Innovative High Strength Glass Microspheres for Extruded and Injection Molded Plastics

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Abstract

High strength, low density glass microspheres (3M™ Glass Bubbles) have been developed and commercialized for use in extrusion and injection molding processes. The new and innovative 3M™ Performance Additives iM30K are low in density, and can survive extremely high compressive forces, providing compounders and processors with new application opportunities. This paper will detail potential extrusion processing benefits and application benefits for injection molded plastic parts containing 3M™ Performance Additives iM30K. These benefits can include low microsphere breakage, lower part weight, improved thermal expansion properties, improved processing, improved dimensional stability and reduced injection cycle times in many applications. Addition of these materials can also result in the maintenance of important thermoplastic physical properties.

Background and Requirements

Low density glass microspheres have been available as plastics additives for years. Graph 1 shows the product range available for 3M Brand glass microspheres. Application of these microspheres has been limited to those where little or no shear or compressive forces are used to form or apply the materials. Most notably are applications relating to plastisols, potting compounds and SMC/BMC[1]. Processors have had limited success incorporating these products into extruded compounds and injection molded thermoplastics. At issue has been the strength of the microsphere and its ability to survive the forces present during processing.

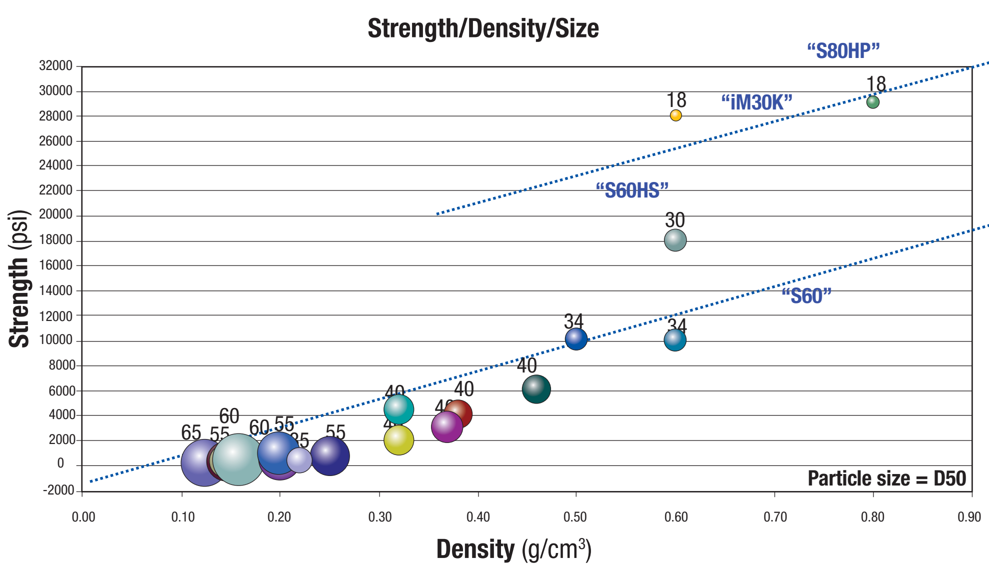
The optimum balance of strength with low density has been difficult to achieve due to trade-offs in acceptable manufacturing efficiencies to produce a microsphere with a consistent, controlled wall thickness. Through innovative process and composition developments, 3M Company has produced the first 30000 psi (~200 MPa) isostatic compressive strength glass microsphere, with a density of 0.6 g/cm^3.

The spherical shape of these microspheres allows for higher filler loading and reduced resin demand, while maintaining a low melt viscosity compared with other highly filled polymeric systems.

Data in this paper show how a new product, 3M Performance Additives iM30K, can be extruded and injection molded to provide significant weight reduction. Also shown are improvements in coefficient of linear thermal expansion and dimensional stability while maintaining important physical properties.

The ability to reduce the weight of thermoplastic materials has been pursued by engineers and designers for various reasons such as fuel economy, buoyancy, improved creep resistance and ease of handling. An example benefit for automotive plastics would be fuel economy. In 2005, approximately 3.1 million tons of plastics were consumed in producing approximately 18,362 million automobiles and light trucks in Western Europe[2]. That is about 169 kg of plastic per vehicle[3]. Assuming a 0.6 g/cm^3 microsphere was used in all plastic materials in a vehicle, providing nominally a 20% weight reduction, a 33.8 kg weight reduction per vehicle would result. The "SWR-ARD Ratgeber Auto" estimates a fuel consumption of up to 0.6 l/100 km for any extra 100 kg in a car[4]. At an average fuel consumption of approximately 7.8 l/100 km[5] about 2.6% fuel could be saved beside a reduction in CO_2 and dust emission.

Graph 1: 3M Brand Blass Microspheres Product Portfolio



Experimental, Results and Discussion

Table 1: Grades of 3M Brand Microspheres Used in Experiments

	Bubble Properties				Status
	Density	Strength*	D50	D90	
S60HS	0.6	18000	30	50	Commercial
iM30K	0.6	28000	17	32	Commercial
S80HP	0.6	30000	18	42	Experimental

*PSI for less than 10% breakage.

Experiments included 3 grades of 3M glass microspheres as detailed in Table 1 and Figure 1. Grades were selected to illuminate processing, handling and property differences. They ranged from high strength bubbles currently used in plastic applications (3M™ S60HS Glass Bubbles), to new and experimental products that are higher in strength (3M™ Performance Additives iM30K and S80HP glass bubbles). Not only are these latter two grades optimized for compressive strength but they have noticeably smaller particle size and narrower particle size distributions (Figure 1) compared with S60HS. Stronger, smaller microspheres will be able to withstand more stringent processing conditions such as higher rpm screws, higher shear rate mixers, etc. These new bubbles also show improved mechanical properties of the final composite properties as discussed below.

Extrusion of the iM30K product is more straightforward than for S60HS. Though side feeding (side stuffing) of the iM30K product downstream is still desirable, experiments adding the microspheres with resin pellets in the extruder hopper or top feeding them near the hopper have shown these approaches to be viable. Many processors and compounders are not equipped to do side stuffing or able to change screw designs. A microsphere that is robust to various processes, such as iM30K additives, can provide an economical solution for many applications. A preferred screw design showing downstream microsphere feeding, along with downstream glass fiber feeding, is shown in Figure 2.

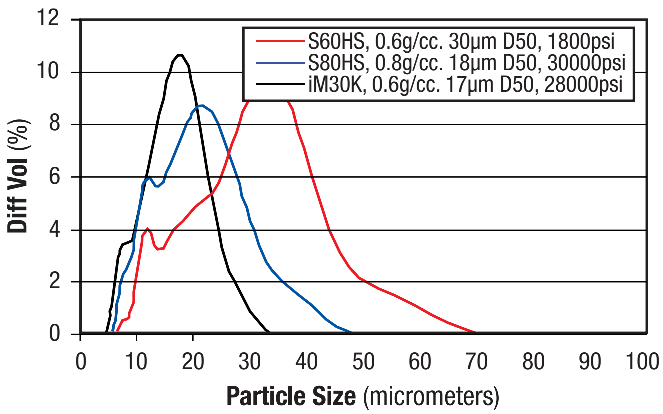


Figure 1: Particle Size Distribution, Density and Hydrostatic Strength of 3M's Extrusion Grade Glass Microspheres

Table 2 shows examples of formulations and typical physical properties achieved in a commercial grade of Nylon 66 (Zytel®6 101LNC010) compounded with S60HS, iM30K and S80HP glass microspheres. A Leistritz ZSE-40 twin-screw extruder was used for compounding the glass microspheres into Nylon 66. The glass microspheres were added downstream using a side stuffer. A general-purpose injection molding machine (BOY 50M) with a three-zone screw (feed, compression and metering) was used to injection mold ASTM test specimens for physical property measurements.

Physical property testing was done in accordance with the following ASTM methodologies;

Physical Property	ASTM Method
Flexular Strength and Modulus	D790
Notched Izod Impact	D252
Tensile Properties	D638
Elongation at Break and Yield	D638

Data in Table 2 show that the part density decreases from 1.14g/cc for regular Nylon 66 to 1.03g/cc at a 20% volume loading of iM30K additives and 0.98g/cc at a 30% volume loading of iM30K additives. This corresponds to a density reduction of ~10% and 14% respectively over standard Nylon 66. The formulations containing S60HS and S80HP also show significant density reductions over Nylon 66.

All the glass microspheres formulations also provide a significant increase in tensile and flex modulus as well as flex strength as compared to Nylon 66. Although there is slight decrease in tensile strength with glass microsphere loading levels, this property reduction can be minimized by using the high strength, small 3M microspheres iM30K and S80HP.

The biggest drawback of adding hollow glass microspheres to Nylon 66 is reduced notched Izod impact strength of the

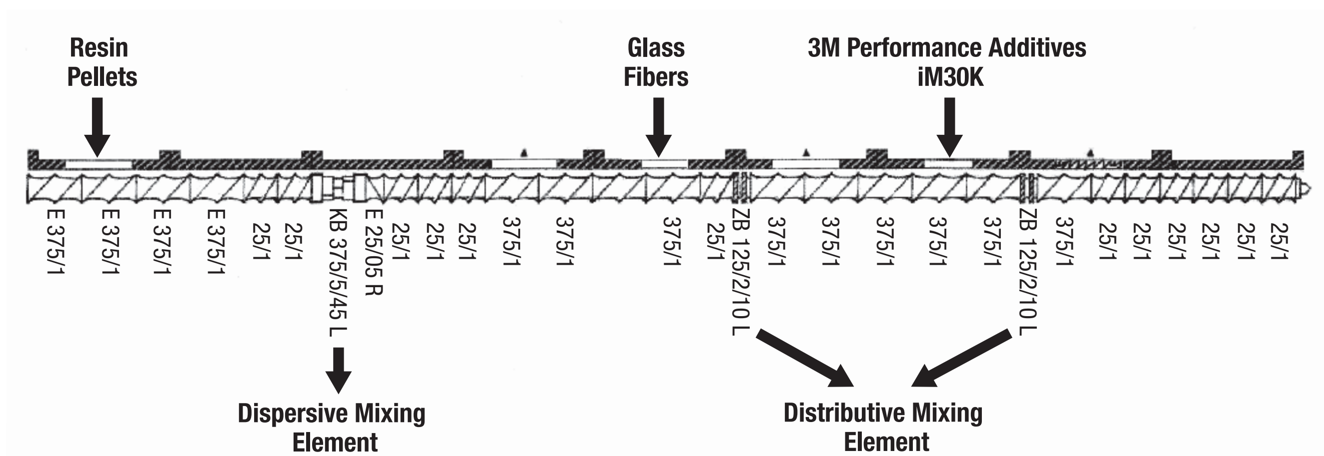


Figure 2: Particle Size Distribution, Density and Hydrostatic Strength of 3M's Extrusion Grade Glass Microspheres

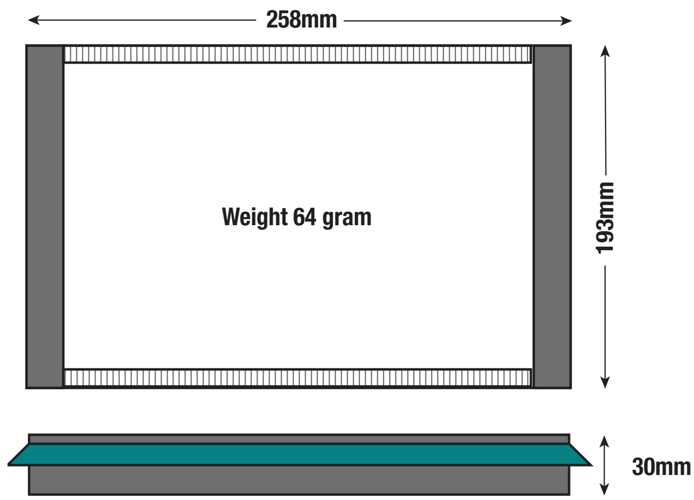
Table 2: Mechanical Properties of Hollow Glass Microspheres in Nylon 66

#	3M™ Glass Microsphere Grade	Volume % Glass Microspheres	Density (g/cm^3)	% Wt. Reduction	Tensile Strength (Mpa)	Tensile Modulus (Mpa)	Flex Strength (Mpa)	Flex Modulus (Mpa)	Notched Izod (ft lb/inch)
1	—	0	1.14	0	75	3200	76	2581	0.72
2	S60HS	20	1.04	8.8	57	3496	103	3103	0.26
3	S60HS	30	0.99	13.2	52	3875	83	3447	0.23
4	S80HP	20	1.07	6.0	59	3792	112	3737	0.42
5	S80HP	30	1.04	8.9	57	4226	85	4123	0.34
6	iM30K	20	1.03	9.5	60	3585	110	3730	0.50
7	iM30K	30	0.98	14.2	59	3930	83	4109	0.37

composite. This is not unexpected as glass microspheres are essentially non-reinforcing fillers dispersed into a plastic material. However, as can be seen in Table 1, over a 50% improvement in the Izod impact strength is realized by using iM30K or S80HP microspheres in the formulations instead of S60HS. This is most likely due to the smaller size of these microspheres compared to S60HS.

Another experiment was conducted with a molded 3M Filtrete™ Cabin Air Filter (CAF) frame consisting of a standard 20% talc-filled homopolymer - black, Piolen® PPTV20A157. This has been compared to a 20% 3M Performance Additives iM30K-filled PP homopolymer - black, Piolen® PPGB20A15. The talc has been replaced with the 3M Performance Additives iM30K and was compounded by the company PIO Kunststoffe GmbH on a conventional twin screw extruder with a standard screw configuration and a side stuffer feeding device. The density of the raw materials were reduced from 1.04 g/cm^3 to 0.84 g/cm^3, indicating that all 3M Performance Additives iM30K survived the compounding process.

The parts were made on a conventional Klöckner Ferromatic Type FM-250 injection molding machine under standard process conditions. Data in Table 3 show that shrinkage of the molded CAF part, particularly in the length and width direction, is significantly lower with the 3M Performance Additives iM30K-filled PP homopolymer compared to the 20% talc-filled PP homopolymer. Furthermore, as expected, the part weight could be reduced by approximately 17% over the standard part weight



while maintaining all relevant mechanical properties.

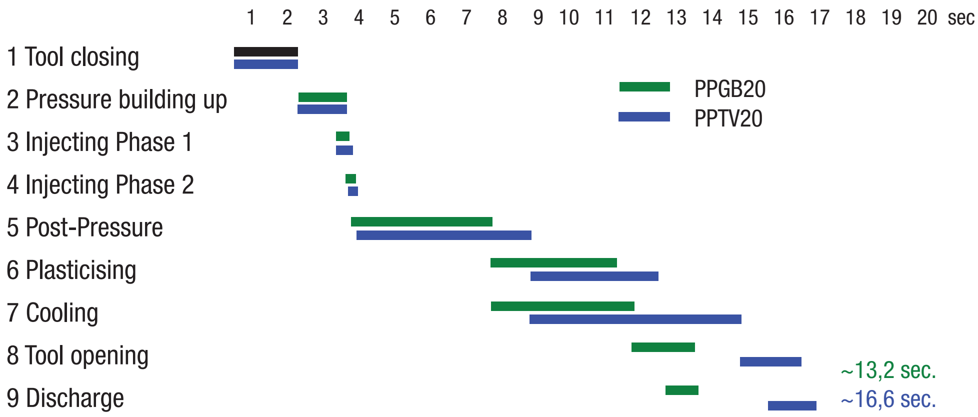
Equally important is the improvement in molding cycle time. The cycle time could be reduced from 16.6 sec down to 13.2 sec due to a reduced post pressure and quenching phase. This is most likely due to increased isotropic flow behavior and less material to be quenched.

This trial also demonstrates that even very small and thin parts or geometries, such as thin sealing lips or bars, can be molded and filled properly with a 3M™ Performance Additives iM30K-filled PP homopolymer. Furthermore, a reduction in shrinkage marks (sink marks) or dents can be noticed and underline the improvement in dimensional stability. This is most likely due to the small particle size of the new Performance Additives iM30K glass bubbles.

Table 3: Mechanical Properties of Hollow Glass Microspheres in PP

Criteria	Target	PPTV20	PPGB20	Difference	Units
Density	1,04	1,043	0,846	-18,8%	(g/cm^3)
Length	258	257,41	258,07	- 0,59 mm	(mm)
Width	193	192,38	192,99	- 0,61 mm	(mm)
Height	30	30,07	30,02	- 0,05 mm	(mm)
Part Weight	64	64,08	53,32	- 16,8 %	(g)

Molding Process for 3M CAF frames E-39



Summary and Next Steps

Hollow glass microspheres can be used in thermoplastics to reduce weight, mold shrinkage, warpage and CLTE. Other attributes unique to hollow glass microspheres are their low thermal conductivity and low dielectric constant. The use of new high strength microspheres, such as Performance Additives iM30K can also provide the additional benefits of improved survivability during stringent thermoplastic processing conditions and improved mechanical properties of the final composite.

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3. http://www.anp-consulting.com/mediapool/19/193403/data/Grafik_AP_06_2006.pdf

4. http://www.neues-fahren.de/neues-fahren/fahrtipp_ballast.htm

5. http://www.ea-nrw.de/infografik/grafik.asp?TopCatID=3107&CatID=3146&RubrikID=3146

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