3M Science. Applied to Life.™

Sep 5, 2018

# New High Strength to Density Ratio Hollow Glass Microspheres for Use in Thermosets and Thermoplastics

ACCE 2018

# Outline

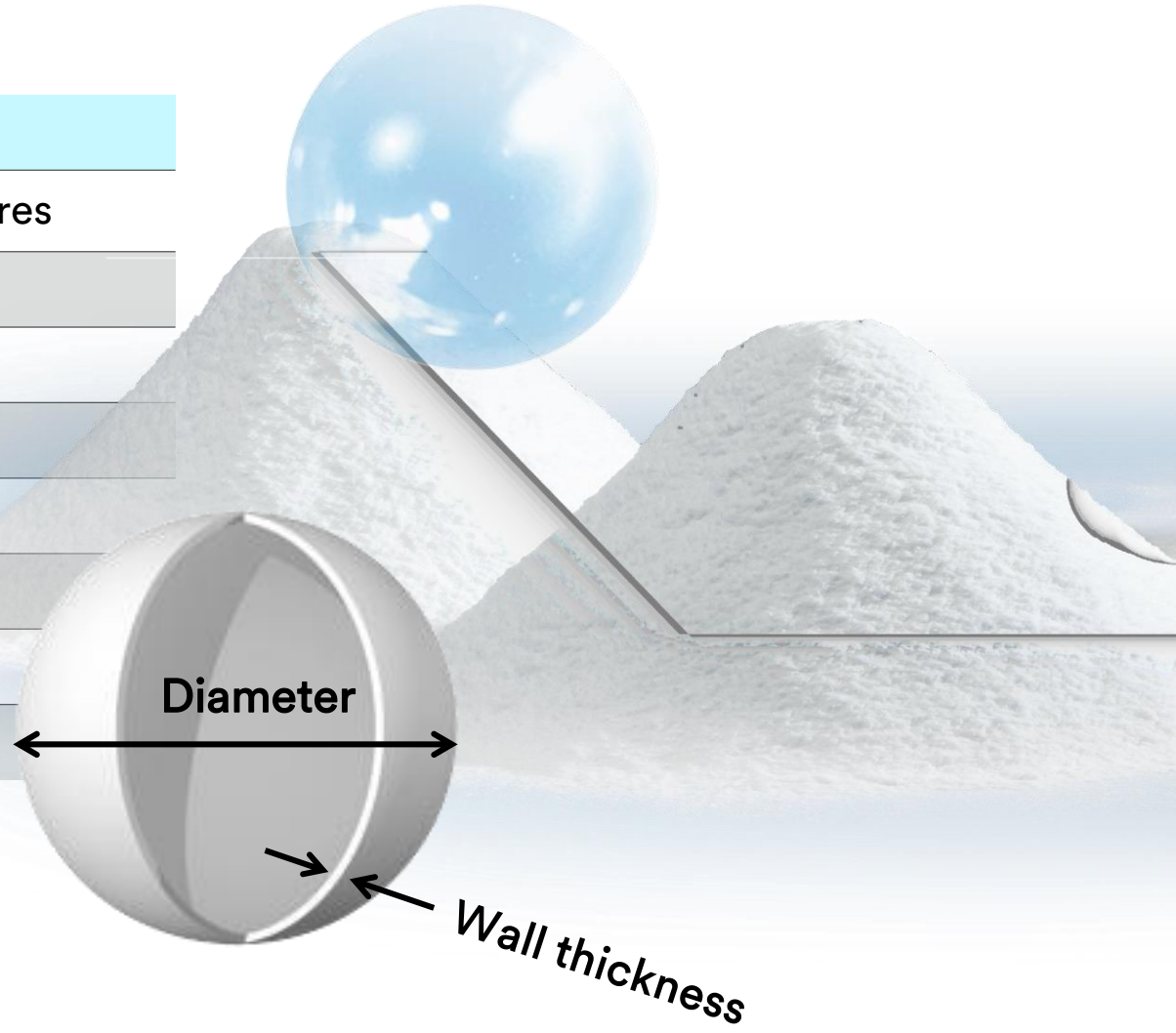
- Overview of Hollow Glass Microspheres
- Automotive Applications
- Benefits in SMC & Product Grades
- Formulating with Hollow Glass Microspheres
- Current Areas of Research

# 3M™ Glass Bubbles

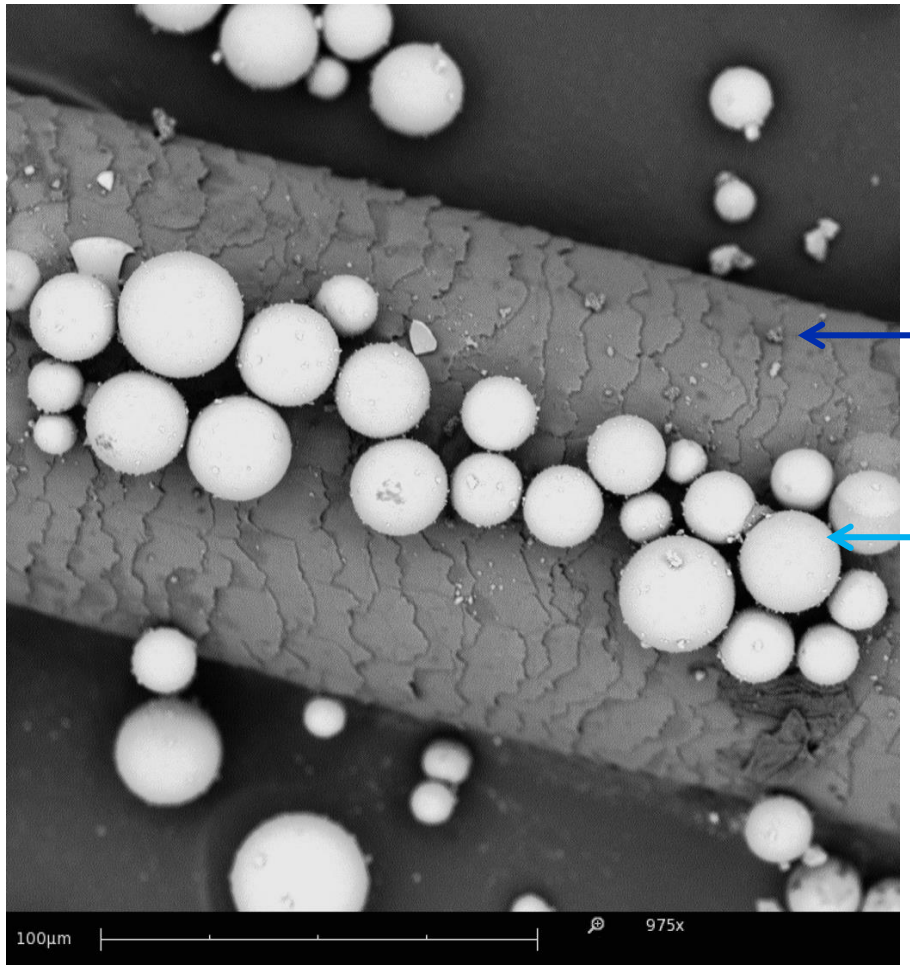
| Property | Value |
|---|---|
| Shape | Hollow, thin walled, unicellular spheres |
| Composition | Soda-lime borosilicate glass |
| Color | White |
| True Density† | 0.12 - 0.60 g/cc |
| Crush Strength* | 250 – 28,000 psi |
| Hardness | Mohs scale 5 |
| Softening Temp | 600° C |
| Average Dia | 15 - 65 microns |

•3M internal QCM

† Helium Gas Pycnometer



# 3M™ iM16K Magnified 975x (Scanning Electron Microscopy)

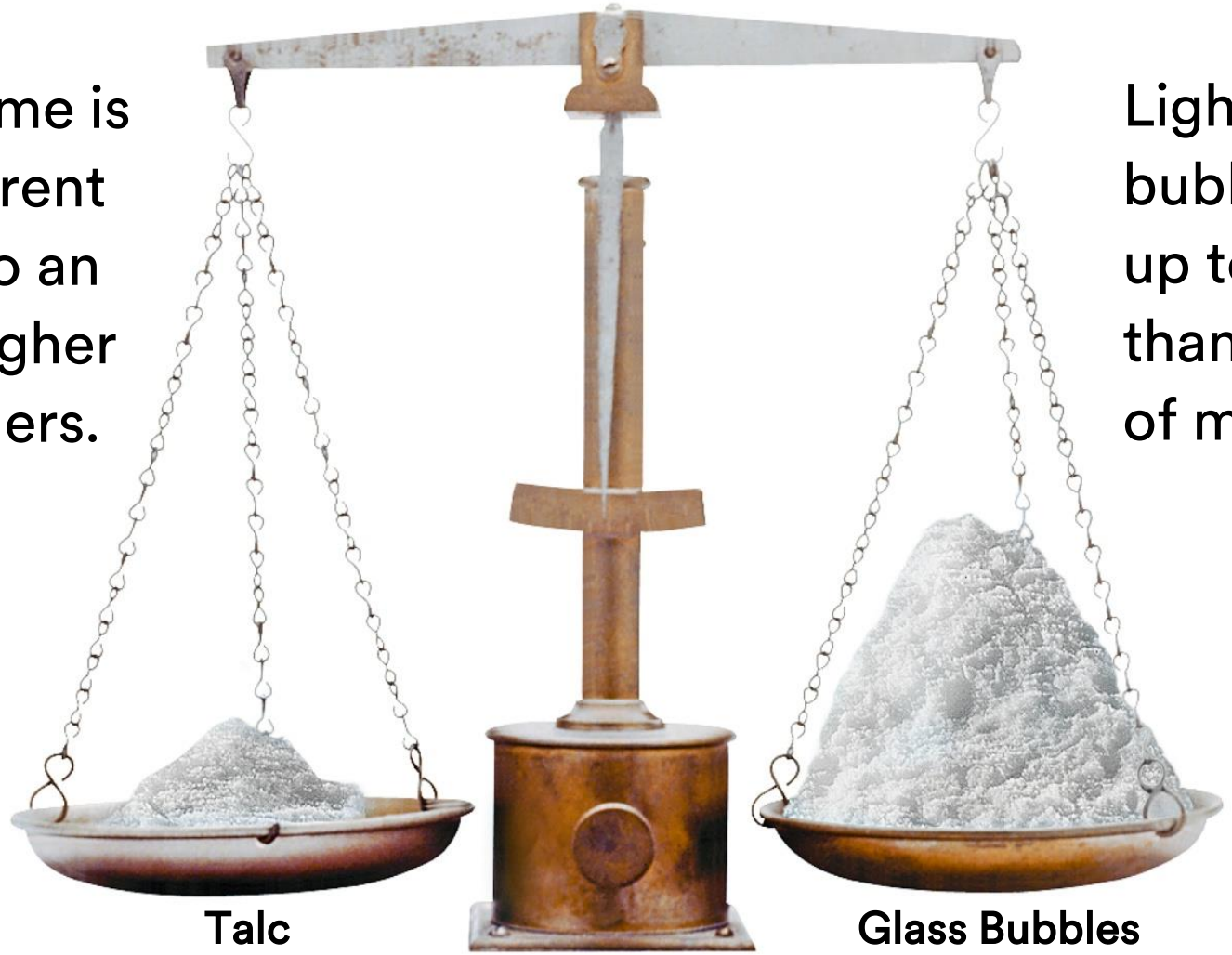



Hair strand

iM16K Glass Bubble

# Formulating with GBs – Weight vs. Volume

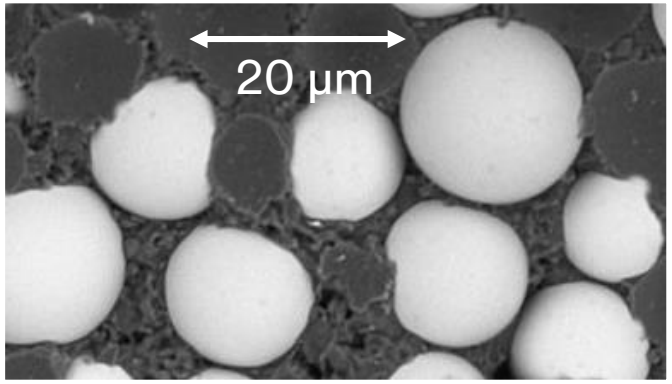
Glass bubble volume is considerably different when compared to an equal weight of higher density mineral fillers.




Lightweight glass bubbles can occupy up to 20x more space than an equal weight of mineral filler.

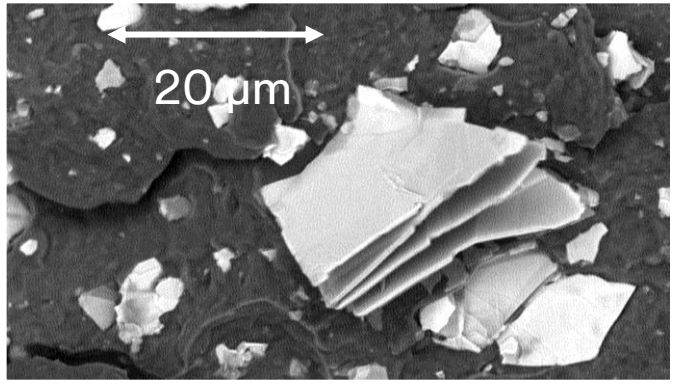
# Comparison of Hollow Glass Microspheres to Typical Fillers

**Hollow Glass Microspheres**



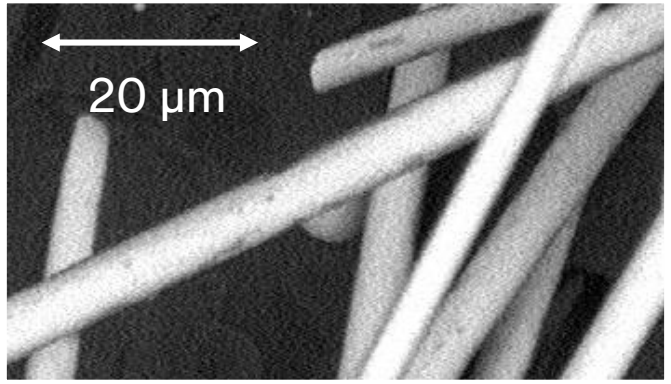

0.46 -0.6 g/cc
1:1

**Talc**




2.8 g/cc
20:1

**Glass Fibers**



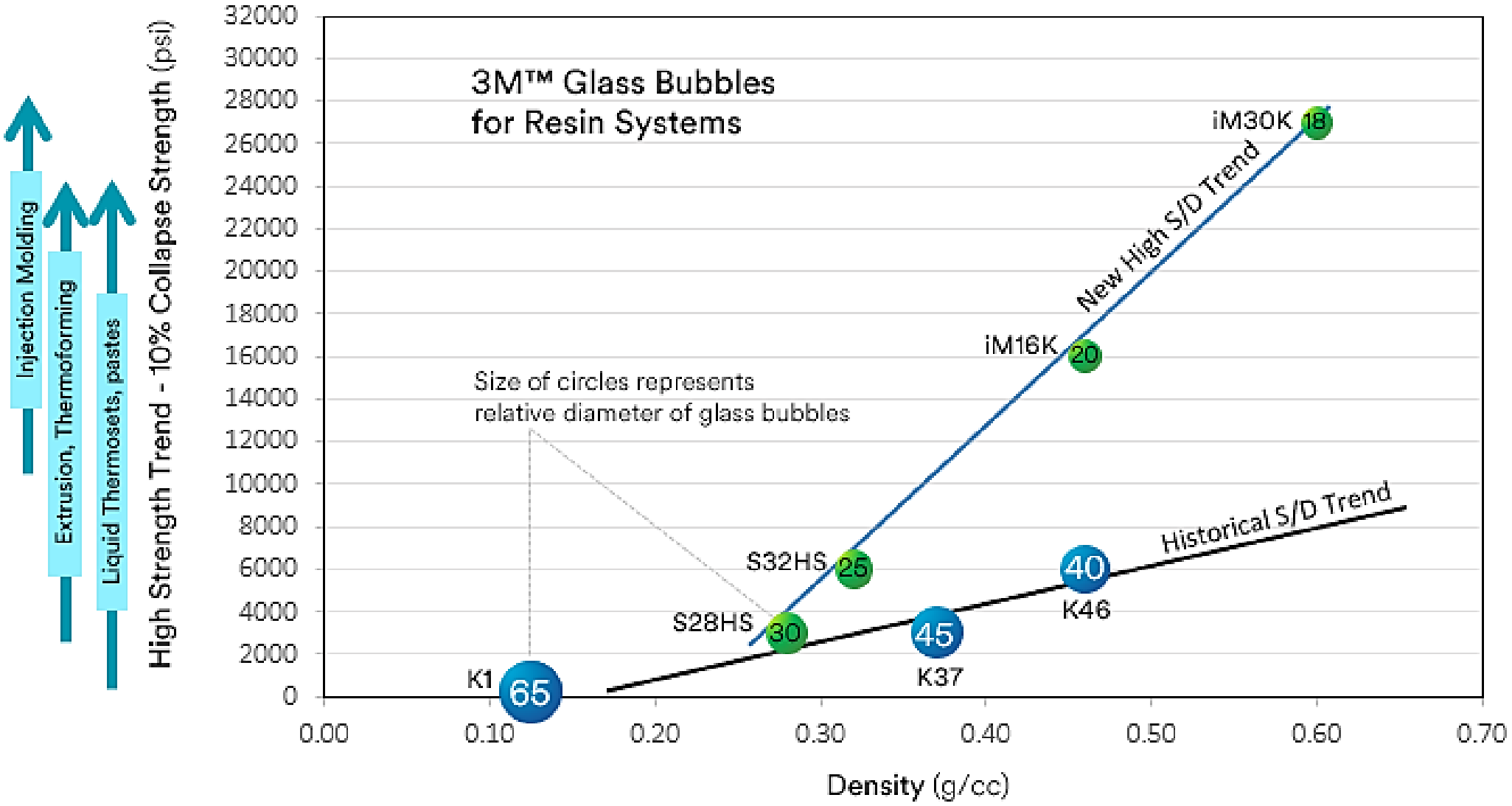

2.5 g/cc
30–50:1

**Low** → **Aspect Ratio** → **High**

High aspect ratio fillers are reinforcing but there are warpage/shrink/CTE issues.

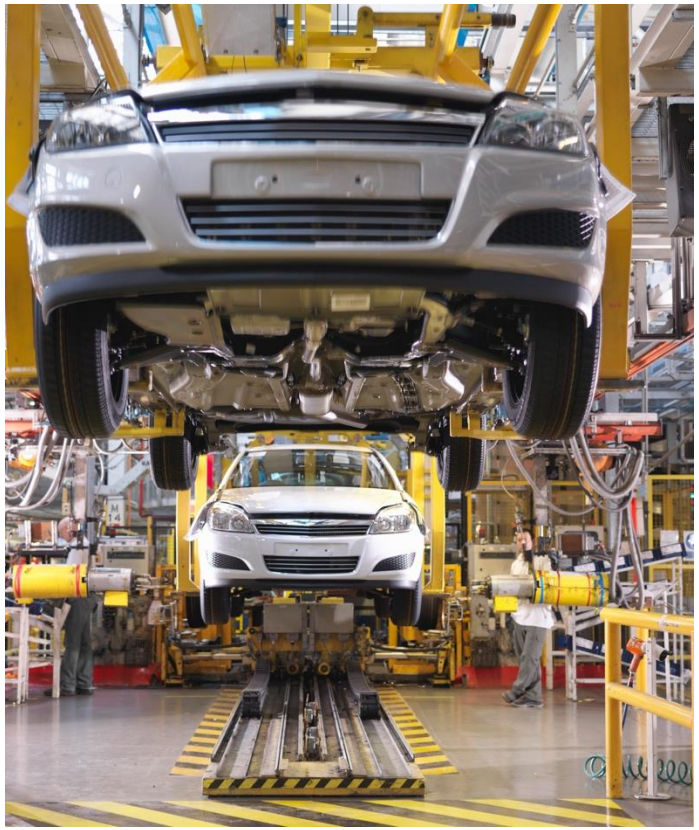
Spheres are not reinforcing but they're ISOTROPIC!

# 3M™ Glass Bubbles Isostatic Collapse



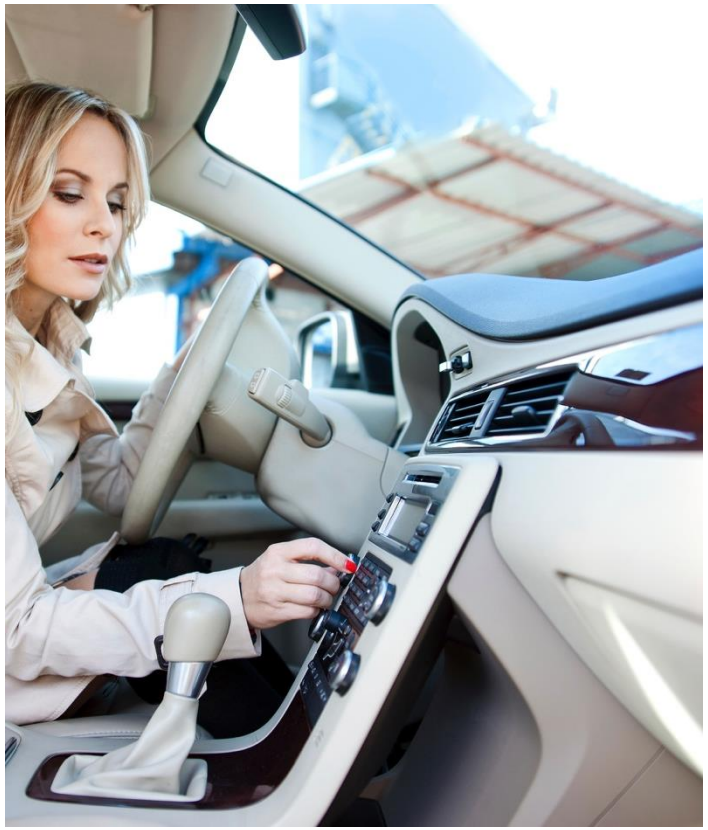
# Automotive Applications for Hollow Glass Microspheres

## Lightweight Seam Sealer & Underbody Coating



## Sheet Molded Composites (SMC)

## Injection Molded Plastics



# Automotive Applications for Hollow Glass Microspheres

## Lightweight Seam Sealer & Underbody Coating

- Up to a 50% Weight Reduction
- Multiple Sealing Applications
- Application benefits including skivability & producing a Class A paintable finish

## Sheet Molded Composites (SMC)

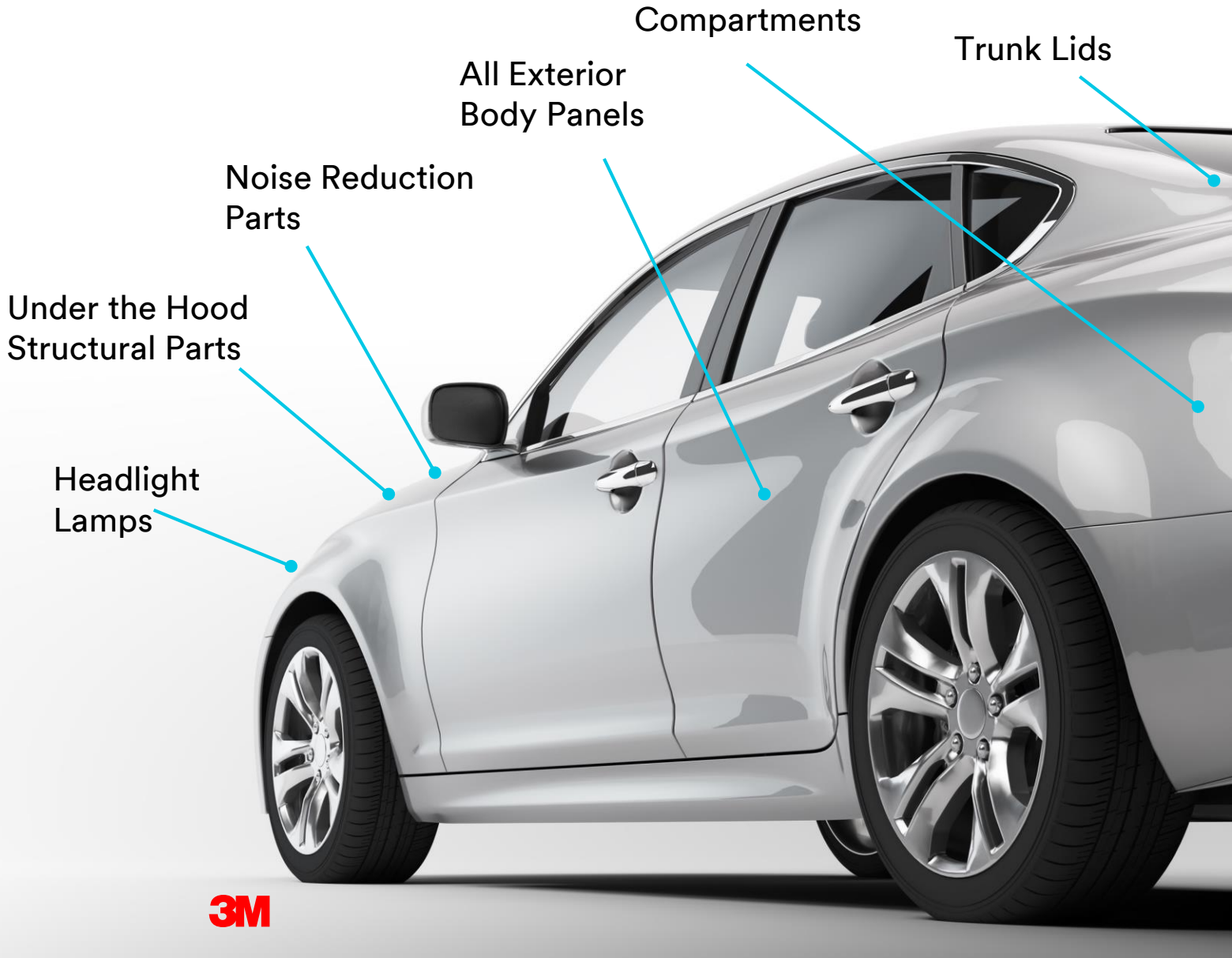
- Up to 40% Weight Reduction
- Class A Paintable
- Lightweight & Ultra lightweight capable at densities of 1.4 – <1.0g/cc

## Injection Molded Plastics

- 15-25% Weight Reduction
- CLTE Reduction
- Cycle Time Reduction

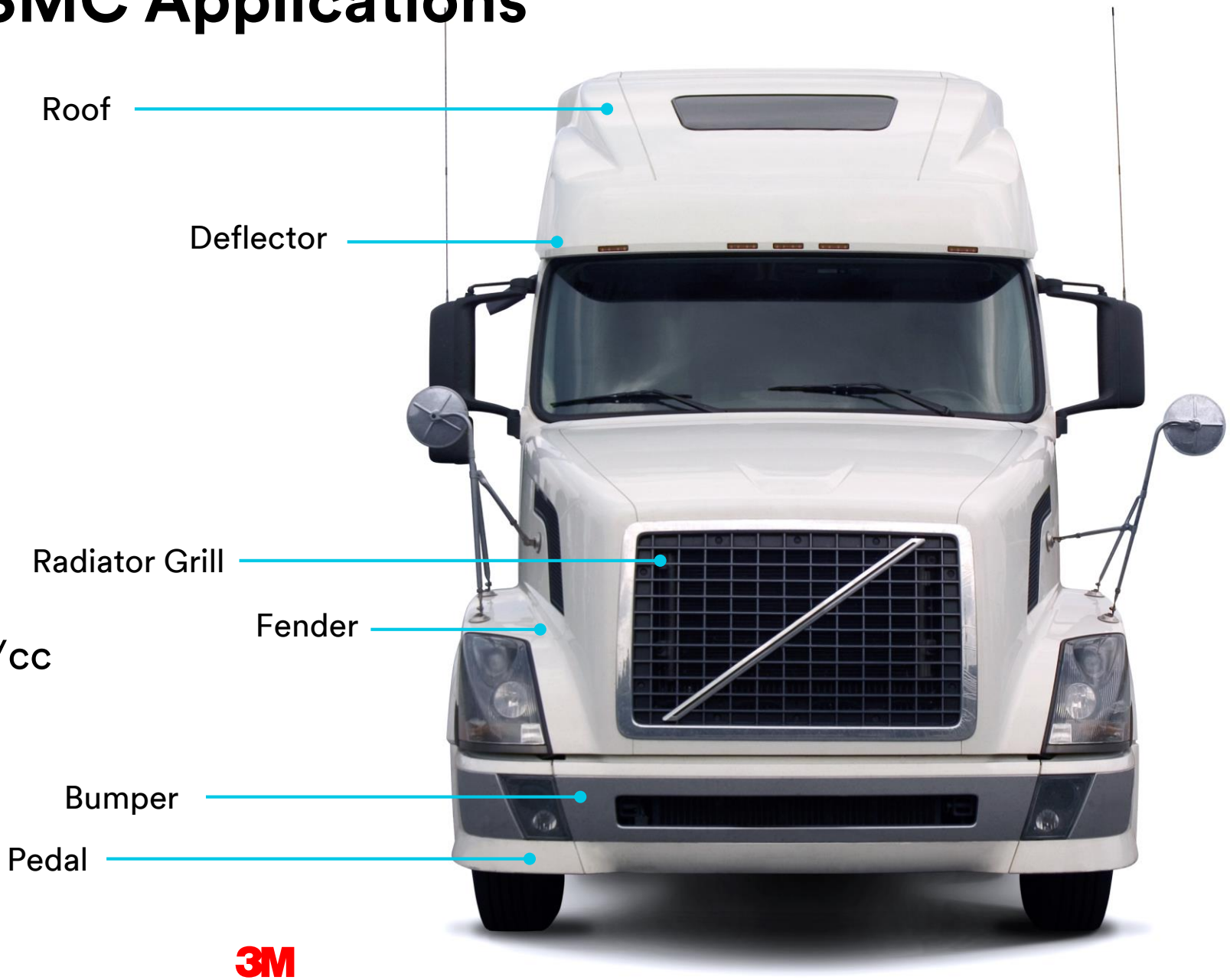
# Automotive SMC Applications

- Automotive
  - »External Class-A surfaces (body panels, roofs)
  - »Internal panels (engine housings, spare tire wells)
  - »Headlamp reflectors

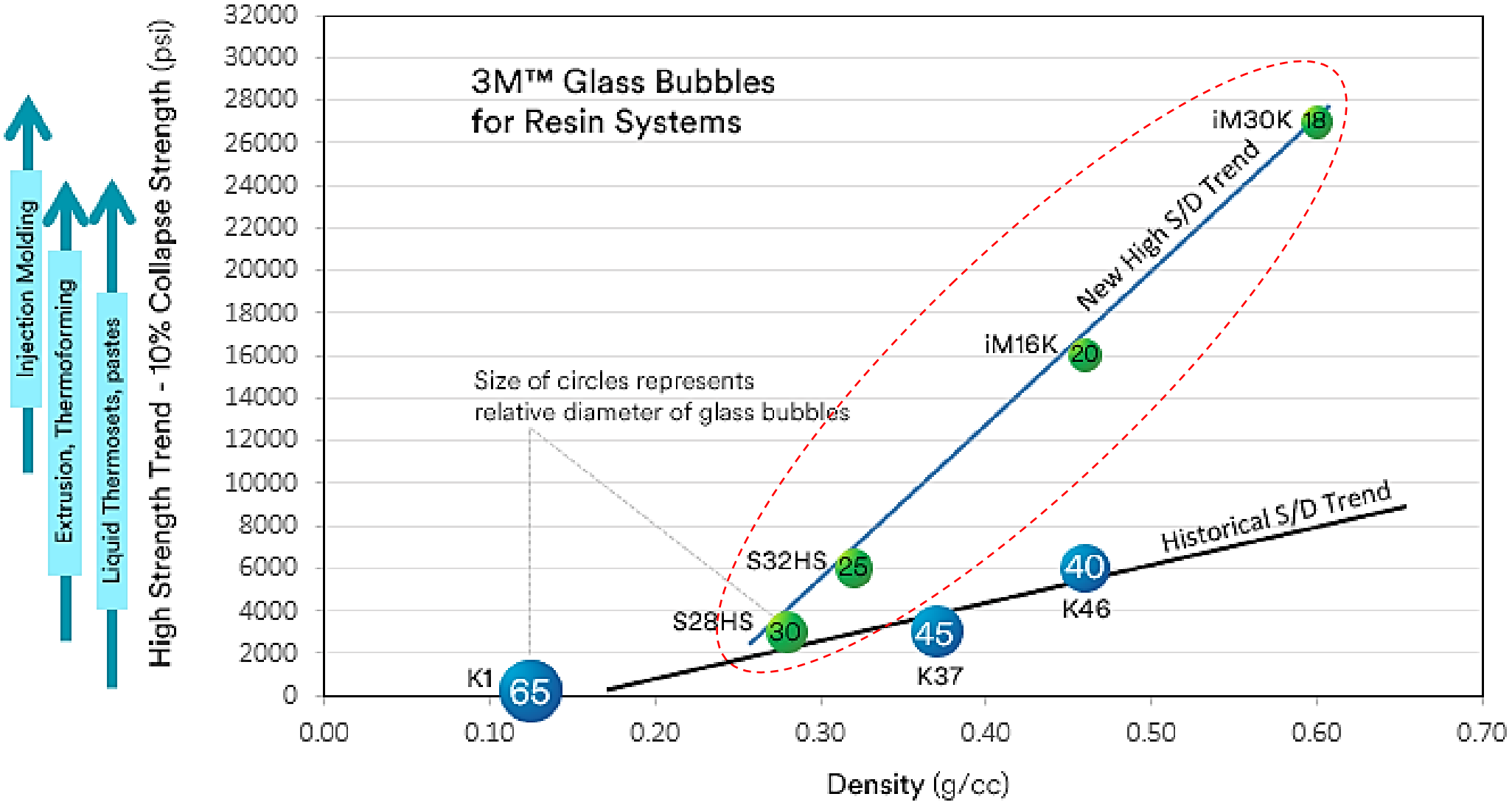


# Commercial Vehicle SMC Applications

- Tractor/Truck
  - » Access doors
  - » Wind deflectors, large external parts
  - » Floor boards
- Marine & Specialty Vehicles
  - » Hoods, body panels
  - » Inherently buoyant 0.95 g/cc SMC



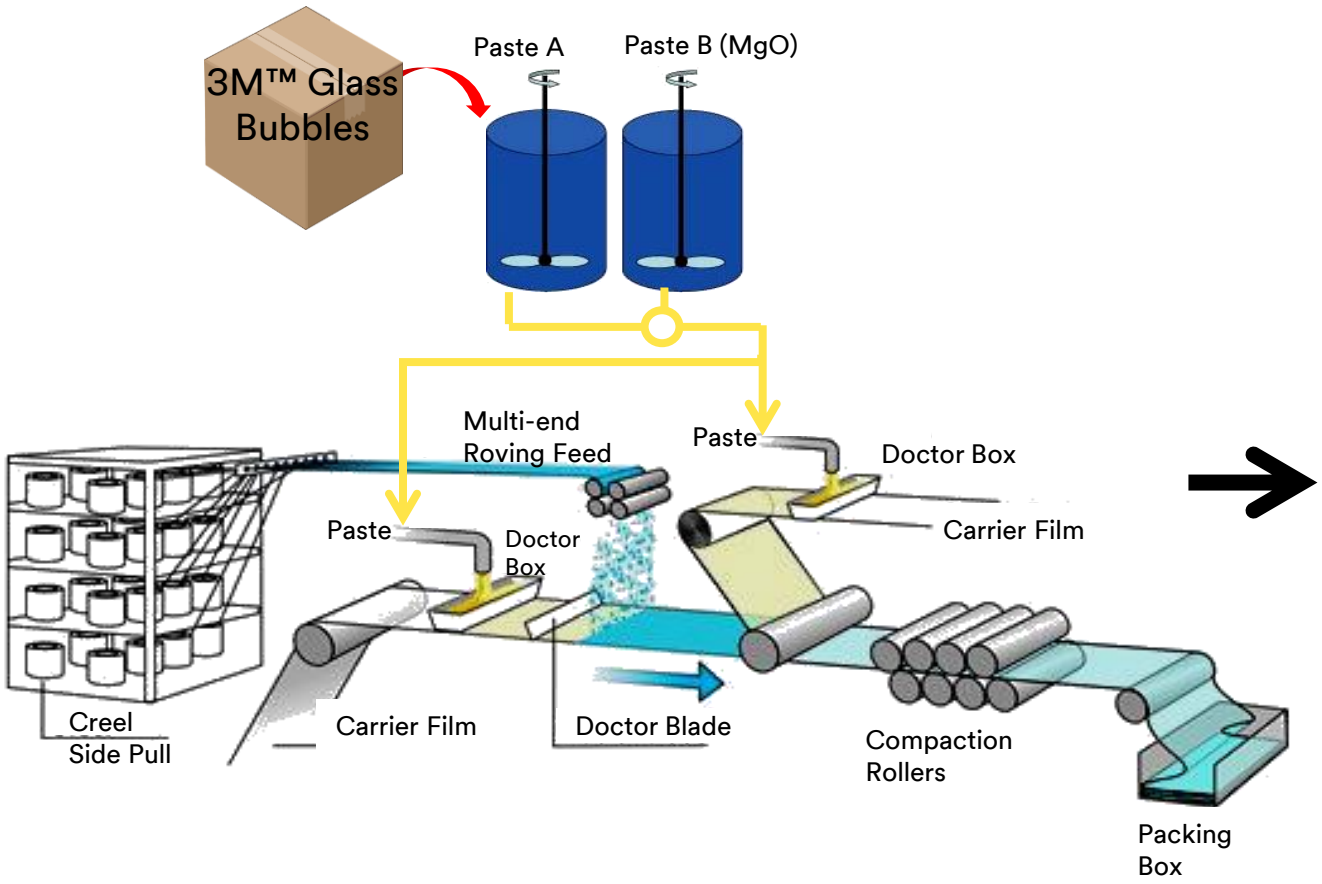
# 3M™ Glass Bubbles for SMC Applications



# 3M™ Glass Bubbles in SMC Applications

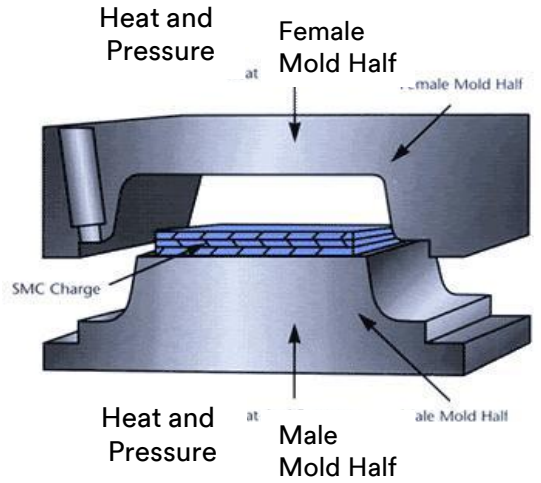
| | Composite Properties | | | Glass Bubble Properties | | | | |
|---|---|---|---|---|---|---|---|---|
| Product Grade | SMC Weight Class | Part Density, g/cc | Average Part Weight Reduction | True Density, g/cc | Isostatic Crush Strength, psi | Minimum Survival Rate by volume | Particle Size 50th Percentile, microns by volume | Particle Size 95th Percentile, microns by volume |
| **Class A Surface Finish** | | | | | | | | |
| NEW **S32HS** | Ultra Lightweight | <1.0 | >40% | 0.32 | 6,000 | 90% | 25 | 45 |
| **iM16K** | Lightweight | 1.2–1.4 | 30% | 0.46 | 16,000 | 90% | 20 | 40 |
| **Structural SMCs** | | | | | | | | |
| NEW **S32HS** | Ultra Lightweight | <1.0 | 40% | 0.32 | 6,000 | 90% | 25 | 45 |
| **S38HS** | Lightweight | 1.3–1.4 | 30% | 0.38 | 5,500 | 80% | 45 | 90 |
| **S28HS** | Lightweight | 1.2–1.4 | 30% | 0.28 | 3,000 | 90% | 30 | 60 |

# Typical Sheet Molded Composite Process

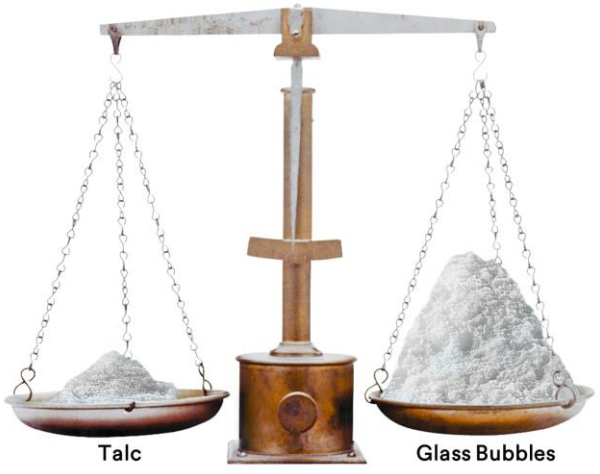



Roll Maturation
RT Curing

Compression
Molding
Shaping & Heat Curing



# Formulation Tips




## Select Hollow Glass Microspheres Grade

- Crush strength depending on max molding pressures
- Particle size Class A vs Structural
- Preferably <55% by volume

## Suggestions with Formulation

- Starting formulation should have similar viscosity and equal volume percent glass fiber to the control
- When replacing heavy fillers with Hollow Glass Microspheres, exchange at equal volume basis (not by weight)
- Viscosity can be adjusted to meet similar viscosity profiles by changing one or more of the processing additives (catalyst or rheology modifier)
- If additional properties need to be met, a coupling agent can be applied to the Hollow Glass Microspheres

## SMC Paste Preparation

- Mix all paste components requiring high sheer first. Then reduce mixing speeds (RPMs) before adding Hollow Glass Microspheres, to avoid bubble breakage
- Maintain mild agitation in holding tanks to prevent Hollow Glass Microspheres float-out
- Avoid transferring using gear pumps, which may break the Hollow Glass Microspheres

# Structural SMC -Formulating with Hollow Glass Microspheres

| | Component | Standard Weight | Light-Wt S38HS | Light-Wt S32HS | Light-Wt S28HS |
|---|---|---|---|---|---|
| A-side Paste | Resin - (vol%/wt%) | 56 / 35 | 47 / 52 | 47 / 53 | 48 / 54 |
| | $CaCO_3$ - (vol%/wt%) | 44 / 65 | 13 / 33 | 13 / 34 | 14 / 35 |
| | 3M™ Glass Bubbles- (vol%/wt%) | - | 40 / 15 | 40 / 13 | 40 / 11 |
| | A-Paste Density (g/cc) | 1.8 | 1.03 | 1.01 | 0.99 |
| Composite | Fibers - (vol%/wt%) | 18 / 23 | 18 / 35 | 18 / 35 | 18 / 36 |
| | Density - (g/cc) | 1.95 | 1.30 | 1.28 | 1.27 |
| | Density Reduction - (wt%) | - | 33 | 34 | 35 |

# Class A SMC -Formulating with Hollow Glass Microspheres

| | Component | Standard Weight | Light-Wt S38HS | Light-Wt S32HS | Light-Wt S28HS |
|---|---|---|---|---|---|
| A-side Paste | Resin - (vol%/wt%) | 56 / 35 | 46 / 58 | 46 / 63 | 45 / 74 |
| | $CaCO_3$ - (vol%/wt%) | 44 / 65 | 6 / 18 | 6 / 19 | 0 / 0 |
| | 3M™ Glass Bubbles- (vol%/wt%) | - | 48 / 24 | 48 / 18 | 55 /26 |
| | A-Paste Density (g/cc) | 1.8 | 0.91 | 0.84 | 0.68 |
| Composite | Fibers - (vol%/wt%) | 18 / 23 | 18/38 | 18 / 40 | 18 / 44 |
| | Density - (g/cc) | 1.95 | 1.20 | 1.15 | 1.00 |
| | Density Reduction - (wt%) | - | 38 | 41 | 48 |

# Mechanical Property Comparison*

| | Flexural Strength (MPa) | % Increase | Impact Strength (J/m) | % Increase |
|---|---|---|---|---|
| 3M Glass Bubbles iM16K | 14.2 | - | 30.4 | - |
| 3M Glass Bubbles iM16K-MAS-1 | 17.2 | 20.9% | 35.0 | 15.1 |

*Typical SMC formulation was used to generate data

# Application Example

Materials used:

- Unsaturated polyester
- Glass fiber
- 3M™ Glass Bubbles iM16K
- 3M ™ Glass Bubbles iM16K-MAS-1

Enabling Features:

- Density reduction from 1.8 to 1.2 g/cc
- 38% reduction in weight
- Class A paintable surface
- Coupling to the resin for improved physicals
- Ease of processability

November 12, 2015

## Glass bubbles lift Corvette body panels to top SPE award

By KERRI JANSEN

SHARE | Automotive | Sustainability | 3M Co. | Fiat SpA | Ford Motor Co. | More +

General Motors Co.

General Motors Co. won the top award from the Society of Plastics Engineers Automotive Innovation awards for its use of hollow glass microsphers in body panels for the 2016 Corvette.

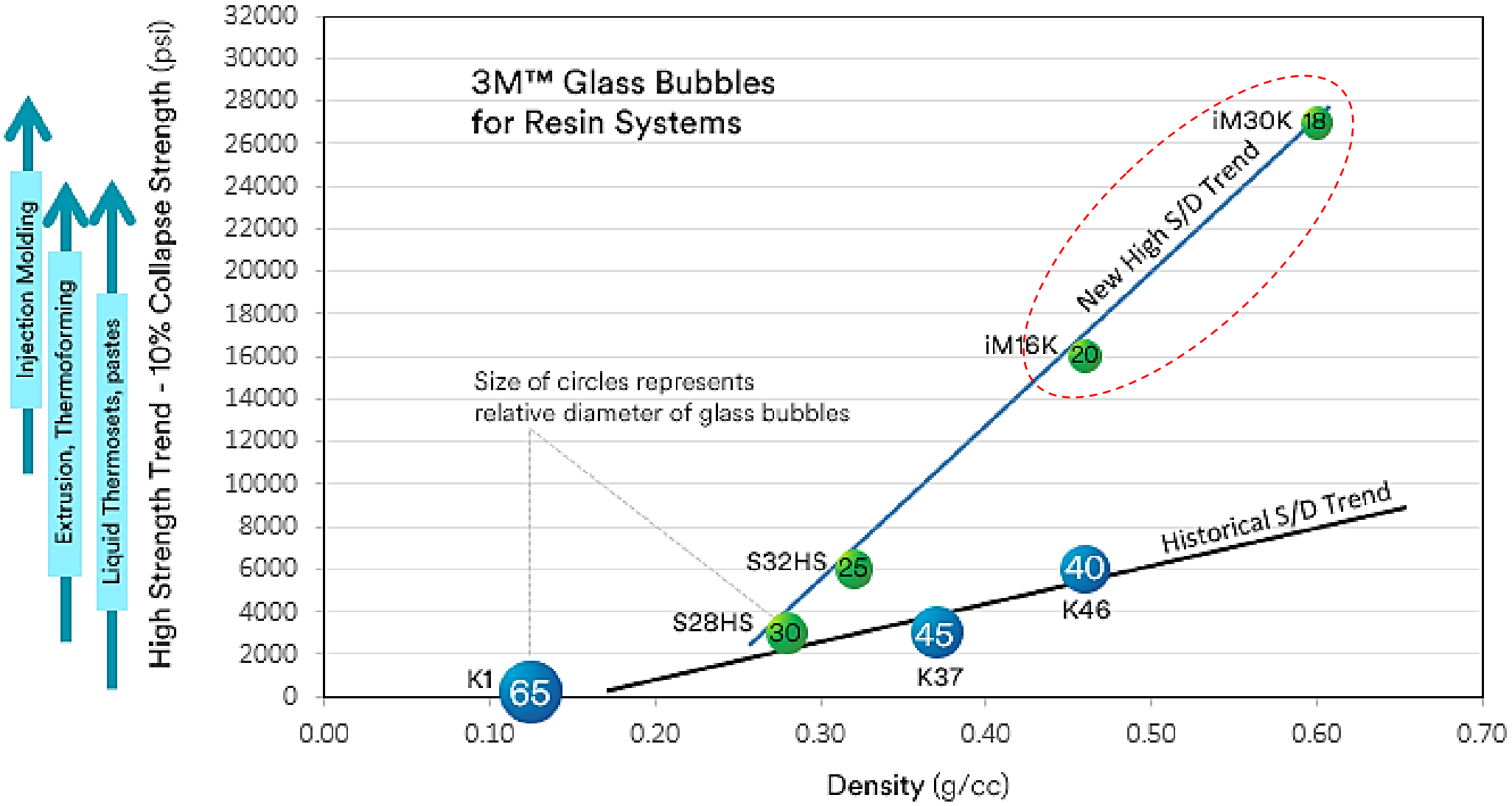
The Society of Plastics Engineers' automotive division announced the category winners for its 2015 Automotive Innovation Awards. SPE honored the winners at its annual Automotive Innovation Awards Gala Nov. 11 in Livonia, Mich.

The top prize went to General Motors Co. for its materials category entry, class A body panels made using TCA Ultra Lite composite material from Continental Structural Plastics. The toolmakers are Century Tool & Gage and Paragon Die & Engineering Co.

CSP replaced calcium carbonate with hollow glass microspheres from 3M Co. and a proprietary surface treatment to achieve 43 percent mass reduction compared to conventional SMC, and 28 percent mass reduction over mid-density grades.

Plastics News 2015

# 3M™ Glass Bubbles for Injection Molding Applications



# Nylon 6 with 30 wt.% Glass Fiber

| Component. | Formula 1 | | Formula 2 | | Formula 3 | | Formula 4 | | Formula 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | PA6 / GF30 | | PA6 / GF30 / GB 3 | | PA6 / GF30 / GB 5 | | PA6 / GF 30 / GB 7 | | PA6 / GF35 / GB 8.1 | |
| | Wt% | Vol% | Wt% | Vol% | Wt% | Vol% | Wt% | Vol% | Wt% | Vol% |
| PA 6-Ult 8202HS | 70 | 83.9 | 67 | 76.3 | 65.0 | 71.7 | 63 | 67.2 | 56.9 | 61.6 |
| Glass Fiber | 30 | 16.1 | 30 | 15.3 | 30 | 14.8 | 30 | 14.3 | 35 | 16.9 |
| iM16K-GB | - | - | 3 | 8.4 | 5.0 | 13.6 | 7.0 | 18.5 | 8.1 | 21.5 |
| Density (g/cc) | 1.368 | | 1.298 | | 1.256 | | 1.216 | | 1.231 | |
| % Reduction in Density | - - | | 5 | | 8 | | 11 | | 10 | |
| Tensile Strength (MPa) | 180.8 | | 167.5 | | 160.4 | | 156.8 | | 179.3 | |
| Tensile Elong. (%) | 4.3 | | 4.03 | | 3.75 | | 3.48 | | 3.60 | |
| Tensile Modulus (MPa) | 6961 | | 6800 | | 6976 | | 6936 | | 7724 | |
| Flexural Modulus (MPa) 1% Secant | 7615 | | 8072 | | 7957 | | 7906 | | 10232 | |
| Flexural Modulus (MPa) 2% Secant | 7585 | | 7845 | | 7716 | | 7695 | | 9774 | |
| Flexural Strength (MPa) | 254.4 | | 236.7 | | 224.4 | | 212.5 | | 251.5 | |
| RT Izod impact Strength (J/m) | 103.6 | | 79.1 | | 79.7 | | 57.3 | | 76.3 | |

# Current Areas of Research

- Structural SMC
- Class A SMC
- Mechanical Properties: Modulus, Impact
- Surface Finish
- Formulations
- Carbon Fiber and Hollow Glass Microspheres
- Hollow Glass Microspheres Surface Treatment

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# Thank you!

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