limited because of high rates of bubble breakage from the high shear forces that they are exposed to during such thermoplastic processing operations as extrusion compounding and injection molding. At issue has been the strength of the glass microspheres.

3M has recently developed innovative glass bubbles which offer resistance to extremely high compressive and shear forces. This allows compounders, thermoformers and injection molders to use them to achieve significant weight reductions without resorting to costly equipment modifications.

This article will showcase how plastics processors could exploit the advantages of these novel glass bubbles while improving end-product properties.

Glass bubbles: Why use them in plastics compounds?

3M™ Glass Bubbles (hollow glass microspheres) (Figure 1) are weight-reducing fillers which can be incorporated into various polymers by melt compounding and processed into articles via thermoforming, blow molding, sheet casting, injection molding, etc.



Figure 1. Hollow Glass Microspheres

Compared to other heavy fillers such as talc, calcium carbonate, glass fiber, and clay (from 2.5 to 2.8 g/cc), glass bubbles for plastics and rubber applications have densities ranging from 0.1 to 0.6 g/cc (Figure 2).



Figure 2. 3M™ Glass Bubbles vs. other heavy fillers

Reducing weight has been a paramount objective in various industries, such as transportation, aerospace, and hand-held electronics. A few words on the historical trends in the transportation industry would be illustrative to set the scene.

The trend of reducing weight, which in turn reduces fuel consumption, became dominant in transportation in the mid-1970s oil crisis, which was the first such crisis to affect the Western World. Reducing weight continues to be an active research field today.

A recent historical analysis of the fuel efficiency of U.S. vehicles¹ before the mid-1970s indicated little change – indeed a net deterioration – in average miles-per-gallon (mpg) of vehicles in the U.S. between 1923 (14 mpg) and 1975 (12 mpg). The steep change in oil prices during the 1970s (Figure 3) triggered a strong interest in improving the fuel efficiency in transportation, which continues to be prevalent today and has resulted in a current fleet fuel efficiency of around 17 mpg¹. In view of the historical data, it is not surprising that the global rise in oil and energy prices in the early 21st Century triggered a renaissance of lightweight material applications. Note that current real (adjusted for inflation) oil prices are higher than what was experienced during the first oil crisis of the 1970s (Figure 3).

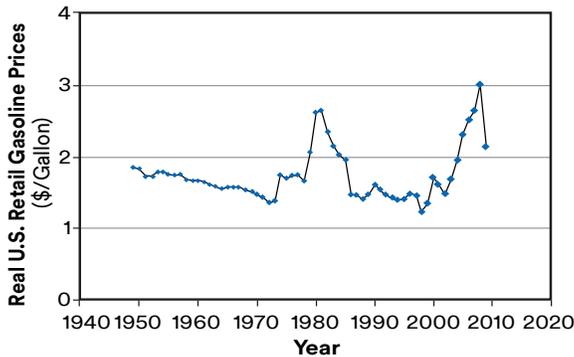


Figure 3. Real (adjusted to inflation) U.S. retail gasoline prices. The plotted data were obtained from: www.eia.doe.gov (accessed December 20, 2010).

The importance of reducing weight and its relationship to fuel consumption is illustrated in the following scenario. One may estimate that body panels, hoses, bumpers, doors, and car interior count for about 50% of the total weight of a standard passenger car. On average, about 300 lbs of filled and unfilled polymers of various densities ranging from 0.9 g/cc to 1.68 g/cc are used in these components². Table 1 summarizes the weight reductions that could be achieved in these parts at different GB wt% loadings with two grades of glass bubbles, K42HS and iM30K. The table indicates that a 50 lb to 100 lb weight reduction can readily be achieved in a car containing 300 lbs of polymeric parts. Based on a recent study, this would result in an increase of fuel efficiency up to 2%³.

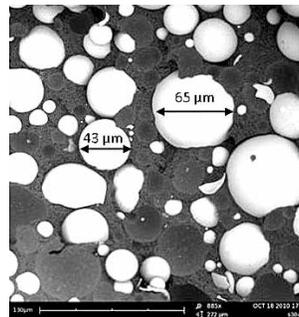
Current interest in new lightweight materials covers a broad spectrum from lightweight metals, such as aluminum and magnesium, to carbon fiber reinforced plastics. Although the majority of these are technically viable solutions, many of them pose challenges both to the producer and to the customer. New materials, such as carbon fibers, are usually significantly more expensive than traditional industrial materials and might require additional processing and assembly steps, which may increase the total cost. Most crucially, new materials usually require additional time and funds for testing, validation, and design trials, which may prolong the product launch and increase cost. 3M™ Glass Bubbles

% Weight reduction at various loading levels (initial part density – 1.1 g/cc)

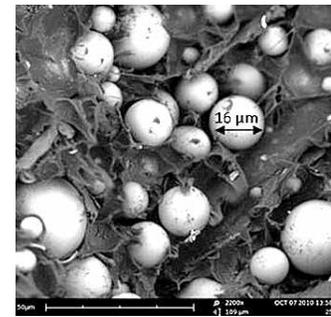
Weight % Loading	3M™ Glass Bubbles K42HS Density – 0.42 g/cc Crush Strength – 7500 psi	3M™ Glass Bubbles iM30K Density – 0.60 g/cc Crush Strength – 28000 psi
5	7.5	4.0
10	13.9	7.7
20	24.5	14.3
% Weight reduction at various loading levels (initial part density – 1.35 g/cc)		
5	10	5.9
10	18.2	11.1
20	31.0	20.0

Table 1. % weight reductions in the presence of 3M™ Glass Bubbles.

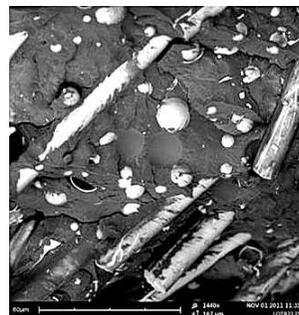
offer a ‘plug-and-play’ solution for reducing the weight of plastic parts without requiring significant material and process changes. 3M glass bubbles can be easily compounded with various polymers using conventional melt processing operations such as extrusion. The resulting compounds are strong enough that the glass bubbles will not break, even in high shear, high pressure processes like injection molding. Figure 4 shows a few examples in different polymer systems.



Matrix: Extruded Impact PP
Filler: 3M™ Glass Bubbles S38XHS (d:0.38 g/cc) at 22wt%
Final Density: 0.65 g/cc (original 0.9 g/cc)



Matrix: Extruded HDPE/Wood Profile
Filler: 3M™ Glass Bubbles iM30K (d:0.6 g/cc) at 18wt%
Final Density: 0.93 g/cc (original 1.14 g/cc)



Matrix: 30wt% GF filled Nylon 6
Filler: 3M™ Glass Bubbles iM30K (d:0.6 g/cc) at 10wt%
Final Density: 1.23 g/cc (original 1.36 g/cc)

Figure 4. Examples of polymer + 3M™ Glass bubble composite systems.

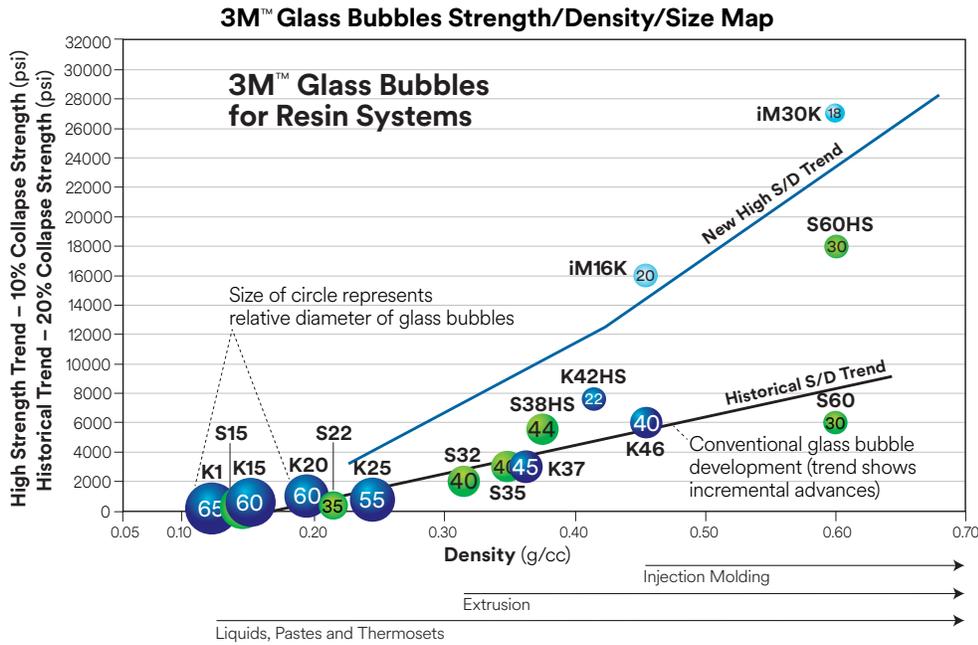


Figure 5. Isostatic crush strength vs. the corresponding true density of the 3M™ Glass Bubbles (the number in the colored circles indicates the average diameter).

The isostatic crush strength (psi) versus the corresponding true density (g/cc) of the glass bubbles are shown in Figure 5 along with their average diameters indicated in the circles.

The recently developed 3M™ Glass Bubbles such as XLD6000, L-21532 (experimental glass bubble), K42HS, and iM30K, which fall onto the “High Strength GB Trend” line in Figure 5, are optimized to improve their compressive strengths. They have noticeably smaller average particle sizes and narrower particle size distributions compared to their same density counterparts, as shown in Figure 6.

The appropriate glass bubble grade for weight reduction is typically the lowest density with the highest survival rate in a given polymer system. The base polymer resin viscosity and the level of pressure fields experienced in the process influence the survival rate of the glass bubbles. High melt viscosity materials in high pressure polymer processes (e.g., injection molding) require stronger glass bubbles such as 3M™ Glass Bubble iM30K. Nevertheless, there is no strict rule and several grades of lower density bubbles (e.g., 0.3 g/cc at 6,000 psi) can still be injection molded successfully with minimal bubble breakage provided that the conditions are set correctly. We will review process parameter considerations in the next section.

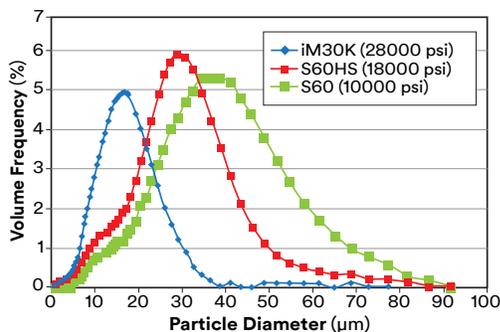


Figure 6. Comparison of the same density 3M™ Glass Bubbles (0.6 g/cc) with different particle sizes and size distributions.

Processing Considerations Extrusion compounding

Co-rotating intermeshing twin screw extruders are typically used for compounding GBs into polymers in a continuous manner. GBs are preferably introduced downstream in the extruder via side stuffing or top feeding ports into a fully molten polymer stream. This is similar to glass fiber feeding where the fiber attrition is kept to a minimum by downstream addition. The second important characteristic of appropriate extruders for GBs is the existence of high free volumes generated by deeply cut screw channels with a high Outer Diameter/Inner Diameter (Do/Di) ratio, e.g. 1.75 or more. As Do/Di increases, channel depth (h) increases. Increased channel depth translates into higher free volume, which is necessary to accommodate GBs and lower shear rates (Figure 7). This is especially important for high loadings of low density GBs at collapse strengths of 5000 psi to 8000 psi.



Where

- $\dot{\gamma}$: Shear rate in screw channel
- Do: Outer diameter of screw
- Di: Inner diameter of screw
- N: Screw speed (rev/min)
- h: Channel depth

$$h = Do - Di$$

$$\dot{\gamma} = \frac{\pi \times Do \times N}{60 \times h}$$

Figure 7. Shear rate in screw channel.

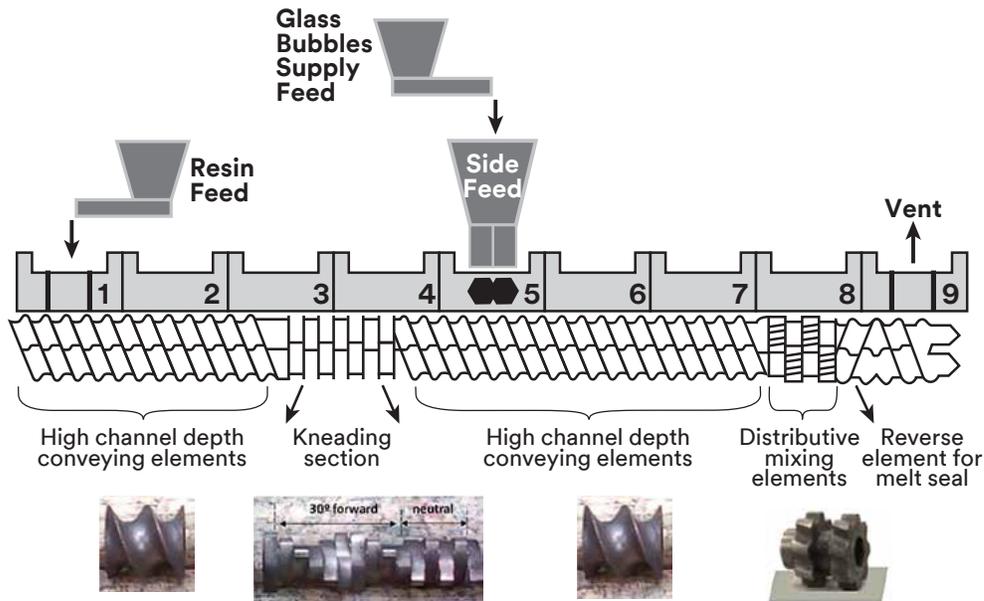


Figure 8. Screw configuration for compounding with glass bubbles

Figure 8 shows a twin screw configuration suitable for compounding with GBs. Polymer resin is starve-fed in Zone 1 via a resin feeder and passed through a set of kneading blocks to ensure its complete melting before GBs are introduced in Zone 5.

GBs should be starve-fed into a side feeder via a supply feeder. As mentioned above, it is crucial that high channel depth conveying elements (D_o/D_i : 1.75 or more) should be used in GB feed Zone 5 as well as subsequent zones. Further downstream in Zone 8, a short set of distributive elements (preferred but can be omitted if necessary) can be used. One of the advantages of GBs during compounding over fillers such as clay and calcium carbonate is their ability to distribute in the molten polymer without having to resort to aggressive kneading and distributive mixing elements. In fact, simply through mere friction from the barrel wall and conveying elements, they can distribute reasonably well. However, a short distributive section is useful especially at very low loadings of GBs. At high loadings GBs occupy the entire resin at their closest packing configuration, making distribution irrelevant. Before the compounded

material is discharged, venting following a reverse element is optional depending on the application. If the compounded pellets are to be injection molded subsequently, venting is not crucial since small amounts of trapped air during compounding can escape through the vents during injection molding.

Figure 9 shows appropriate auger configurations for GB side feeder (left) and supply feeder (right). Note that a tight melt seal is necessary for the side feeder. GBs can also be safely compounded along with various fillers such as glass fiber, talc or clay. Clay fillers should be added in Zone 1 as they need to be dispersed efficiently via the use of kneading blocks. Talc can be added either in Zone 1 or by dry blending with GBs first and together in Zone 5. Since both GBs and talc are in powder form, they do not phase separate in spite of the differences in density. However, this should be checked for each supply and side feeder auger system configuration.

Glass fibers cannot be dry blended with GB powders since they phase separate quickly due to the differences in their physical forms, i.e. chopped fibers vs. powder. Glass fibers can be added after GBs in Zone 7.

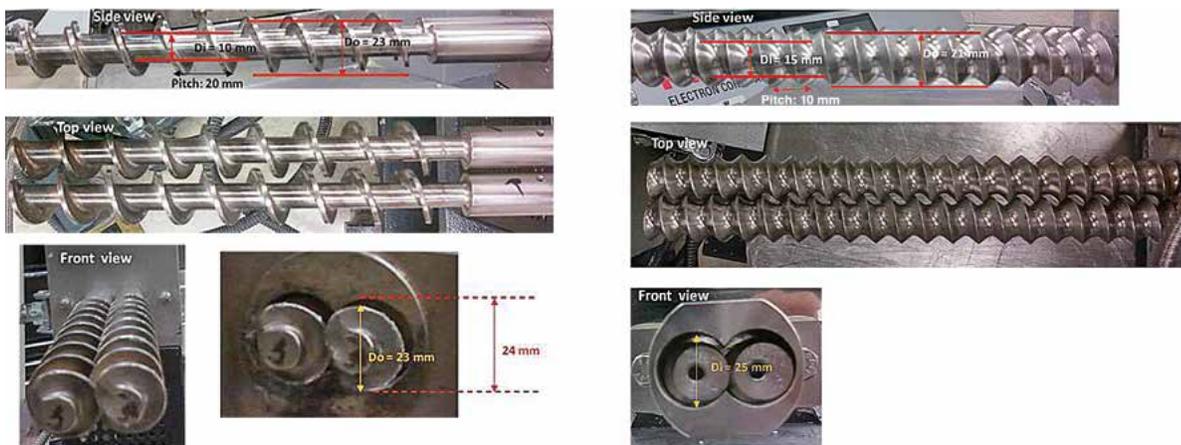


Figure 9. Auger configuration for the glass bubbles side feeder (left) and supply feeder (right)

Injection Molding

Injection molding involves high pressure fields and hence more attention is required to prevent glass bubble breakage. There are two zones in the process where bubble breakage can occur. The first one is the plasticating zones where the polymer is molten and conveyed to prepare for injection into the mold. Back pressure, which increases shearing of the polymer melt, must be set low enough to prevent glass bubble breakage but high enough to provide a compact melt and prevent air bubble formation in the plastic melt and eventually in the finished part. Next, the injection rate should be kept low enough to prevent injection pressures from exceeding the isostatic crush strength of the glass bubbles. Likewise, holding pressure should be lower than the isostatic crush strength rating of the glass bubble. Injection pressure is also determined by the intensification ratio (i.e., area of the ram/area of the screw) and should not exceed the pressure ratings of the glass bubble⁵.

A Case Study on the Properties of 3M™ Glass Bubbles in Glass Fiber Filled Nylon 6,6

Glass bubbles are excellent strength/weight optimizers when they are used in filled polymer systems such as glass fiber, talc, and calcium carbonate filled thermoplastics. Replacing a certain percentage of these high density fillers with glass bubbles results in weight reduction while maintaining the original mechanical properties. The following example is a case study with glass fiber filled nylon 6,6.

Materials

Commercially available, high strength (18000 psi isostatic crush strength), low density (0.60g/cc) glass microspheres (3M™ Glass Bubbles S60HS) were selected for these experiments. A commercially available, injection molding grade of polyamide 66 was obtained from E. I. DuPont de Nemours Company under the trade name Zytel®101LNC010. Glass fibers, PPG™ ChopVantage® 3540, with a density of 2.65 g/cc, were obtained from PPG Industries.

Compounding and injection molding

All samples were compounded in a Berstorffsm Ultra-Glide twin screw extruder (TSE 25 mm screw diameter; length to diameter ratio of 36:1) equipped with top feeders for microspheres and glass fibers (GF), a water bath, and pelletizer with the screw design shown in Figure 10. Screw speed ranged from 140 to 160 rpm. Temperature set points ranged from 500°F to 575°F. Test specimens were then molded on a 150 ton Engel injection molding machine using an ASTM four cavity mold. The screw diameter was 30 mm and the injection pressure was maintained below 18000 psi to prevent glass bubble breakage.

Testing and Characterization

Flexural strength and flexural moduli were determined according to ASTM D790. Notched Izod impact properties were determined according to ASTM D252. Tensile mechanical properties were determined according to ASTM D638. The density of the injection molded parts was determined using a helium gas pycnometer.

Results and Discussion

The results in Table 2 indicate that the presence of 3M™ Glass Bubbles S60HS significantly reduced the density of the injection molded parts. One can also note the strength/weight optimization via the use of glass bubbles in glass fiber filled nylon 6,6. Glass bubbles allow the end product properties to be retained to a large extent while decreasing the density. For instance, the formulation with the 10wt% GF and 90wt% nylon 6,6 (C-3) has a final part density of 1.20 g/cc with a tensile strength (TS) of 73 MPa, tensile modulus (TM) of 5.47 GPa, flexural strength (FS) of 147 MPa, flexural modulus (FM) of 4495, unnotched impact (UI) of 2.8 J/cm and notched impact (NI) of 0.6 J/cm. If one desires to double all of the mechanical properties, the GF content must be increased from 10wt% to 33% (see formulation C-1). This would increase the density from 1.20 to 1.39 g/cc. The doubling of these properties can also be obtained using formulation #4, with a density of 1.19 g/cc, which contains glass bubbles.

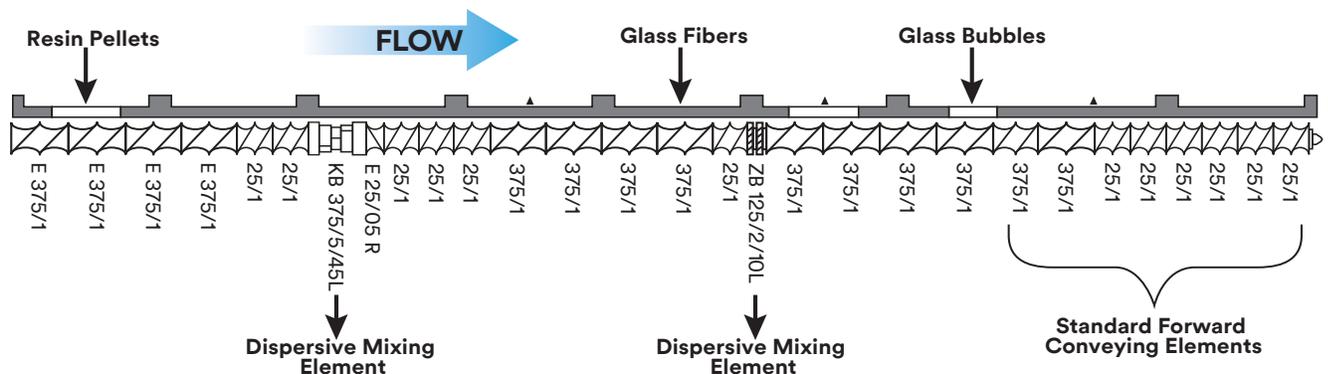
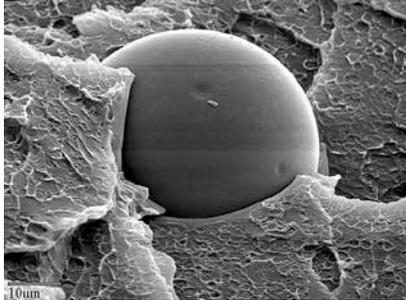


Figure 10. Extruder Screw Design For Compounding 3M™ Glass Bubbles

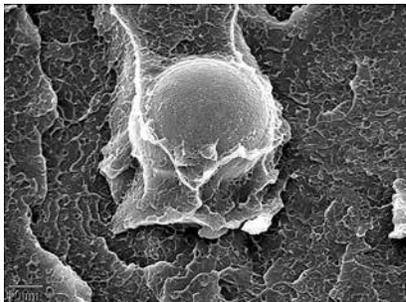
	GM	GF	Nylon	Density	Tensile Strength	Tensile Modulus	Elongation	Flexural Strength	Flexural Modulus	Unnotched Izod	Notched Izod
	wt%	wt%	wt%	g/cc	MPa	GPa	%	MPa	MPa	J/cm	J/cm
C1	0	33	67	1.39	177	11.95	2.2	280	9266	6.3	1.1
1	5	31	64	1.33	170	11.53	2.3	260	9607	7	1.4
2	10	30	60	1.28	165	11	2	239	9000	7.4	0.9
3	15	28	57	1.23	142	10.74	2.1	226	9786	6.8	1.1
4	20	26	54	1.19	132	9.08	2.1	203	9545	5.8	1.1
C2	0	20	80	1.27	108	7.95	1.8	196	6060	3.9	0.8
1	5	19	76	1.22	103	8.37	1.7	189	6393	4.3	0.9
2	10	18	72	1.18	118	8.36	2.4	184	6244	4	0.5
3	15	17	68	1.14	113	7.75	2	174	6868	4.2	0.9
4	20	16	64	1.1	99	8.69	2	160	6895	4.5	0.8
C3	0	10	90	1.2	73	5.47	1.6	147	4495	2.8	0.6
1	5	10	86	1.16	82	6.26	1.9	140	4428	2.5	0.7
2	10	9	81	1.11	80	5.42	2	136	4706	2.5	0.6
3	15	8	77	1.07	77	6.23	2	128	4800	2.3	0.6
4	20	8	72	1.03	70	6.14	1.9	116	4997	2.4	0.4

Table 2. Physical Properties of 3M™ Glass Bubbles S60HS filled Nylon 6,6 Composites.

In order to improve the properties of composites further, glass bubbles are surface treated with silanes to improve compatibility with various polymers. Figure 11 shows silane treated 3M™ Glass Bubbles iM30K, which shows improved adhesion to the polymer matrix.



Untreated Bubble



Treated Bubble

Figure 11. Scanning Electron Microscopy image showing improved adhesion to the polymer matrix via silane treatment.

Additional Benefits

There are several other benefits of adding glass bubbles into thermoplastics compounding formulations. These can be outlined as reduced cycle time in thick molded parts, decreased mold shrinkage and part warpage, and reduced coefficient of thermal expansion as discovered during numerous laboratory and plant trials. Figure 12 shows the effect of glass bubble loading on the Coefficient of Linear Thermal Expansion (CLTE) of the nylon 6,6 at different temperature intervals. 25 to 30% decrease in CLTE can be achieved in nylon 6,6 with the addition of glass bubbles up to 30 vol %. Likewise, Linear Mold Shrinkage (LMS) decreases as the amount of glass bubble loading is increased. 50% reduction in LMS is observed in injection molded polypropylene containing 30% by volume iM30K (Figure 13).

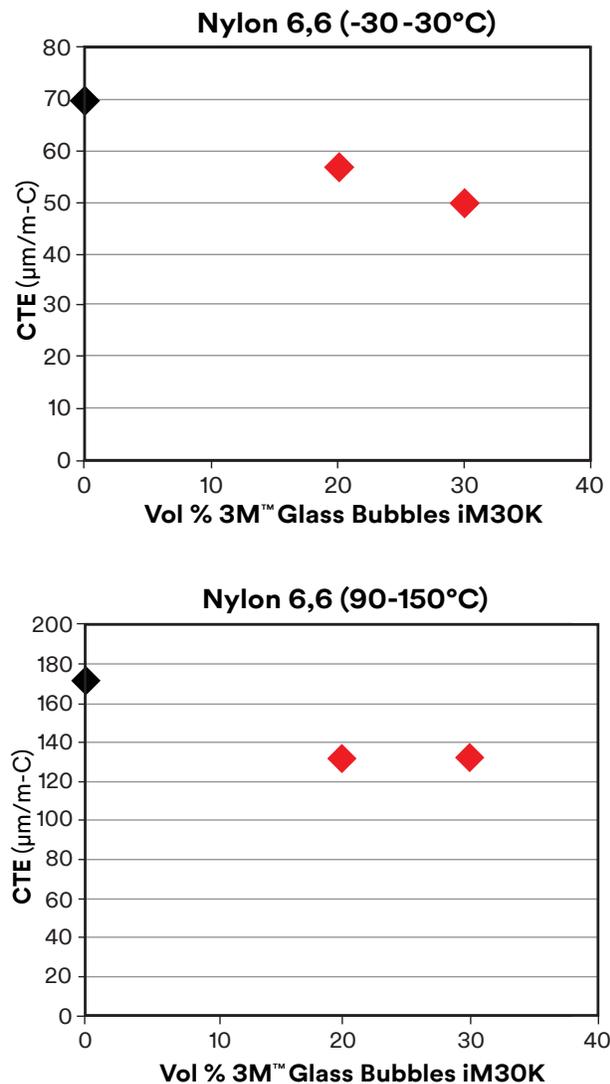


Figure 12. Coefficient of Linear Thermal Expansion (CLTE) of Nylon 6,6 as a Function of Glass Bubble Loading

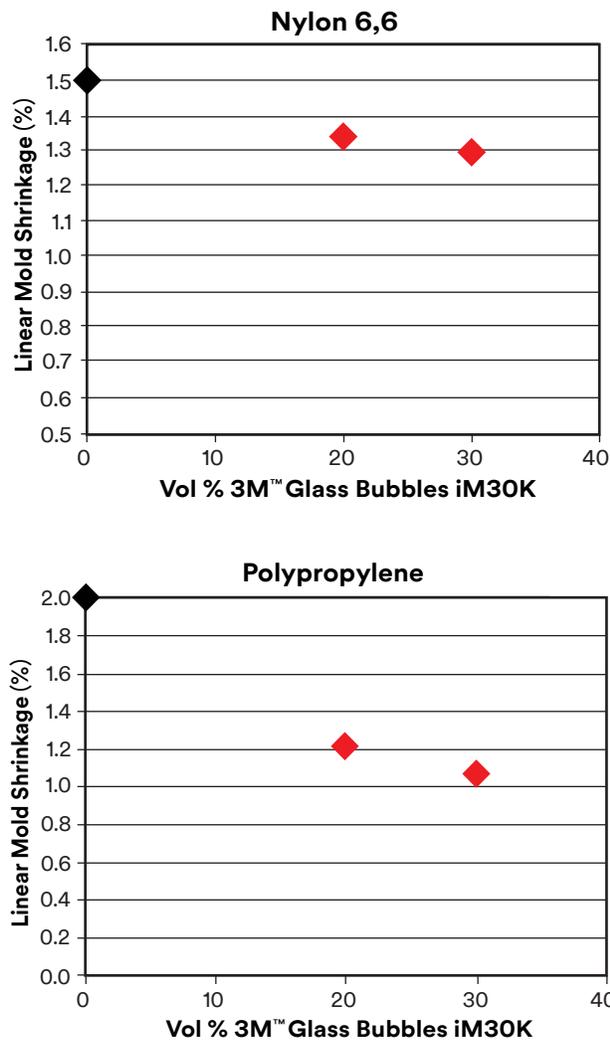


Figure 13. Effect of Glass Bubbles on Linear Mold Shrinkage

Conclusions and Future Outlook

Compounding 3M™ Glass Bubbles with polymers offers a ‘plug-and-play’ weight reduction solution. The method is rapid, cost effective, and does not require any complex material or process modification.

3M glass bubbles can be added along with high density fillers (talc, glass fiber, carbon black, calcium carbonate, etc.) to polymer composites to optimize density and mechanical strength.

In addition to weight reduction, laboratory and plant trials also indicated that additional processing and material related improvements can be achieved by the addition of glass bubbles into compounding formulations. These can be summarized as: reduced cycle time, especially in thick injection molded parts; decreased part warpage due to the isotropic nature of the fillers; reduced coefficient of thermal expansion; and decreased mold shrinkage.

References

- ¹ M Sivak, O. Tsimhoni. Fuel efficiency of vehicles on U.S. roads: 1923–2006. *Energy Policy* 37, pp. 3168-3170, 2009.
- ² N. G. McCrum, C. P. Buckley, C. B. Bucknall. *Principles of Polymer Engineering*, 2nd ed. Oxford University Press, New York, pp. 8-10, 1999.
- ³ J. Pflug, B. Vangrimde, I. Verpoest. Material efficiency and cost effectiveness of sandwich materials, SAMPE Conference, Long Beach, CA USA, 2003.
- ⁴ 3M™ Glass Bubbles iM30K Product Information, Issued by 3M Company in August 2006.
- ⁵ 3M™ Glass Microspheres Compounding and Injection Molding Guidelines, Issued by 3M Company in March 2008.

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