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Glass Microspheres

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Abstract: Glass microspheres are microscopic spheres of glass manufactured for a wide variety of uses in thermal insulation coating, putty, plastic casting polyester, radome, synthetic foam, adhesives, printed circuit board substrate, bowling, fan blades, and caulking materials, emulsion explosives, golf, sealant, pipeline insulation materials, artificial marble, PVC, low density oil drilling, light cement etc. Glass microspheres are usually between 1 and 1000 micrometres in diameter, although the sizes can range from 100 nanometres to 5 millimetres in diameter. Microspheres are spherical particles that can be distinguished into two categories; solid or hollow. This paper presented a general overview of glass microspheres.

Keywords: Glass microspheres, history, property, application, development.

Cam Mikro Kürecikleri

Öz: Cam mikro küreler, ısı izolasyon kaplaması, yapıştırıcı, polyester, radar, sentetik köpük, bağlayıcılar, elektronik devre altlıkları, üfleç bıçakları, sıvı patlayıcılar, bowling, golf, sızdırmazlık elemanı, boru hattı izolasyon malzemeleri, sunni mermer, PVC, düşük yoğunluklu deliciler, hafif çimento vb. alanlarda çok çeşitli kullanımlar için üretilmiş mikroskobik cam kürelerdir. Bunların çapı genellikle 1 ila 1000 mikrometre arasındadır. Ancak, boyutları 100 nanometre ile 5 milimetre arasında değişebilir. Mikro küreler, katı veya içi boş olmak üzere iki kategoriye ayrılabilirler. Bu makale cam mikro kürelere genel bir bakış sunmaktadır.

Anahtar Kelimeler: Cam mikroküre; tarihçe; özellik; uygulama; gelişim

1. Introduction

Microspheres are spherical particles that can be classified in two categories; solid or hollow. They typically range from 1 to 200 μm in diameter, and are made from glass, ceramic, carbon or plastic depending on the types of applications. Solid glass microspheres (SGM) are manufactured by direct burning of glass powders while hollow ones (HGM) are produced by adding blowing (bubbling) agent to glass powder [1–2].

2. History

Glass microspheres have been employed for at least 100 years, with solid glass beads produced in New York as far back as 1914. In 1922 considerable amount of glass beads with high refractive–index was fabricated for coating movie screens. In 1950s hollow glass microsphere technology was developed [3]. Since then, many sectors started to depend upon SGMs and HGMs as a main constituent in their products and production processes. In 1960s they were at first employed as a filler for plastics and found opportunities in countless number of applications such as aerospace and military materials, moulded plastic components, retro–reflective main road marks, oil and gas,

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recreation, paints and coatings, transportation, building, mining blasting materials, individual care, cosmetics etc. [4–6].

Recently, glass microspheres inhibited marvellous growth because of innovative high–value, highly growing industries emerged and high quality glass microspheres of perfect sphericity, strict tolerances and particle size distributions became commercially available. The relevant sectors cover bio–medical, life sciences, microscopy, automotive, high technology equipment and special implementations [7].

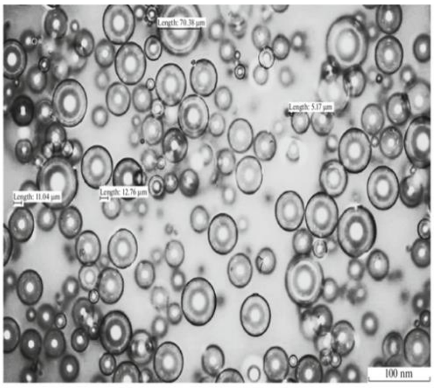

Figure 1. Image of glass microspheres

3. Types of Glass Microspheres

Glass microspheres are spherical particles possessing various implementations covering composite polymer technology, medicine, analytical chemistry, abrasive explosive, paints, and coatings. They are largely employed in the fabrication of road and pavement signing materials, like traffic paints, thermoplastics, and pre–formed signs [8–10].

3.1. HGMs

HGMs, sometimes named as micro–balloons or glass bubbles, possess diameters changing in the range of 10 to 300 μm. They are typically made of borosilicate–soda–lime glass batch formulation and supply the properties like low density, high heat and chemical endurance [8, 11–12].

The walls thickness determined the crushing strength of hollow spheres and, as expected, when the density of sphere gets higher the crushing strength increases. The light–weight hollow glass spheres are chemically steady, non–combustible, non–porous, and have excellent water resistance [13].

Hollow spheres are employed as a light–weight filler in composite materials like bubbly foam and light–weight concrete. Micro–balloons supply bubbly foam light–weight, low–speed thermal conductivity, and compression strength exceeding when compared to other types of foams. The mentioned features are taken into an account in the submersibles and deep–sea oil drilling devices, for which other kinds of foam would implode. Hollow spheres belonging to various systems form syntactic foams with different features [14–15]. They also possess storage usages and low–speed release of pharmaceuticals and radioactive tracers for searching in controlled storage and hydrogen release. Microspheres can be evaluated in composites for filling polymer resins to obtain special features. When making surf boards for instance, formers seal the EPS foam blanks with epoxy and micro–balloons for forming an impervious and easily sanded surface over which fibre glass laminates would be applied [16]. HGMs offer conductive coatings having optimum thickness providing spherical particles possessing decent conductivity and shielding features while keeping the weight–saving profit accompanied with hollow–core low–density materials, and they are suitable for the uses in military implementations, bio–technology, medical instruments, electronics, and other special sectors [17]. An example for hollow microsphere is presented in Fig. 2.

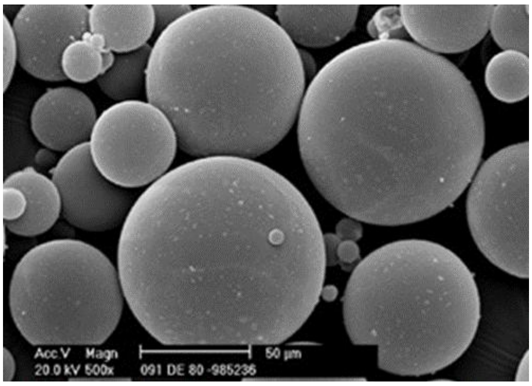

Figure 1. HGMs for composite (50 µm)

3.1.1. History of HGMs

By the late–1930s, solid glass beads being produced of waste soda–lime glass were fabricated by a company, highway departments used the product for reflective road paint. Till 1950s, it was selling reflective sheets containing low–refractive index glass beads (called "Army Cardboard") to the French army. They were made to be retro–reflective for light being perpendicular to the sheet plane, and mounted on the back of convoy vehicles to assist avoiding night–time accidents. During his investigation, Beck discovered clouds of micro–bubbles in close vicinity of the beads surface and sorted out that maintaining the particulate glass feeds, for a long time in moist condition, supplies suitable situations for forming hollow bubbles. To overcome such a handicap, he suggested to crush the glass and use it at once. However, he also knew to precede work within the company making an attempt to form such hollow glass beads, and an earlier work was patented by Standard Oil of Ohio. After some experimental studies, he sorted out that the achievement of hollow beads or "HGMs" by double–stage melting and forming process was possible. In the year 1963, a patent application covering careful formulation of glass frit, milling it to a specific particle size, afterwards, reheating the particles for forming single–wall HGMs was made by Beck [18–20].

3.1.2. Characterisation of HGMs

The properties to be mentioned here are density, strength, thermal and electrical features, which are limited to those being a straight forward consequence of glass microspheres hollow nature [18, 21].

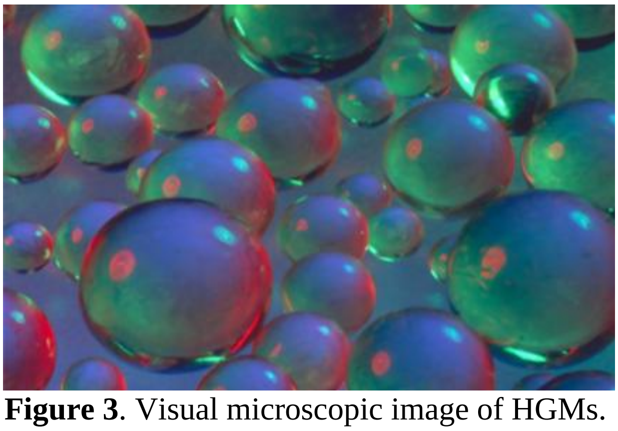
Figure 3. Visual microscopic image of HGMs.

3.1.2.1. Density

It is a main feature for HGMs besides isostatic collapse strength. Particulate filler providers describe it variously and compare its values unknowing that the absolute process employed for the determination could misguide the user. In the case of bulk density, it is the well–known fact that the holder's volume contains both the HGMs volume and the air voids between the microspheres. Another measurement method evaluates tapped powders volume. However, such a process, likewise bulk density, include the voids between the HGMs and could not be employed for formulations [18].

3.1.2.2. Thermal Conductivity

HGMs thermal conductivity could be defined as a function of their hollow volume and wall thickness. Determining a bulk quantity of HGMs is misguiding because of the voids between them. Consequently, it can be said that it is most suitable to approximate the HGMs thermal conductivity from theoretical models. Unsurprisingly, there is a linear relation between density and thermal conductivity (Fig. 4) [18, 22].

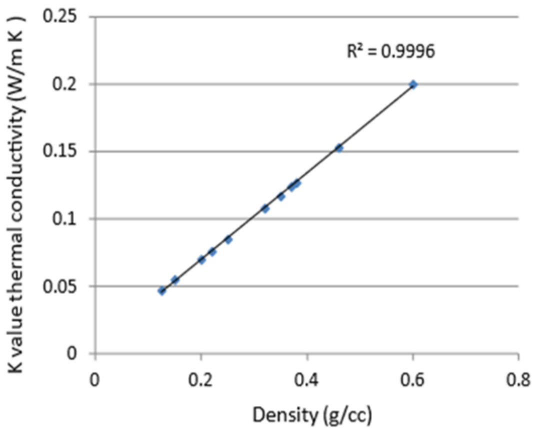

Figure 4. Correlation between density and thermal conductivity

3.1.2.3. Electrical and Dielectric Properties

The values of low dielectric constants and low loss tangents typically characterize HGMs–filled materials. Highly large–scale integration of electronic circuits fundamentally decreased the size of circuit boards employed in electronic equipment, which led to develop compounds having the properties such as low dielectric constant, high strength, low–density, low–moisture absorption, and high endurance. Integrated circuit boards, forming the heart of computers, request electrical insulators with low and desirably tuneable dielectric features. Polymers and polymeric composites found themselves applications in the regarded areas thanks to their low dielectric features.

The values of impedance are employed for calculating dielectric constant at varying frequencies. It is seen that HGMs volume fraction possesses a noticeable influence on the dielectric constant of syntactic fillers, which makes their usage, for instance, in radomes, circuit substrates, packing materials, and other kinds of products where light–weight compounds of expected electrical features are requested. Low dielectric constants and low loss tangents raise the speed of signal propagation while decreasing signal weakening escaping from main losses of radiation energy, when the working frequency raises [18, 23–24].

3.1.2.4. Microscopic Imaging of HMG's Density

Topography mode of imaging either describes the HGMs or HGM pockets when removed from their situations as preparing sample under freeze fracture, supplying satisfactory locational knowledge of the HGMs where several measurements between or on each sphere can be made [18, 25–26].

Figure 5 indicates scanning electron microscope (SEM) images of HGMs in different scales, where one can clearly see the small, perfect spherical shaped bubbles with the diameters varying in a certain range [27].

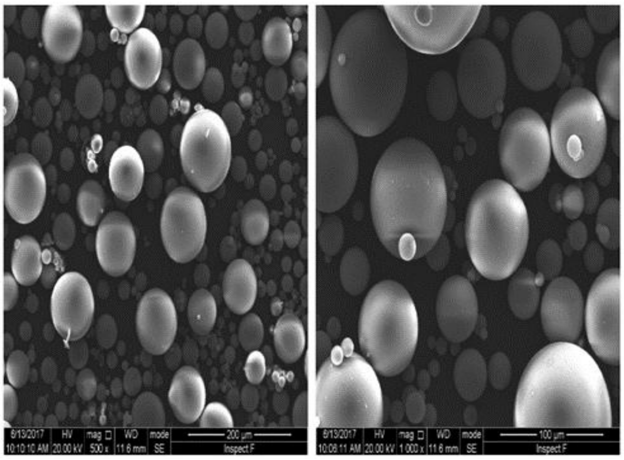

Figure 5. SEM images of HGMs

The diameter distribution of microspheres, from which the microsphere's size falling in the interval of 30 μm 70 μm is seen, can be followed in Figure 6 [27–28].

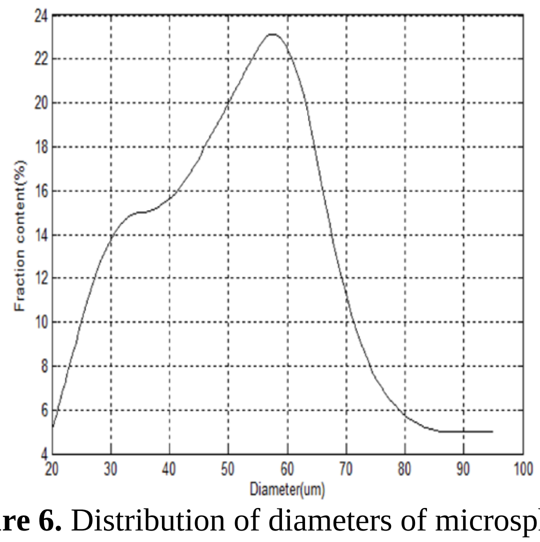

Figure 6. Distribution of diameters of microspheres

Figure 7 exhibits the cross–section of a typical cracked microsphere. It is determined that the microspheres wall thickness varies within the ranges of 1.2 to 2.2 μ. On the other hand, the void content to the microsphere remains about 85 % unchanged, while HGMs wall thickness raises in association with the rise of its diameter [27, 29–30].

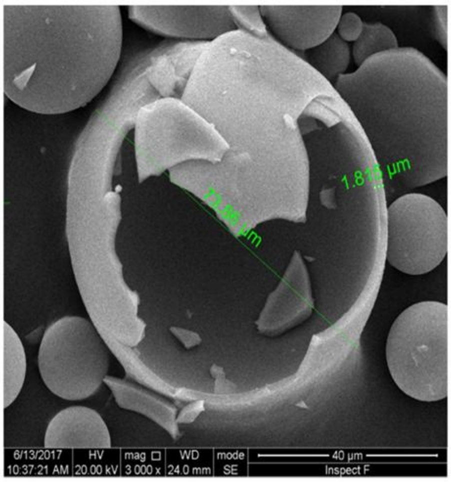

Figure 7. SEM image of cracked HGMs

3.1.3. Reasons of choosing HGMs

Reducing viscosity and increasing fluidity:
HGMs are quite tiny particles of a higher ball–type rate, "ball–bearing" influence of which could raise the flowability and decrease the resin’s viscosity and its internal stress. Consequently, the composite causes less amount of heat in dynamic processing, being away from insufficient lubrication and partial thermal decomposition. When injection moulded, they are more easily squeezed out, either reducing the product imperfection, or enhancing the production efficiency [31–33].

More substitution capability for resin:
HGMs comparingly fill less surface area and have low–level oil–absorption, and evenly dispersion in mixture. Their capability of being easily compressed and integrated allow high level of filler loadings. It considerably decreases the resin’s usage, raises the filler content, and efficiently diminishes VOC indicators, beside cost [31, 34].

Reducing products shrinkage and warpage:
Properties of high filling ratio and isotropic characteristics lead to high–level dimensional stability of final products and lower the rates of shrinkage and warpage. As occupying a convenient portion, it can enhance the crushing and final products impact strength and surface hardness clearly [31–32, 34]

More economical by volume:
The high–performance HGMs density is just a friction of that of resin. So, less usage of HGMs is required rather than large amount of resin. As taking the costs into an account per unit in volume instead of in weight, high–performance HGMs could considerably lower costs [31–32].

Altering the products density:
The HGMs density is generally 0.20–0.60 g/cm^3, and the mineral filler’s density is usually about 2.7–4.4 g/cm^3. So, the desired ideal density could be achieved by incorporating suitable amounts of HGMs [31–33].

3.1.4. Storage

The HGMs could be packed with plastic boxes or texture bags and carried in bulk by different means.

To prolong the storage time, humid environment should be avoided and the storage to be done in a cool and dry place. Since HGMs are ultra–fine powder with medium alkali, the stimulation of respiratory tracts is possible, when HGMs are exposed in air for a long time, so wearing a qualified mask or respirator is necessary [11, 35].

3.1.5. Applications of HMGs

Glass bubble and HGM's applications are made in the areas such as thermal insulation coverages, plastic casting polyester, radome, synthetic foam, adhesives, printed circuit board substrate, bowling, fan blades, golf, pipeline insulation compounds, artificial marble, low–density oil drilling, light–weight cement etc. To overcome industrial problems:

Usage of HGMs in paint:
HGMs possess the tiniest surface area and low–oil absorption level, considerably reducing the usage of other components in paint.

The glassified microspheres surface could supply the chemical corrosion endurance, and light reflection. So, the paint could be prevented from fouling, corrosion, UV, yellowing and scratching etc.

Gas inside HGMs with rigid orientations results in low thermal conductivity, so that paint coating can be expected to have a noteworthy effect on heat insulation. HGMs could effectively improve the coating's fluidity, smoothness and flexibility and lower the cracking and peeling problems.

Dosage suggestion:
The incorporation is usually approximately 10–20 % of the total weight. HGMs are supposed to input at the final stage, and distributed with low–velocity, low–shearing force mixing device. Because of their satisfactory liquidity and low level of friction, they will easily be dispersed into mixture for keeping fully wet condition within a short while. Thanks to thoroughly and slightly prolonging mixing time uniform dispersion can be obtained [18, 36–38].

One can expect that application of HGMs in putty compared with the conventional putty supply certain advantages:

Ease of preparation and production leading to light–weight and large volume. In comparison to ordinary putty, 10–20 % of talc, calcium carbonate, bentonite could be replaced by new one with 5 % of HGMs. Its volume could be in comparison enlarged 15–25 % more than that an ordinary putty having and approximately 8 % resin is saved.

The HGMs oil absorption level is considerably less than those of talc and other filling agents. Therefore, they have considerably decreased viscosity. Putty with HGMs could be easily polished saving time and labour and reducing dust [38–39].

3.1.6. Types of HGMs

3.1.6.1. Silver–coated HGMs (conductive)

Ag possess a number of features making it desirable as a coating component for micro–particulates. As well as being highly electrically and thermally conductive, it also possesses excellent reflectivity across the complete visible spectrum and into the infrared (IR) region. Additionally, Ag surface slowly oxidizes, which matters for other electrical conductors, like Cu or Ni, as it diminishes charge transfer efficiency between surfaces. The considerably conductive nature of Ag also means that it

could be employed to protect sensitive electronic components from electro–magnetic interference coming from other current carrying equipment.
Nowadays, solid Ag particles or flakes are evaluated in special paints, polymers and adhesives to cover or encase structures and components where efficient dissipation of electrostatic charge build–up is needed. This feature is of importance in the aerospace industry, where protection of sensitive components and dissipation of lightning strikes is desirable.

Using particle coating technology, these density and cost issues can be addressed simultaneously. The usage of a low density core material, no matter hollow glass or polymer, as support for a nanometre thin shell of metal, decrease both the density of final composite and the amount of metal needed per unit of final product.

Despite the low levels of conductive metal presence on the coated particles, it is still enough to supply useful functionality. An Ag coating thickness of 50 to 100 nanometres on a 20 μ sphere is satisfactory to allow passage of an electrical current through a coat of paint into which the particles have been formulated at 30 % by volume [34, 39–45].

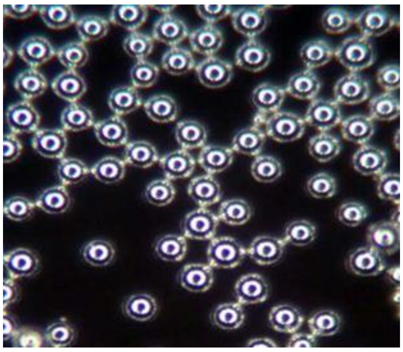

Figure 8. Conductive Ag metal coated HGMs

3.1.6.2. Zinc Oxide (ZnO) Coated HGMs

ZnO is an inorganic component with various outstanding features, like being semiconductor with the association of a large band gap offering advantages of higher breakdown voltages, possessing capability to maintain large electric fields, lower electronic noise, and high–temperature and high–power operation. Additionally, ZnO has high refractive index, high thermal conductivity, binding, antibacterial and ultra violet (UV)–protection features. Applying its coating on HGMs supplies additive functionality of flowing low–weight substrate of controlled shape and size [46–47].

3.1.6.3. Nickel–plated HGMs (conductive)

Conductive Ni–plated HGMs are frequently preferred as a light–weight, lower–cost, electrically conductive incorporation and an alternative option to expensive Ag fillers. To obtain this functionality HGMs are coated with a thin layer of Ni metal for achieving an electrically conductive surface. This light–weight filler is frequently employed in paints, adhesives, composites, and specialized research and development applications to supply cost–effective electrical conductivity [47].

3.1.6.4. Photospheres– titanium dioxide (TiO_2)–coated HGMs (photo–catalytic)

Photospheres are HGMs covered with anatase, photo–catalytic TiO_2, to give a high temperature, buoyant, filterable, and reusable alternative to solid TiO_2 nano–particles. This product line was especially designed for photo–catalytic water treatment. Photospheres can be used, collected and re–used, making it an environmentally friendly and efficient product [40, 48].

3.1.6.5. TiO_2–coated HGMs (light scattering)

Isospheres are HGMs covered with rutile and designed to be high quality seeding material with perfect light scattering features for elevated temperature applications in the experimental fluid dynamics and particle image velocimetry sector. Isospheres are hydrophilic in nature making them to be employed with no surfactant [48].

3.2. SGMs

SGMs supply multiple advantages like improved processing, perfect chemical endurance and heat resistance, thermal stability, low oil absorption, and are employed in automotive, electrical, household devices, adhesives, packaging, paint and construction sectors.

When compared to other types of microspheres, like plastic or hollow glass, SGMs possess a high density, approximately 2.2 g/cc, for borosilicate, 2.5 g/cc for soda–lime, and 4.49 g/cc for barium titanate glass spheres. SGMs have high crushing strength making them suitable for high stress applications where microspheres are exposed to lots of stress during processing or implementation [18, 49–51].

The advantages of glass microspheres are those:

- Solid glass microbeads behave as mini–magnifying glasses for delivering visually more real colour.
- They supply a richer, wetter, deeper look.
- They visually expand expensive colour–shift pigments to obtain cost–effective new appearances.
- They favour even dispersion of colorants and reflectors.
- They behave as mini–ball bearings to enhance material flowing and lower flow lines.
- They supply colour consistency from all viewing angles.
- They improve chemical endurance and chipping strength thanks to the glass hardness, and
- They supply a durable, non–deformable spacer particles for bond line applications [50–51].

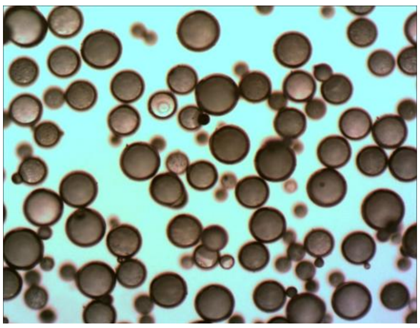

Figure 9. Au–coated SGMs–high density–transparent slightly conductive Au coating on glass particles

3.2.1. Soda–lime (soda–lime–silicate) Glass Microspheres

This group of glass is one of several glass formulations fabricated in a sphere shape. In general, soda–lime glass spheres contain approximately 75 mole % silica, 14 % mole sodium carbonate, 10 mole % calcium carbonate and small amounts of other additives. Specific physical features vary by product. For example, true particle density approximate value is 2.5 g/cc. Annealing temperature is around 500 °C. Softening temperature is 650 °C. Thermal expansion coefficient value (α) is about $80x10^{-7}$/°C. Additionally, they are chemically resistant to acid attacks [18, 52].

3.2.2. Spacer Grade Solid Soda–Lime Glass Microspheres

They are currently supplied in soda–lime glass formulation in particle size varying between 18 and 219 μ. Spacer grade beads possess high sphericity and a quite distinct particle size distribution. They are available as dry powder meshed to > 95 % of particles. This is very high–quality high–value product–just a little content of spacer grade microspheres serves a controlled gap, beside defining and maintaining specified bond line thickness.

3.3. Borosilicate SGMs

Borosilicate glass has high water and acid endurance, low α, low density and high softening point compared to other glass formulations. α for borosilicate glass is about 1/3 of other glass compositions leading it to be resistant to thermal shock being crucial for those application where momentary deviations in shape may matter.

Specific physical features for borosilicate glasses vary by product:

- True particle density: ~2.2 g/cc
- Refraction index: ~1.48
- Annealing temperature: ~560 °C
- Softening temperature: ~820 °C
- α: ~ 30 x 10^{-7}/C
- Chemical endurance: resistant to corrosive environments [11, 53–55].

3.4. Conductive Au–coated solid barium–titanate glass–microspheres

Thin Au coating (about 20 nm) is applied to solid barium–titanate glass microspheres 30–100 μm, obtaining slightly conductive, high density glass particles. Their density value is approximately 4.49 g/cc [11, 55].

3.5. Barium–titanate glass microspheres

This system glass is a distinct optical one with high level of BaO and TiO_2, unlike other conventional counterparts being mostly silica. It gives a much higher refractive index in comparison with other glasses. Refractive index is a parameter showing how light decelerates while passing through an optical compound. Microspheres possessing this property are crucial when employed for optical systems where high refractive power is needed by certain branches such as endoscopy, micro–optics, defence and microscopy. Barium–titanate glass microspheres reflect more light directly back to the viewer’s eye. High refraction index makes retro–reflectivity frequently seeked for in guard rails, traffic signs, reflective paint, tape or clothing. Barium–titanate glass covered hemispherically with aluminium makes sure that the light bounces off the half of the sphere aluminium–coated and gives the retro–reflective influence for high visibility in dark [11, 55].

3.6. Fluorescent–coated glass microspheres

SGMs could be hemispherically covered with fluorescent solvent resistant coatings applied to half of each microsphere, causing the glass particles to be seen colourful, fluorescent, and highly visible in daylight. Coated glass microspheres inhibit bright fluorescent reply under UV light leading these particles to behave spectacularly as fluorescent tracers or as a high visibility option with a specific spectrum reply. Glass microspheres offer fluorescent coated colours of blue, green, yellow, orange–yellow, orange, red and violet and three glass options (borosilicate glass, soda–lime glass, barium–titanate glass) [55].

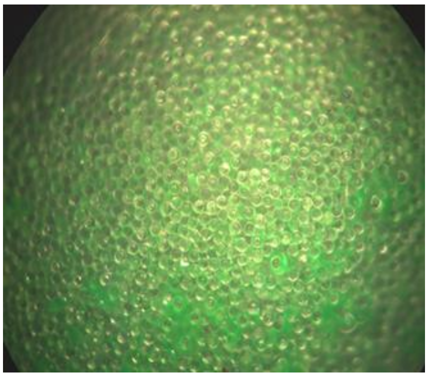

Figure 9. Fluorescent coated glass microspheres

4. Overview of Metal–coated Microspheres and Chalcogenide (Ch) Glass Microspheres

Metal–coated microspheres, either fully or partially, are frequently employed for obtaining a conductive or retro–reflective surface beside taking advantage of precise spherical shape and controlled particle size of microspheres. Metal–coated microspheres are employed as catalysts, laser fusion targets, and compounds for preparing:

- Composite and strengthened polymers,
- The pastes of Cu and Ag for the usage in the field of electronics,
- Thermo–electrical elements,
- Meltable coatings,
- Electrically conducting bond line spacers.

Metal–coated spheres are produced by electro less auto–catalytic accumulation of metals or metal alloys on all types of solid or HGMs with the diameters changing from 1–1000 μm. Metals for coating purposes are nickel, copper, silver, and gold. Multi–layered metal coatings having various metals/alloys could be manufactured. The metal coating's adhesion capability to glass substrate is outstanding; the former one does not defoliate while processed or being ultrasonically treated. Such spheres do not contain uncoated glass microspheres or metal particles. Their coating features are quite similar to those of the bulk metal.

The following features could be given to the glass substrate with metal coating:

- High electrical and thermal conductivity,
- Chemical endurance and ferro–magnetism,
- High specific weight,
- Mechanical strength,
- Electro–magnetic absorption [55].

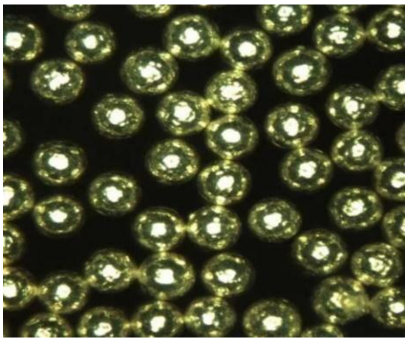

Figure 11. Metal–coated microspheres

Chalcogenide (Ch) glasses obtained mainly from one or more chalcogen elements (S, Se, and Te) are challenging compounds in the field of photonic thanks to non–linear features, photo–sensitivity, low level of phonon energy and IR transparency. Because Ch optical fibres can be found in the market commercially, the manufacturing mean based upon the melting of the tip of a fibre could be employed in such a case too. For dropping the particulate glass through a vertical furnace cleared with an inert (generally argon) gas is a frequently used process. The usage of such an atmosphere is inevitable because of the reactive nature of molten Ch glass. These mentioned spheres have applications in bio–sensing, temperature sensing, lasers and amplifiers. Two, three and four components metal–Ch nano–crystals (like CdSe, PbTe, $CuInS_2$, Cu_2ZnSnS_4 etc.) attract much attention in the renewable energy fields for improving the effectiveness of energy conversion apparatus [56].

Figure 12 indicates a microscope image of the Ch microsphere. The surface of Ch microsphere appears smooth and uniform.

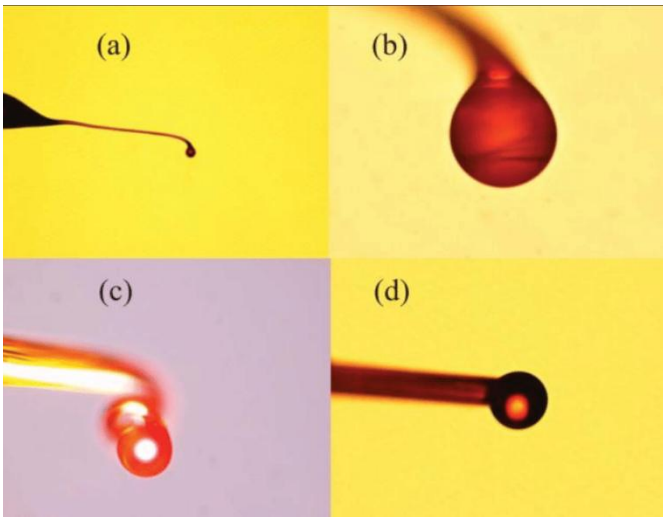

Figure 12. Microscope image of the Ch glass microsphere sample

5. Production of Glass Microspheres

5.1. Flame forming particles

- Frit, other dry granules or solutions having forming components can be feeding material.
- Compositions generally depend on the soda–lime silicates, sodium–borosilicate systems, etc.
- Feed has to possess a blowing (bubbling) agent, which is a constituent decomposing and releasing gas at high temperature.
- Usually S–containing materials.

- Feeding is given into a flame at high temperatures of ~ 1100–1400 °C.
- Gas released when the bubbling agent decomposed leads granules or droplets being enlarged to the hollow glass shells.

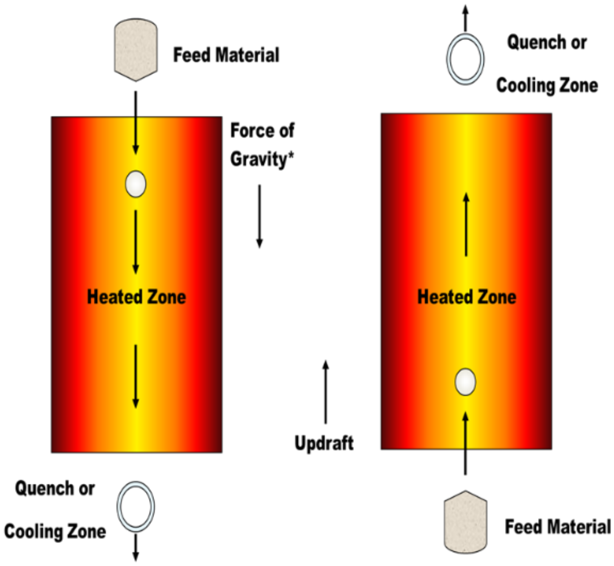

Figure 13. An experimental apparatus developed by SRNL for forming HGMs

Particles may go into the flame in the way of:

- Moving downward thanks to the gravity force,
- An updraft may be employed for controlling holding time in the flame,
- Particles stay shortly in the heated sector,
- Resulting in HGMs with smaller diameters,
- Rising upward by a gaseous stream,
- Holding time in heated sector is longer,
- larger diameters HGMs will be formed [57].

5.2. Sol–gel processing

HGMs are manufactured from a sol–gel derived sodium–borosilicate glass with a composition suitable for photo–enhanced hydrogen diffusion in the hydrogen storage application. The heat–treated xerogel is suspended and doped with iron sulphate or iron chloride to give the transition metal and bubbling agent and is spray dried, the granules of which are afterwards flame sprayed in an oxy–propane flame to obtain glass–microspheres. N–hexa decyl tri methyl ammonium chloride is incorporated to selected suspensions before spray drying for achieving hollow spray–dried particles, which inhibits promise for improved HGMs. Agglomeration of the spray–dried granules results in lowered flowability of the granules and reduces the effectiveness and quality of the HGMs manufacture [58]. The following pictures describe the manufacturing of microspheres by sol–gel method.

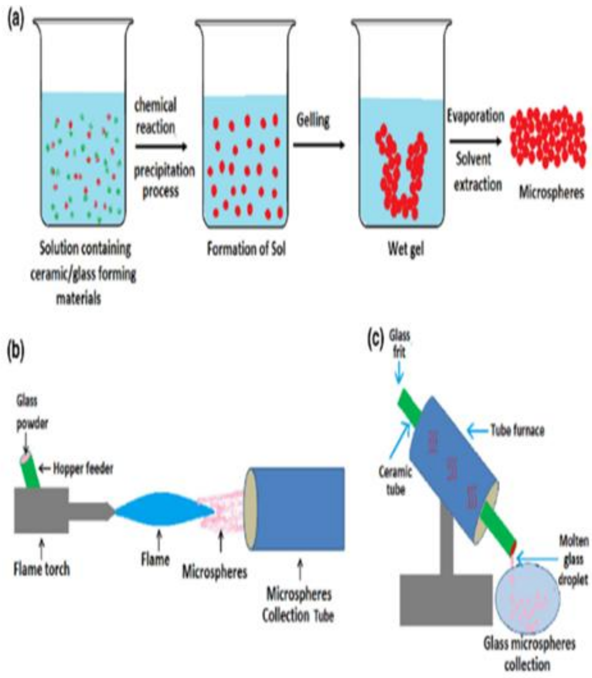

Figure 14. The glass microspheres production by (a) sol–gel, (b) flame spheroidisation and (c) tube furnace methods

5.3. Fly ash

FACs, a type of hollow granules in fly ash, are produced by fast cooling of glass during coal combustion.

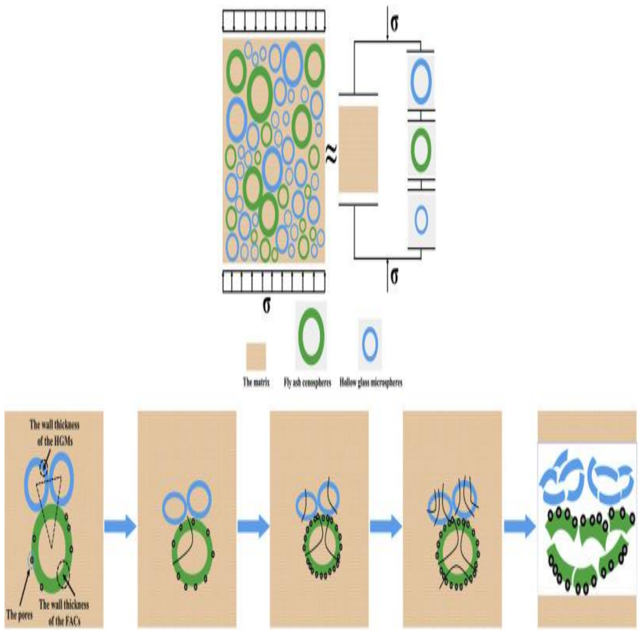

Figure 15. Fabrication of fly ash cenospheres–HGMs

Fly ash over more than 70 million tons, being by–product of thermal power plants, is annually formed in US, only 40 % of which inhibits useful implementations, with the rest dumped, causing crucial environmental pollution. Based upon pozzolanic features, fly ash is evaluated as (i) alternative batch component of Portland cement branch, (ii) for designing concrete mixtures [59].

Ceramic foams evaluating fly ash and red mud were manufactured. Consequently, it was demonstrated that the resultant foams inhibited low–density, high–level of porosity and low–compression strength. Schematic representation is given in Fig. 15.

5.4. Other methods

- Liquid droplet
- Rotating electrical arc
- Argon plasma jet [60–61].

5.5. Industrial production

- Feeding is charged at the bottom of the furnace.
- Feed is carried upward by means of hot gaseous stream.
- Holding time within the hot zone is an action of granule mass and upward speed of the gas flow.
- Holding time is crucial.

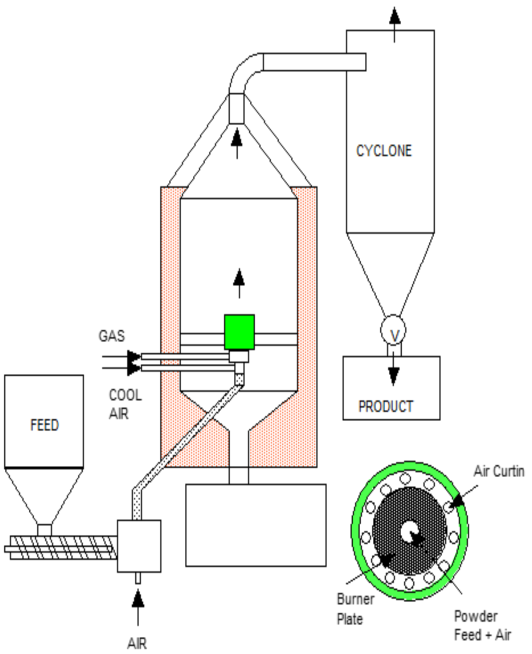

Figure 16. Mechanism of industrial production

- Hollow sphere afterwards has to be got rid of at the max. expansion point and moved through areas of continuously lowering temperatures.
- Outer skin" cools and solidifies supplying mechanical strength.
- The cyclone detaches HGMs from gases.
- HGMs of the diameters varying ~ 10–350 μm are formed.
- Feeding is charged at the top of the heating chamber by a vibratory funnel.
- A "fluidizing component" can be incorporated to the granules for enhancing dispersion.

- A carrier gas transports the particles the flame and dissociates granules more falling through the flame front fusion taking place.
- A cyclone cools and separates HGMs from the gas mixture.
- HGMs of the diameters being less than 125 μm are formed [57].

5.6. Flame spherodization method

For achieving glass microspheres Flame Spherodization Method (IFSM) is also employed, in which irregular glass particles are given into a flame at a temperature high above the glass transition one. The glass particles inside the flame raise their temperature for a few milli seconds, giving a simultaneous viscosity decline adopting a spherical form because of the surface tension action.

Figure 17 presents the IFSM scheme where the powder feeder system consisting of a vibratory sieve set slowly gives the irregular glass particles to the hot zone of the flame and afterwards, at the central part of the flame the glass particles become spheroidized. Finally, the achieved microspheres move through the cool zone of the flame [62].

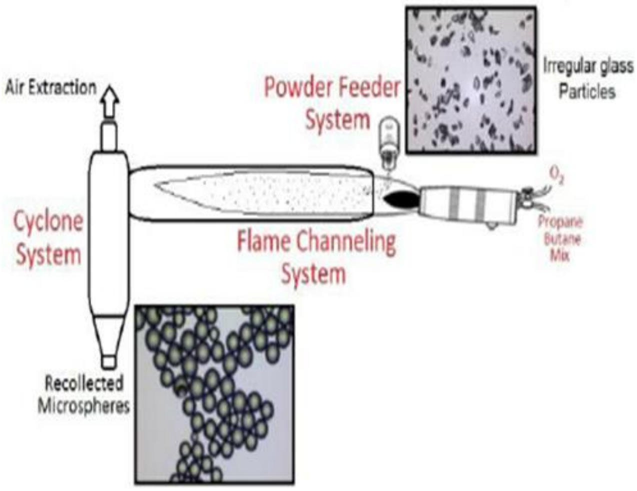

Figure 17. IFSM scheme

6. Present Time Usage Areas

Solid and hollow microspheres possess various implementations, relying on the features of the constituent and the size, and involve a large spectrum of technologies. At present time healthcare and bio–technology are the major fields, specifically thanks to the evolution seen in drug delivery systems. It occupies more than 50 % of the world market with the cosmetics and personal care. The building, paints, coatings and automotive industries can be mentioned as the other regarded industrial application fields. Depending upon the usage, sometimes ceramic or crystalline microspheres may serve better features, being also true in the case of energy implementations [63].

7. Energy Saving

Hollow glass and polymeric microspheres have large range of applications in the area of thermal insulation, thanks to their outstanding features, like high compression strength, low–density, low water absorption level, low–speed heat conduction, and high chemical endurance. HGMs assist us to decrease energy consumption when employed in oil and gas drilling and extraction works. HGMs possess good rolling properties, which could considerably enhance the drilling performance; additionally, drilling fluids with HGMs inhibit resistance to elevated temperatures, stability, and endurance, supplying a prolonged service life of the drilling device as well.

The energy–saving usages of HGMs are especially relevant in the building branch, where the residential energy consumption is progressively rising, specifically because of numerous number of buildings having insufficient insulation and air conditioning, sometimes assumed to be more than 50 % of the total electricity usage in buildings. A cost–effective solution for decreasing such an energy consumption consists in minimizing the solar heat load and the heat dispersion through the roof and walls by employing insulating compounds possessing low–speed thermal conductivity and high IR radiation reflectivity [64].

8. Design

When designing the insulating structures, searching the long–life endurance of the compound as a function of various environmental parameters is an important matter. The HGMs size has to be decently chosen to supply balanced performance on either anti–corrosion or heat insulation. An approach for obtaining high IR reflection and surface preservation from fouling, and so prolonged lifetime, is based upon HGMs coverage by anatase and a super–hydrophobic component. The utilization of including HGMs for improving the thermal and mechanical features of isolation foams was proved for a long time; a polysiloxane foam has recently been formed by foaming and cross–linking processes and strengthened with hollow microspheres being altered with vinyl tri methoxy silane to enhance the consistence of filler and matrix. The thermal stability and the mechanical features of strengthened foam have been considerably improved.

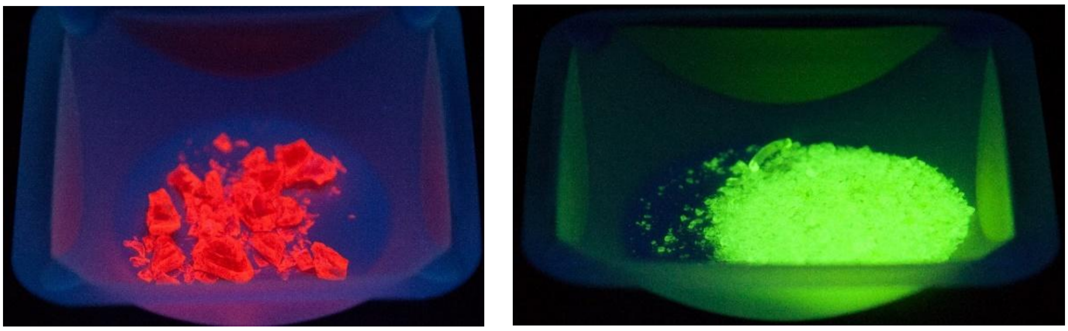

Figure 18. Red and green phosphorescent glass microspheres

HGMs behaved supplying many nucleation sites, being favourable for forming a uniform cell morphology, beside only disadvantage of being easily aggregated in the polymer matrix. Depending on HGMs, one could achieve a higher compression strength or a lower level of thermal conductivity [64].

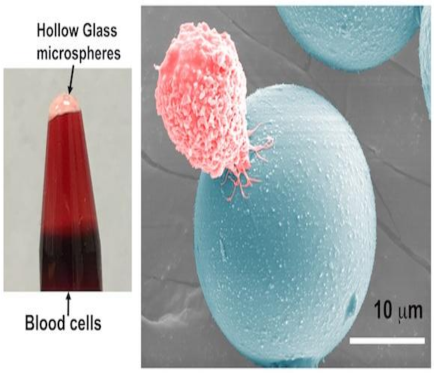

Figure 19. A cancer cell in pink is attached to the surface of the hollow glass bubble in blue (colours are simulated)

Another challenging implementation of HGM was recently indicated effective day–and night–time radiative cooling by employing an innovative meta–material produced by a high–throughput, economical roll–to–roll process. Such compound has SiO_2 microspheres, with the size ranging from 4 to 8 μm, randomly scattered in a polymethyl pentene (TPX) matrix that has a tremendous solar transmittance. Because the encapsulated silica microspheres possess neglectable absorption in the solar spectrum, the compound is not heated by direct solar light; additionally, it inhibits an IR emissivity bigger than 0.93 across the atmospheric window [65].

9. The Latest Studies on Glass Microspheres

Due to wide range applications of glass microspheres, many scientific researchers have been conducted and several articles were hereby written:

According to Patankar et al. [66], by processing HGM to obtain high density polyethylene (HDPE) composites via mixing and compounding is possible leading to composite with high volume fraction of HGMs in HDPE matrix. In the research of Martinelli et al. [67] they mentioned that glass microspheres having radio–nuclides were employed to treat liver cancer and chemical resistant glass microspheres with the potential use in hypothermic therapy were produced. Schmid et al. [68] established that fragile glass spheres could uniformly be covered by a magnetron sputtering process. Dong et al. [69] demonstrated that the microsphere could form single–and multi–mode micro–laser in communication band with a pumping laser of wavelength 780 nm band. Porous wall (PW) HGMs having a tortuous network of nanometre–scale channels are new forms of glass micro particles. They stayed in place after mouse intra tumoral injection, advising a probable application for anti–cancer drugs delivery. Li et al. [70] presented an initial characterization of PW–HGMs, an exclusive material differentiated by large, solvent–accessible inner volume and mesoporous walls.

Porous HGMs possess various usages including porosity enhancers for lead–acid batteries. A fast, facile and high yield synthetic method for manufacturing porous HGMs with the diameters around 45–55 μm was stated by Xie et al. [71]. HGMs could be applied in the insulation field as fillers thanks to the hollow structure being not conductive to the transfer of heat. Bing Li et al. [72] mentioned that hollow microspheres with low thermal conductivity and conduction heat transfer is the most important means for transferring heat within the HGMs. The thermal conductivity of the system can be lowered by the combined usage of the former and the latter methods. Xu et al. [73] prepared intact hollow glass–ceramics microspheres with spherical morphology using organic template method with PAM as template. According to the researches of Shetty et al. [74] an easy flame spraying method for forming cobalt–doped HGM was developed by recycled amber glass frit coated by a transition metal salt. Poorbaygi et al. [75] aimed to sort out whether glass microspheres impregnated with two radionuclides, ^{90}Y as source of therapeutic β emissions and ^{177}Lu as source of diagnostic γ emissions could be useful for spec imaging during or after applying ^{90}Y microspheres for treating hepatic tumours. To manufacture uniform HGMs for the hydrogen storage application, a sol–micro–emulsion–gel process combined with a T–shaped junction microfluidic technology was developed to produce mono–sized precursor gel microspheres. Huang et al. [76] inhibited that the precursor gel microspheres possess uniform diameter, density, microstructure, composition and high sphericity. The mono–sized dried gel microspheres can be converted into uniform HGMs, with high yield and quality for hydrogen storage, in an elevated temperature vertical furnace under the optimized working condition. In the research of Gao et al. [77] cuprous oxide (Cu_2O) microcrystals with sea urchin–like morphologies were prepared on the surface of HGMs employing sodium sulphite (Na_2SO_3) as the reducing agent and sodium acetate–acetic acid (NaAc–HAc) as buffer solution in copper sulphate ($CuSO_4$) solution. Liu et al. [78] directly synthesized HGMs–$CoFe_2O_4$ (HGMs–CF) core–shell particles by the homogeneous co–precipitation method at 90 °C without calcination. The experimental study on compressive features of syntactic foams with three different

HGMs of different grades with varying volume % has been done by Swetha et al. [79]. Bioactive glass inlays and coating failed to improve biological osseo integration of Ti and CoCr alloy implants in the research of Keränen et al. [80]. Hollow glass–ceramics microspheres (HGCM) were manufactured by a simple technique employing polyacrylamide microspheres (PAM) as template in the study of Nan Xu et al. [81].

Bortot et al. [82] developed a simple theoretical mathematical model to help the process of glass particles spheroidization in a propane–butane–oxygen flame. The study of Lakhkar et al. [83] exhibited the successful production of titanium–phosphate glass microspheres. In the work of Peroni et al. [84], the mechanical behaviour of syntactic foams made of HGMs mixed in an iron matrix was searched. Qi et al. [85] investigated the effects of the initial glass compositions of gel particles, the pressure and composition of furnace atmosphere, the temperature and length of refining zone on the diffusivity, quality and yield of the resulting HGMs. Intact HGCM with spherical morphology were prepared by organic template method with PAM as template according to the research of Xu et al. [86]. Magnetic Fe–Ni–P nanoparticles have been produced on HGMs via electro less plating for the implementation of light–weight microwave absorbers by Zhou et al. [87].

Jiao et al. [88] discussed the influences of SBF concentration, immersion time, solid/liquid ratio and activation of HGM on the deposition rate and coating characteristics. They found that the activation process in the entity of bio glass benefits the deposition of hydroxyapatite coating on HGMs. The poly(butylene succinate)/hollow glass microsphere (PBS/HGM) composites were prepared with various HGM contents by Li et al. [89]. In the researches of Hu et al. [90] the matrix was silicon rubber (SR) and the filler was the mixture of different ratio of intact and broken HGM. The magnetic features of cobalt–coated glass microspheres composite achieved from the typical synthesis were investigated at room temperature by Zhou et al. [91]. Mesoporous bioactive glass microspheres synthesized by acid or acid–alkali catalysis can be good candidates as drug carriers for bone disease and filling materials in bone repairment in the future thanks to the study of Miao et al. [92]. The effective application of RSM for determining optimal conditions for hydroxyl radical production and rapid destruction of dimethyl phthalate indicated that HGM–TiO_2 photo catalysis is a promising material for water treatment according to Jiang et al. [93].

Dalai et al. [94] pointed out that a suitable metal loading in required proportion on the HGMs assists in improving the hydrogen storage capacity. As reported in the publication of Sorge et al. [95], the PHGM additives did enhance electrolyte storage and porosity in the electrodes. Dalai et.al. [96] reported the preparation and characterization of cobalt loaded HGMs from amber glass powder for hydrogen storage application. The paper of Guimaraes et al. [97] described the application of a Monte Carlo code to simulate both the irradiation effects and the imaging of ^{166}Ho and ^{90}Y sources localized in different parts of the liver. Liu et al. [98] exhibited that a suitable amount of HGM loading fraction in the EVA/MH composites leads to a significant synergistic influences, increase in their fire retardancy capabilities and thermal stability. Since hydroxyapatite is chemically similar to the mineral component of bones and hard tissues in mammals, its formation on HGMs classifies them as bioactive components and since HGMs possess considerable mechanical strength, so upon coating over metal implants it would impart more strength to the implant material reported by Shrivastava et al. [99]. Pereira et al. [100] pointed out that the use of HGM composites in the fabrication of reactors is a way to lower costs and make large scale outdoor microalgae production feasible. HGMs were demonstrated to be a promising hydrogen storage material with many advantages over other hydrogen storage techniques and the raw materials for the HGMs production are generally recycled culets and so are cost effective and need low energy usage for production according to the work paper of Dalai et al. [101]. In the study of Sun et al. [102], TiO_2 nano–particles were successfully coated on the HGMs surface in the form of core–shell structure by sol–gel method. Cenospheres retain their integrity even during sintering according to Lehmhus et al. [103]. This is reflected in a major increase in mechanical performance, up to the degree of weight–

specific strength exceeding that of the unfilled reference material, while ductility remains on a promising level. Strain rate sensitivity is not significantly affected by filler content. Domanická et al. [104] exhibited that photoluminescence emission spectra of Nd–doped glass microspheres prepared by flame synthesis were not affected by SiO_2 content, while emission intensities of Er–doped glasses decreased with increasing SiO_2. Particles–filled composites and special models developed for hollow microsphere filled composites are employed to analyse the experimental trends of thermal conductivity and dielectric constant by Zhu et al. [105]

The research of Lyubimov et al. [106] dwells upon the comparative analysis of the methods of the glass microsphere metallization. One must be aware to minimize the compression, impact, and shear forces upon the HGMs to ensure they are not damaged during processing and transport [18]. And Yalcin touched briefly on the subject of HGMs as a key component of repairing compounds for auto, wall, plaster, etc. Fusing of ceramics using lasers as energy sources is one of the promising processes for the future of ceramic technologies according to Hmood et al. [107]. Comparison of some changes occurring in PLA due to its modification by glass filler being in the form of GM was the objective of the study of Malinowski et al. [108]. Ce–doped (Y, Gd)$_3$Al$_5$O$_{12}$ nano–ceramics were manufactured by the method of hot–pressing sintering of glass microspheres followed by heat treatment according to the work paper of He et al. [109]. In the study of Ahn et al. [110] organic/inorganic composite membranes based on sulfonated poly(phenylene oxide) (SPPO) and HGMs were prepared for the usage as proton exchange membranes in direct methanol fuel cells (DMFCs). A miniaturized chemical vapour sensor probe was developed using a porous glass microsphere (PGM) as the alignment–free optical micro resonator as a result of studies of Wang et al. [111].

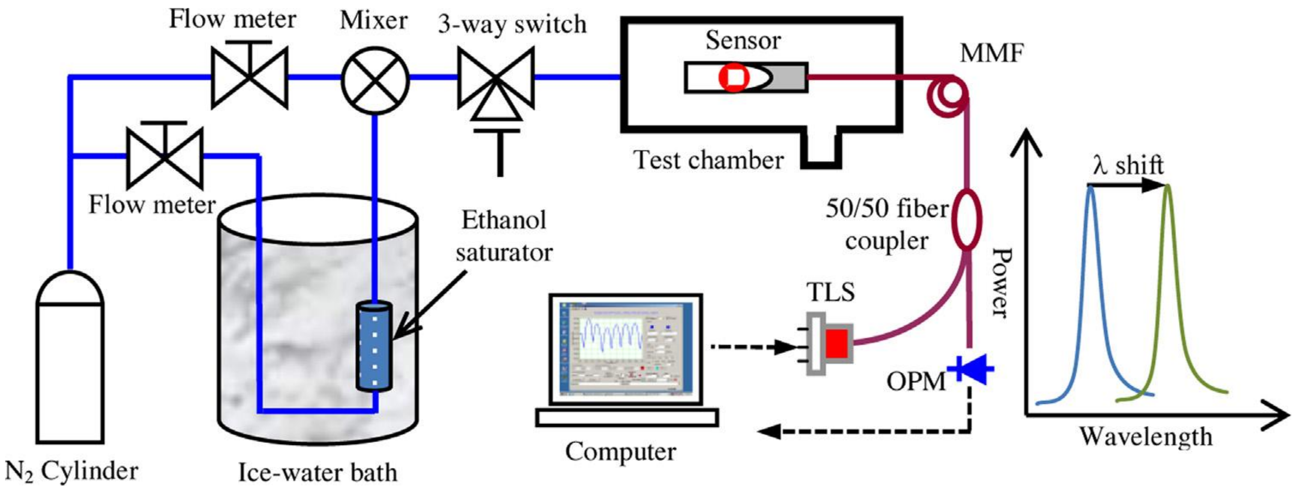

Figure 20. Block diagram of the experimental setup of Wang et al. [111] to test the integrated PGM resonator sensor for chemical vapour detection (TLS: Tunable laser source OPM: Optical power meter and MMF: Multimode optical fibre)

The hybrid filler of HGMs and nitride particles was filled into low–density polyethylene (LDPE) matrix via powder mixing and then hot pressing technology to achieve the composites with higher thermal conductivity as well as lower dielectric constant during the studies of Zhu et al. [112] A microsphere made from a strontium–barium–niobate glass co–doped with Er^{3+} and Yb^{3+} ions is proposed to be employed as an optical temperature sensor. By means of the fluorescence intensity ratio technique, the effect of temperature changes in the emission bands of the erbium thermalized levels is characterized by Paez et al. [113]. A new method to examine the luminescent features of Tm^{3+}/ Er^{3+}/Yb^{3+} tri–doped oxyfluoride glass ceramic was proposed in the study of Huang et al. [114]. High dimensional stability and load–bearing capacity combined with thermal stability of syntactic foams make them attractive in aerospace, automotive, civil as well as marine structural applications compared to the conventional materials used with GM in these implementations [18]. A novel catalyst format, TiO_2–coated hollow glass spheres was studied by Pestana et al. [115].

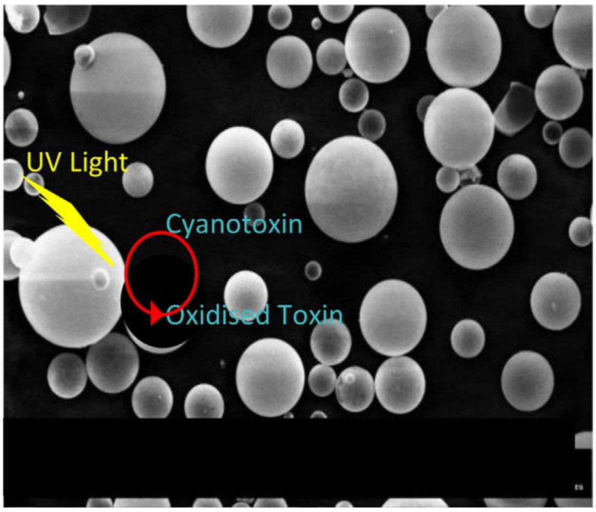

Figure 21. The photocatalytic degradation of eleven microcystin variants and nodularin in water using photospheres [115]

The article of Perfilov et al. [116] deals with the problem of rising ecological safety, effectiveness and quality of mortars and grouting mortars. Ghosh et al. [117] investigated the effects of the size of HGMs (20 µm vs. 40 µm) and composition on the energy absorption capacity of the silicate glass foams under both the quasistatic (~10^{-3} s^{-1}) and high–strain rate (~$10^{3}s^{-1}$) loading conditions. The effect of acid leaching time on porosity properties of porous microspheres was searched for by Moosavi et al. [118] changing leaching time cumulative volume became 7–fold. In the study of Mingfei et.al. [119], glass microspheres were prepared from CRT funnel glass, together with lead recovery by carbon thermal reduction enhanced acid leaching.

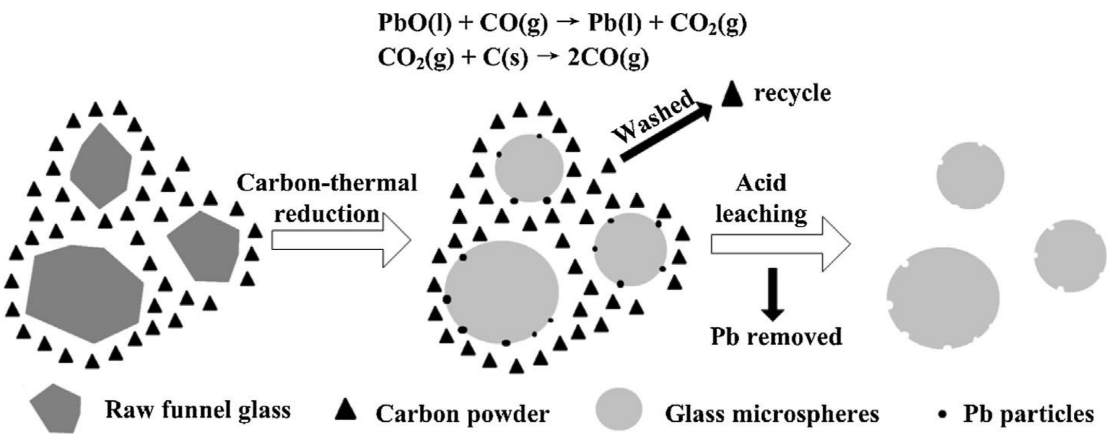

Figure 22. New process for detoxification and reutilization of waste cathode ray tube (CRT) funnel glass development [119]

The composite of HGMs coated by $Ni_{0.7}Zn_{0.3}Fe_2O_4$ particles was fabricated via sol–gel method, and then the ternary composite (HMG/$Ni_{0.7}Zn_{0.3}Fe_2O_4$/PT) was synthesized by in situ polymerization by Li et al. [120]. A temperature resistance buoyancy material was manufactured by means of a tert–butyl alcohol gel casting process with borosilicate glass (BG) and HGMs as the matrix and filler, respectively by Ren et al. [121]. The article of Oreshkin et al. [122] was devoted to the study of properties of light–weight extruded fine–grain cement concrete with HGMs. In the study of Geng et al. [123] heat–resistant syntactic foams with relative high compressive strength, elastic modulus and low bulk density were manufactured through binding HGMs by phosphate adhesive. According to Zhang et al. [124] HGMs filled polymers exhibit strong strain rate sensitivity, and the strain rate sensitivity factor decrease with the increase of volume fraction. Geometrical parameters of the HGMs were measured by Li et al. [125]. Selective internal radiation therapy of hepatic malignancies is a ground breaking therapeutic modality that needs the combined efforts of multiple medical disciplines to ensure the safe delivery of ^{90}Y–labelled microspheres in the studies of Westcott et al. [126]. Materials with light–weight, high–strength and low thermal conductivity were manufactured by bonding HGMs with different content of ACP and TEOS by the study of Wang et al. [127]. The super–hydrophobic and IR–reflectivity HGMs was synthesized by being coated with anatase TiO_2 and a super–hydrophobic material by Yan et al. [128]. Titanium–doped HGMs with different levels of Ti doping have been manufactured from dried gel precursors for application in ICF programs by Li et al. [129]. During the studies of Duan et al. [130] hollow mesoporous bioactive glass microspheres (HMBGMs) were formed via a hydrothermal–assisted self–transformation method employing cetyl trimethyl ammonium bromide (CTAB) as a mesoporous template. In the paper of Delogu et al. [131] environmental and economic assessments were combined to evaluate the sustainability of adopting an innovative light–weight material for an automotive component. Novel HCMs from mixtures of fumed silica (FS), HGMs, polyester chopped strand fibres, titanium dioxide and carbon black powders were successfully manufactured by the dry powder mixing method HGM additions led to a shift in the average pore diameter of HCMs toward a finer value and more concentrated distribution but posed a decrease on the specific surface area of the HCMs according to the studies of Li et al. [132].

Nanometre ZnO was deposited on HGMs using a sol–gel method by Lu et al. [133]. The optical features of the composite pigments were strongly affected by the morphology of ZnO nanostructures. Ren et al. [134] indicated that the composite composed of the iM30K HGMs with small mean particle size inhibited high compressive strength. In the studies of Li et al. [135] the effect of Ti–doping on the compositional homogeneity and the difference between the two classes of HGMs, Ti–doped gel precursors and HGMs were characterized by XRD, XRF, SIMS, SEM and EDS. Herrera–Ramírez et al. [136] have taken the advantage of both low density and thermal conductivity of HGMs, and high mechanical and electrical conductivity of carbon–based nano–fillers, micro– and nano–sized fillers can be combined into a single composite material. In the searches of Ren et al. [137] a high–temperature resistance buoyancy material HGMs/SiO_2 composite with the HGMs as the filler and the SiO_2 as the matrix was successfully prepared through a compression moulding process. Yang et al. [138] used a Tm^{3+}–Ho^{3+} co–doped tellurite glass as the laser medium to build active microsphere laser resonators. A droplet method is implemented and hundreds of high quality microspheres can be fabricated simultaneously. In the work of Anbuchezhiyan et al. [139], an endeavour has been made to synthesis HGM reinforced magnesium matrixes based syntactic foams and analyse its mechanical properties. As the conclusion of publication of Jiao et al. [140], HGMs can significantly reduce the smoke production and the heat release of the TPU composites by catalysing TPU carbonization and change the structure of char residue layer during the combustion process. Dalai et al. [141] have fabricated cobalt–loaded HGMs via air–acetylene flame spheroidisation and nano–crystalline CoO–loaded HGMs were prepared using cobalt nitrate hexahydrate blended with glass powder. In this field assisted alignment process, the micro columns also exhibit gradient structure according to Liu et al. [142]. A combustion route with wet creams as the starting precursor was developed by An et al. [143] for the formation and seemly of Ni–NiO composite shells on silicate HGMs. Treated HGMs and short bamboo fibre HGMs based PP composites have been prepared by Kumar et al. [144] and investigated in this study for their mechanical properties and morphology. Based on the results of various analysis of Kang et al. [145], the optimal weight of HGMs is in between 1 and 7 wt. % without compromising the superior characteristics of SWNT in the syntactic foam was suggested.

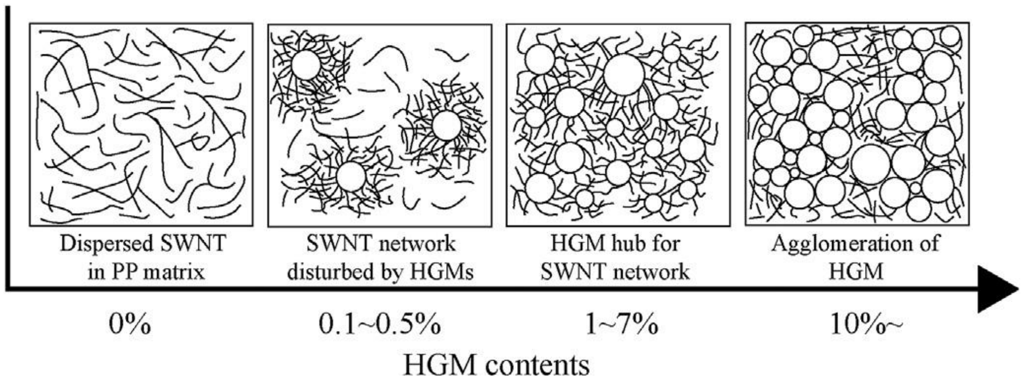

Figure 23. Schematic representation of effect of HGM contents on SWNT network [145]

Ultra low weight Ag–coated glass microsphere composites exhibit the most excellent reliability for high performance conducting polymer–matrix composites according to Wang et al. [146]. Pontiroli et al. [147] obtained a mesoporous bioactive glass in the SiO_2–CaO system for the first time by spray–drying an aqueous synthesis solution under mild acidic conditions. In the work of Bianchetti et al. [148] a refractometric air pressure sensing platform based on spherical whispering–gallery mode micro–resonators was presented and analysed. The "operator maximum dose" study of Ralite et al. [149] suggests that the radiologist and the NM manipulator receive significant exposure on their hands by using internal radiation therapy with ^{90}Y glass microsphere.

The manuscript of Zakir Hossain et al. [150] highlighted a simple cost–effective one–step process for fabricating porous calcium phosphate–based glass microspheres with varying control over surface pores and fully inter–connected porosity via a flame spheroidisation process. Tian et al. [151] presented a new point of view to develop retro–reflective polyurethane (GMPU) composed of polyurethane and amino–functionalized glass microspheres (NH_2–GM), the latter was founded to be chemically bonded onto the PU successfully. According to Araque et al. [152] composite films of PHB, HGM and PP–g–MA were developed through the melt intercalation technique to evaluate the properties of the materials by means of morphological, thermal, and mechanical properties. Ren et al. [153] manufactured a temperature–resistant FACs–HGMs/BG composite with different contents of FACs. $BiOCl_{1-x}I_x$ coated HGM was synthesized as a novel near IR reflective pigment for super–hydrophobic cool roof coatings. $BiOCl_{1-x}I_x$ micro–flowers or microspheres were deposited on HGMs by a simple chemical liquid deposition method by Gao et al. [154].

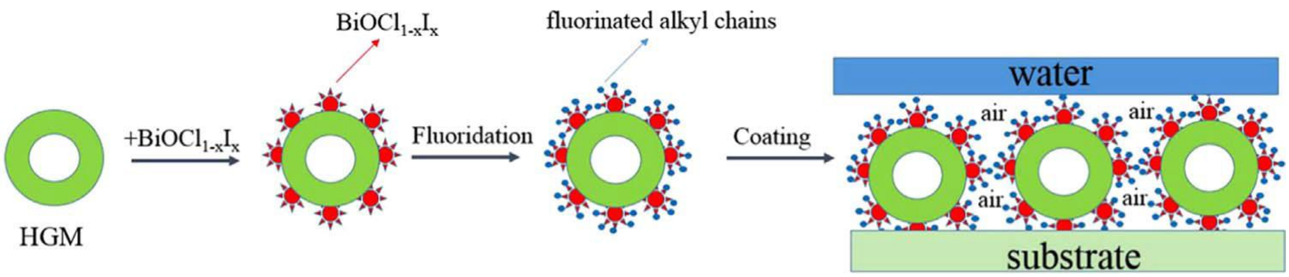

Figure 24. Schematic illustration of the fabrication of super–hydrophobic cool films derived from HGM/BiOCl $_{1-x}$ I_x composites through a facile brush technique process [154]

The results of Vieira et al. [155] can be summarized that when a calibrated Ho^{3+} doped YAS microsphere is excited and heated up with a laser, its temperature can be estimated by measuring the WGM peaks displacement, and that the emission band centred at 1200 nm can be used if medical applications are considered. The cement–based composites made from graphene nano–

platelets (GN) and HGMs were prepared and its electromagnetic waves absorbing properties were researched by Lv et al. [156]. HGM@TiNiY pigment with core–shell structure which has good thermal reflectivity has been prepared by a novel mixing slurry–sintering method, according to the knowledge of the Zeng et al. [157]. In the studies of Huang et al. [158] the fibre taper I_x microsphere coupled device with WGM is used to efficiently generate the UC luminescence, about 5 times than the case of optical fibre end directly illuminating. Ohta et al. [159] developed human haemoglobin (hHb) and albumin (HSA)–based microspheres using Shirasu porous glass (SPG) membrane emulsification. In the publication of Al–Gemeel et al. [160], the effect of various combination ratios of PVA and SF fibres and the usage of hollow glass powder admixture on the compressive strength, flexural behaviour and energy absorption of ECC were investigated. In the searches of Nbuchezhiyan et al. [161], an endeavour has been made to investigate the mechanical features of HGMs–reinforced die cast magnesium alloy under vacuum die casting process. The morphologies, structures, components and thermal stabilities of the amorphous $La_4Ti_9O_{24}$ microspheres manufactured by a container less flame spraying method, were investigated by SEM, optical microscope, XRD apparatus, EDX analysis and DSC measurement during the studies of Li et al. [162].

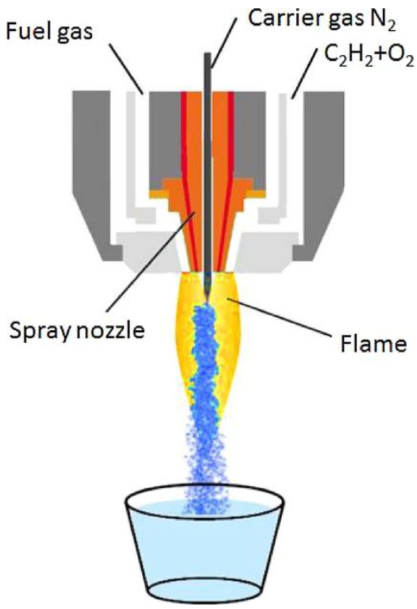

Figure 25. Schematic illustration for synthesis of various microspheres by flame spraying [162]

Kafrouni et al. [163] analyzed the differences between ^{99m}Tc–MAA SPECT and ^{90}Y–microsphere PET dosimetry investigating imaging and clinical factors. In the work presented by Greppi and Fabbri [164] the effect on the dispersed heat produced by inserting air containing microspheres in the case material of a hybrid solar tile has been investigated.

A new NaF roughening and NaOH washing strategy instead of HF was successfully applied in the study of Zhang et al. [165] to alleviate the damage and breakage of HGMs. In the study of Hong et al. [166] hierarchically porous bioactive microspheres were fabricated by an extended electro spraying technique assisted with non–solvent induced phase inversion. As a result, the ESBG microsphere with regular spherical shape and interconnected porous microstructure have potential applications in bone tissue engineering, drug delivery and injection medications. According to the study of Ding et al. [167] the compressive strength and relative density of the ceramics increased exponentially with the solid loading. Er^{3+}–doped silica glass microspheres with diameters of ~25–40 μm were fabricated by using an electrical discharge method by Nguyen et al. [168]. In the study of Cheng et al. [169], MCRT method, combined with Mie theory, was used to investigate the radiative transfer of radiative–cooling coatings with non–uniform size–distribution SiO_2 particles. Vereshchagina et al. [170] have realized a sustainable approach to the synthesis of the microsphere composite with a hollow core–shell structure displaying the function of a specific ion sorbent by coating cenosphere derived microsphere glass supports with nano sized $ZrMo_2O_7(OH)_2(H_2O)_2$ as a result of their research. According to Fang et al. [171] the degradation rate of PLGA, mass loss, water uptake, and swelling of microspheres in vivo all increased compared with incubation in vitro.

10. Conclusions

Scientific and commercial implementations of solid and HGMs have been continuously growing day by day, besides the advances in their manufacturing with high quality and large batches. Glassy microspheres could easily be doped with chemical elements and compounds to improve their functionality. Additionally, they could be produced as porous or hollow, permitting for encapsulation of other chemical or bio–medically relevant components. All these features led to develop micro–lasers, micro–sensors, bio–labelling or drug–delivery bullets or even to examine matter–radiation interactions at the very high power density made possible. As well as industrial applications it seems that there is a constant or increasing demand from the healthcare and construction (e.g., paints and coatings) field.

References

[1] Saferstein R., Criminalistics, an introduction to forensic science, Cram101 Text Book, 11th edition, 2017.

[2] Stuart M. L., Handbooks of composite reinforcements, VCH Publishers, California, pp. 248–50, 1993.

[3] Glass beads & retro reflectivity, ALL Glass Limited, 49 Burnbrae Road, Linwood Industrial Estate, Linwood, PA3 3BD Scotland (Access Date: 15. 03. 2019).

[4] Çelebi H., J. of Sci. and Techn. A–Appl. Sci. and Eng. 2017, 18: 3.

[5] Ochoa O. O., Reddy J. N., Finite element analysis of composite laminates. Dordrecht: Springer Science & Business Media, 1992

[6] Sorensen L., Gmür T., Botsis J., in: Proceedings of the 3rd International Conference on Composites Testing and Model Identification Comp Test, University Press, Porto, pp. 174–175, 2006.

[7] Beyatricks K. J., Kavimani S. et al., Earth Journals, 2013, 2: 1, 2013.

[8] Righini G. C., Glassy microspheres for energy applications, Micro machines (Basel), Published online 2018 Jul 30. doi: 10.3390/mi9080379 (Access Date: 18.03.2019).

[9] Standard specification for roadworks, November 2015, accessible on http://www.nt.gov.au/infrastructure/techspecs/index.shtml (Access Date: 18.03.2019).

[10] Evans M. R., Pavement marking demonstration projects: State of Alaska and state of Tennessee, FHWA–HRT–12–048, November 2013.

[11] Product information: Floated product series, 3M Glass Bubbles, accessible on www.3M.com/oilandgas (Access Date: 29.03.2019).

[12] Yung W. K. C. et al., Comp. Sci. and Techno., 2009, 69(2): 260–264.

[13] Verweij H., G. de With, Veeneman D., J. of Mater. Sci., 1985, 20(3):1069–1078.

[14] Whatever floats your boat, Clemson student chapter of the American Society of Civil Engineers, Wayback Machine. ces.clemson.edu, 2009.

[15] Erikson R., Foams on the cutting edge, Mechanical Engineering–CIME, 1999.

[16] Shelby J. E. et al., A radically new method for hydrogen storage in hollow glass microspheres, DOE Technical Report FG26–04NT42170, 2017.

[17] Mee S. J., The synthesis, characterisation and properties of self-assembled hollow and low density microspheres, PhD Thesis, College of Engineering and Physical Sciences, University of Birmingham, May 2011.

[18] Amos S. E., Yalçın B., Hollow glass microspheres for plastics, elastomers, and adhesives compounds, PDL Handbook Series, William Andrew, Elsevier, 2015.

[19] Big world, professional producer for glass beads!: Products manual, Landscapus INC., accessible on http://www.landscapusinc.com/ (Access Date: 20.03.2019).
[20] Gauthier M. M., Glass processing, pp 1115–1170, 1995 (Access Date: 20.03.2019).
[21] Garza–Cruz T. V., Nakagava M., Granular Matter, 14. 10.1007/s10035–012–0315–6, 2012.
[22] Liang J. Z., Li F. H., Measurement of thermal conductivity of hollow glass–bead–filled polypropylene composites polymer testing, 25. 527-531. 10.1016/j.polymertesting.2006.02.007., 2006 (Access Date: 21.03.2019).
[23] Wang J. H. et al., DOI: 10.3144/expresspolymlett.2008.16, December 2007.
[24] Shunmugasam V. C., Pinisetty D., Gupta N., DOI 10.1007/s10853–013–7691–0, 2013.
[25] Rosato D., Density in plastics engineered product design, 2003.
[26] Zhu, B. L. et al., J. Reinf. Plast. Compos., 2012, 31: 1311–1326.
[27] Bing L. et al., Modelling and characterization of effective thermal conductivity of single hollow glass microsphere and its powder, materials, 11. 133. 10.3390/ma11010133., 2018.
[28] Mukund J. Y. et al., Brazilian J. of Pharmaceutical Sci., 2012, 48: 1.
[29] Awaja F. et al., Progress in Mater. Sci., 2016, 83.
[30] Li Z. et al., J. Phys. Chem. C, 2009, 113: 7, 2792–2797.
[31] Liang J. Z., Li F. H., Polym. Test., 2006, 25: 527–531.
[32] Wong Y. et al., J. Vis. Exp., 2017, 122.
[33] Debasmita M., Alok S., Plast. Polym. Technol., 2013; 2: 39-47.
[34] Zhang H. et al., Electroplating Finishing, 2007, 26(1): 26–29
[35] Kureha. Available online: http://www.kureha.co.jp/en/business/material/microspheres.html (Access Date: 25.03.2019).
[36] Han M. G. et al., J. Magn. Mater., 2009, 321(9): 1125–1129.
[37] Li, B. et al., J., Mater. Lett. 2011, 65, 1992–1994.
[38] Ari, T. C., Akin, S., in Proceedings of the World Geothermal Congress, Melbourne, Australia, pp. 1–7, 2015.
[39] Budov V. V., Glass Ceram. 1994, 51, 230–23.
[40] Minhas A. et al., Hollow–glass sphere application in drilling fluids: Case study, in Proceedings of the SPE Western Regional Meeting, Garden Grove, CA, USA, 2015.
[41] Ganesan P. et al., Am. J. Drug Discov. Dev., 2014, 4: 153–179.
[42] Nussinovitch A., Polymer macro– and micro–gel beads: Fundamentals and applications, Springer Sci. & Business Media: Berlin, Germany, 2010.
[43] Gu G. et al., Chin. Opt. Lett., 2013, 11: 101401.
[44] Rembaum A., Tokes Z. A., Microspheres: Medical and biological applications, CRC Press Revivals: Boca Raton, FL, USA, 2017.
[45] Veatch F. et al., Method of producing hollow glass spheres, U.S. Patent 2,978,339, 4 April 1961.
[46] Fan K. C. et al., Meas. Sci. Technol., 2010, 21: 054002.
[47] Nogami M. et al., Rev. Laser Eng., 1980, 8: 793–797.
[48] Li T., Fundamental tests of physics with optically trapped microspheres, PhD Thesis, University of Texas, Austin, TX, USA, 2013.
[49] Liepins R. et al., Progr. Polym. Sci., 1980, 6: 169–186.
[50] Gulyaev I., Experience in plasma production of hollow ceramic microspheres with required wall thickness, Ceram. Int. 2015, 41: 101–107.
[51] Okamot S. et al., Sci. Rep., 2014, 4: 5186.
[52] Sanghera J. et al., C. R. Chim., 2002, 5: 873–883.
[53] Lim K. L. et al., Chem. Eng. Technol., 2010, 33: 213–226.
[54] Schmid G. H. S. et al., Int. J. Energy Res., 2017, 41: 297–314.
[55] https://www.cospheric.com/ (Access Date: 30.03.2019).
[56] Righini G. C., Glassy microspheres for energy applications, Micromachines (Basel), 2018 Aug; 9(8): 379, Published online 2018 Jul 30. doi: 10.3390/mi9080379.

[57] www.glass-bubble.com/blog/archives/tag/hollow-glass-microsphere (Access Date: 01.04.2019).
[58] Schmitt M. L. et al., J. of Non–Crys. Solids, 2006, 352(6): 626–631.
[59] Ranjbar N., Künzel C., Cenospheres: A review, Fuel, 2017, 207:1–12.
[60] Bica I., Mater. Sci. and Eng. B, 2002, 88 (1): 107–109.
[61] Marchand C. et al., J. of Thermal Spray Techno., 2007, 16(5): 705–712.
[62] Watkins I. G., Prado M., Procedia Mater. Sci., 2015, 8: 1057–1065.
[63] Budov V. V., Hollow glass microspheres. use, properties, and technology (Review), Glass and Ceramics, 1994, 51(7): 230–235.
[64] Righini G. C., Righini N., Glassy materials based microdevices, ISBN 978-3-03897-618-9 (Pbk); ISBN 978-3-03897-619-6, Feb. 2019.
[65] Bermel P. et al., Optics Express, 2015, 23(24): A1533–A1540.
[66] Patankar S. N., Kranov Y. A., Mater. Sci. and Eng. A, 2010, 527: 1361–1366.
[67] Martinelli J. R. et al., J. of Non–Cryst. Solids, 2010, 356: 2683–2688.
[68] Schmid G. et al., Surface and Coatings Techn., 2010, 205(7): 1929–1936.
[69] Dong C. H. et al., Optics Commun., 2010, 283: 5117–5120.
[70] Li S. et al., Nanomedicine: Nanotechnology, Biology, and Medicine, 2010, 6: 127–136.
[71] Xie Y. et al., J. of Power Sources, 2011, 196: 10727–10730.
[72] Li B. et al., Mater. Letters, 2011, 65: 1992–1994.
[73] Xu N. et al., Ceram. Int., 2011, 37: 2663–2667.
[74] Shetty S., Hall M., Hydrogen Energy Publications, 2011, 36: 9694–9701.
[75] Poorbaygi H. et al., Appl. Radiation and Isotopes, 2011, 69: 1407–1414.
[76] Huang W. et al., Fuel and Energy Abst., 2011, 36(16): 9758–9766.
[77] Duan X. J. et al., Mater. Letters, 2011, 65: 243–250.
[78] Liu J. et al., Mater. Letters, 2011, 65: 929–932.
[79] Swetha C., Kumar R., Materials and Design, 2011, 32: 4152–4163.
[80] Keränen P. et al., J. Mech. Behav. Biomed. Mater., 2011, 4(7): 1483–91.
[81] Xu N. et al., Mater. Research Bull., 46, 2011, 92–97.
[82] Bortot M. B. et al., Procedia Mater. Sci., 2012, 1: 351–358.
[83] Lakhkar N. J., Park J. H., Acta Biomaterialia, 2012, 8: 4181–4190.
[84] Peroni L. et al., Mater. Sci. and Eng. A, 2012, 552: 364–375.
[85] Qi X. et al., Int. J. of Hydrogen Energy, 2012, 37: 1518–1530.
[86] Xu N. et al., Comp. Sci. and Tech., 2012, 72: 528–532.
[87] Zhou S. et al., Mater. Chem. and Phys., 2012, 134: 224– 228.
[88] Jiao Y. et al., Mater. Sci. and Eng., C, 2013, 33: 2744–2751.
[89] Li J. et al., Mater. and Design, 2013, 46: 902–909.
[90] Hu Y. et al., Comp. Sci. and Techn., 2013, 79: 64–69.
[91] Zhou R. et al., Mater. Letters, 2013, 112: 97–100.
[92] Miao G. et al., Mater. Sci. and Eng., C, 2013, 33: 4236–4243.
[93] Jiang W. et al., J. of Photochem. and Photobio. A, 2013, 262: 7–13.
[94] Dalai S. et al., Int. J. of Hydrogen Energy, 2014, 39: 16451–16458.
[95] Sorge M. et al., J. of Power Sources, 2014, 266: 496–511.
[96] Dalai S. et al., Int. J. of Hydrogen Energy, 2014, 39: 3304–3312.
[97] Guimaraes C. et al., Radiation Phys. and Chem., 2014, 95: 185–187.
[98] Liu L. et al., Polymer Degradation and Stability, 2014, 104: 87–94.
[99] Shrivastava P. et al., Microelectronic Eng., 2014, 126: 103–106.
[100] Pereira D. A. et al., Bioresource Techn., 2014, 158: 98–104.
[101] Dalai S. et al., Microelectronic Eng., 2014, 126: 65–70.
[102] Sun L. et al., Separation and Purification Techn., 2014, 125: 156–162.
[103] Lehmhusa D. et al., Procedia Mater. Sci., 2014, 4: 383–387.
[104] Domanická A. et al., Ceram. Int., 2014, 40: 6005–6012.
[105] Zhu B. L. et al., Comp. Part B, 2014, 58: 91–102.

[106] Lyubimov V. V. et al., Procedia CIRP, 2015, 37: 107–111.
[107] Hmood F. J. et al., J. of the Euro. Ceram. Soc., 2015, 35: 4143–4151.
[108] Malinowski R. et al., Comp. Part B, 2015, 76: 13–19.
[109] He G. et al., Mater. Research Bull., 2015, 66: 45–50.
[110] Ahn K. et al., Polymer, 2015, 56: 178–188.
[111] Wang H. et al., Sensors and Actuators B, 2015, 216: 332–336.
[112] Zhu B. L. et al., Comp. Part B, 2015, 69: 496–506.
[113] Páez L. L. et al., Sensors and Actuators A, 2015, 233: 422–426.
[114] Huang J. et al., J. of Luminescence, 2015, 157: 215–219.
[115] Pestana C. J. et al., J. of Hazardous Mater., 2015, 300: 347–353.
[116] Perfilov V. A. et al., Procedia Eng., 2016, 150: 1479–1484.
[117] Ghosh D. et al., J. of the Euro. Ceram. Soc., 2016, 36: 781–789.
[118] Moosavi S. S., Alizadeh P., Mater. Letters, 2016, 167: 98–101.
[119] Mingfei X. et al., J. of Hazardous Mater., 2016, 305: 51–58.
[120] Li L. et al., J. of Magnetism and Magnetic Mater., 2016, 417: 349–354.
[121] Ren S. et al., Mater. Sci. & Eng. A, 2016, 674: 604–614.
[122] Oreshkin D. et al., Procedia Eng., 2016, 153: 638–643.
[123] Geng H. et al., Mater. and Design, 2016, 95: 32–38.
[124] Zhang X., Wang P., Comp. Part B, 2016, 101: 53–63.
[125] Li F. et al., Int. J. of Hydrogen Energy, 2016, 41: 12705–12713.
[126] Westcott M. A. et al., Adv. in Radiation Oncology, 2016, 1: 351–364.
[127] Wang Q. et al., Ceram. Int., 2016, 42: 4886–4892.
[128] Yan H. et al., J. of Phys and Chem. of Solids, 2016, 98: 43–49.
[129] Li F. et al., J. of Non–Crys. Solids, 2016, 436: 22–28.
[130] Duan H. et al., Mater. Letters, 2016, 167: 201–204.
[131] Delogu M. et al., J. of Cleaner Produc., 2016, 139: 548–560.
[132] Li C. et al., Energy and Buildings, 2016, 125: 298–309.
[133] Lu D. et al. Ceram. Int., 2017, 43: 9164–9170.
[134] Ren S. et al., J. of Alloys and Comp., 2017, 722: 321–329.
[135] Li F. et al., J. of Non–Cryst. Solids 2017, 458: 52–60.
[136] Herrera–Ramírez L. C. et al., Comp. Sci. and Techn., 2017, 151: 211–218.
[137] Ren S. et al., J. of Alloys and Comp., 2017, 721: 213–219.
[138] Yang Z. et al., Optical Mater., 2017, 72: 524–528.
[139] Anbuchezhiyan G. et al., J. of Alloys and Comp., 2017, 719: 125–132.
[140] Jiao C. et al., J. of Hazardous Mater., 2017, 332: 176–184.
[141] Dalai S. et al., Mater. Today: Proceedings, 2017, 4: 11608–11616.
[142] Liu X. et al., Comp. Sci. and Techn., 2017, 153: 62–70.
[143] An Z., Zhang J., Mater. Research Bull., 2017, 93: 230–237.
[144] Kumar N. et al., Comp. Part B, 2017, 109: 277–285.
[145] Kang D. H. et al., Comp. Part B, 2017, 117: 35–42.
[146] Wang Y. et al., Comp. Sci. and Tech., 2017, 140: 89–98.
[147] Pontiroli L. et al., Mater. Letters, 2017, 190: 111–114.
[148] Bianchetti A. et al., Optics Commun., 2017, 394: 152–156.
[149] Ralite F. et al., Physica Medica, 2017, 44: 28–45.
[150] Zakir Hossain K. M. et al., Acta Biomaterialia, 2018, 72: 396–406.
[151] Tian S. et al., Progress in Organic Coatings, 2018, 115: 115–121.
[152] Araque L. M., de Morais A. C. L., J. of Mater. Research and Tech., 2018.
[153] Ren S. et al., Ceram. Int., 2018, 44: 1147–1155.
[154] Gao Q. et al., Solar Energy Mater. and Solar Cells, 2018, 180: 138–147.
[155] de Sousa–Vieira L. et al., Optical Mater., 2018, 83: 207–211.
[156] Lv X. et al., Construction and Building Mater., 2018, 162: 280–285.
[157] Zeng G. et al., Ceram. Int., 2018, 44: 8788–8794.

[158] Huang Y. et al., J. of Alloys and Compounds, 2018, 748: 93–99.
[159] Ohta S. et al., J. of Biosci. and Bioeng., 2018, 126(4): 533–539.
[160] Al–Gemeel A. N. et al., Construction and Building Mater., 2018, 171: 858–870.
[161] Anbuchezhiyan G. et al., Archives of Civil and Mech. Eng., 2018, 18: 1645–1650.
[162] Li X. et al., Mater. Research Bull., 2018, 97: 567–571.
[163] Kafrouni M. et al., Physica Medica, 2018, 56: 33.
[164] Greppi M., Fabbri G., Energy Procedia, 2018, 148: 948–953.
[165] Zhang J. et al., Surface and Coatings Tech., 2019, 359: 62–72.
[166] Hong W. et al., Ceram. Int., 2019, doi: https://doi.org/10.1016/j.ceramint.2019.03.241.
[167] Ding J. et al., Ceram. Int., 2019, 45: 10126–10132.
[168] Nguyen V. A. et al., Optics Commun., 2019, 440: 14–20.
[169] Cheng Z. et al., Int. J. of Thermal Sci., 2019, 140: 358–367.
[170] Vereshchagina T. A. et al., J. of Environmental Chem. Eng., 2019, 7: 102887.
[171] Fang Y. et al., J. of Drug Delivery Sci. and Tech., 2019, 51: 430–437.