Chapter

Glass Beads for Road Markings and Other Industrial Applications

Tomasz E. Burghardt

Abstract

Solid sphere glass beads designed for the use in road markings, as filler beads for plastic composites, as blasting beads for abrasive surface cleaning and peening, and as filtering media are described. Their production process from recycled float glass and from virgin glass melt is briefly discussed; the associated carbon footprint is provided. Environmental or health issues that could be caused by the presence of crystalline silica or toxic elements are refuted based on results from laboratory analyses. For the main commercial application—reflectorization of road markings—the role of glass beads in providing visibility for drivers and in protecting the road markings from abrasion is illustrated. The effect of increasing refractive index on both the functional service life and the visibility of road markings is shown based on the outcome from field studies. Selected research related to the use of the same type of glass beads for other industrial applications is briefly reviewed. The described glass beads cannot be currently replaced because they are relatively inexpensive, environmentally benign, readily available, and highly effective in furnishing the desired effects.

Keywords: retroreflectivity, filler beads, blasting beads, peening, crystalline silica, toxic elements, refractive index, road markings, service life, road safety, carbon footprint

1. Introduction

Solid sphere glass beads (GB), sometimes called microspheres or microbeads, are important for various commercial uses [1]. They play specific roles that, within the currently known and practically available technologies, make them irreplaceable. Excellent performance at reasonable cost, relatively low environmental impact, stability under various conditions, and the absence of meaningful safety concerns are among their chief advantages. Since the mass production of GB coincided with rapid industrial development, their presence in the environment was proposed as one of the tracers for the Anthropocene [2, 3]. The main usage of such GB is in road markings (RM), where they provide retroreflection and protect the markings from abrasion [4]. GB are also broadly utilized as filtration media [5], for abrasive cleaning and peening of surfaces [6], and as fillers in polymer composites [7]. Their retroreflective properties are also exploited in preparation of heat-reflecting envelopes [8]. Review of GB designed for strictly medical or analytical laboratory applications that are made to meet much higher quality and purity standards, porous GB for special applications, hollow GB, or sub-micron particles is beyond the scope of this chapter despite interesting properties [9]. Similarly, GB with diameters >2.0 mm are not considered; their selected characteristics were described elsewhere [10].

Herein, the following aspects related to the solid sphere GB designed for industrial applications shall be briefly described: (1) production process from recycled float glass, with brief mention about the manufacture from virgin raw materials; (2) carbon footprint for the production of such GB; (3) possible environmental issues associated with the presence of crystalline silica or toxic elements; (4) the role of GB in RM, along with the effects of increasing refractive index (RI) of the GB on (5) the visibility of RM and (6) their functional service life along with the long-term carbon footprint of the applied RM are quite broadly discussed; and (7) the usage of such GB in other industrial applications with particular accent on composite materials.

2. Manufacture

2.1 Production

The production procedure of GB from crushed glass in vertical thermal flame process seems to have been first described in a patent from the 1940s [11]. Despite technological advances, the production principles remain unchanged. The raw material for the production of such GB is recycled float glass (the cullet) [12], which is mechanically ground to form a glass granulate of desired dimensions, and then fed into the flame region of a special vertical oven powered by natural gas. Inside the oven, at temperature of approximately 1300°C, the irregular shards of glass granulate melt and, to minimize the surface tension, acquire spherical shape within circa <0.1 s. Because of the flow of the gases within the oven, the liquid spherical particles travel to the cooler region, where their temperature drops below the vitreous transition and the GB are formed. With this technology, GB with diameters up to circa 0.85 mm can be conveniently produced. Control of the production process is of critical importance to assure quality: high roundness and the absence of fused beads, air entrapments, milkiness, surface defects, and appropriate resistance to chemicals—selected requirements for GB used in RM are listed in the standard EN 1423 [13]. Among the parameters that control the outcome, one has to list the quality of the raw material, temperature gradient within the oven, flows of air and the natural gas, feeding rates, glass granulate particle size, movement of the glass and gases within the oven, and so forth. All of these parameters are optimized by manufacturers and remain proprietary to them, so literature related to the details is not available; no important new developments that would be practically applicable were described either. This type of GB, prepared from recycled glass, shall be called herein "Standard" (to differentiate from other types, prepared from virgin glass melts); due to the utilized raw material, their RI is 1.5. The external appearance of "Standard" GB—from broken float glass, through glass granulate, until manufactured GB with visible surface imperfections—is illustrated in **Figure 1**. The presence of pendant mini-beads seems unavoidable contamination resulting from the commercial large-scale manufacturing process; the extent of such impurities is miniscule and has not been reported to affect any of the desired properties.

GB can also be manufactured from virgin raw materials, which permits not only for the obtention of larger diameters but also for increased surface quality, and, through modification of the composition of the melt, increased RI. The recycled float glass can

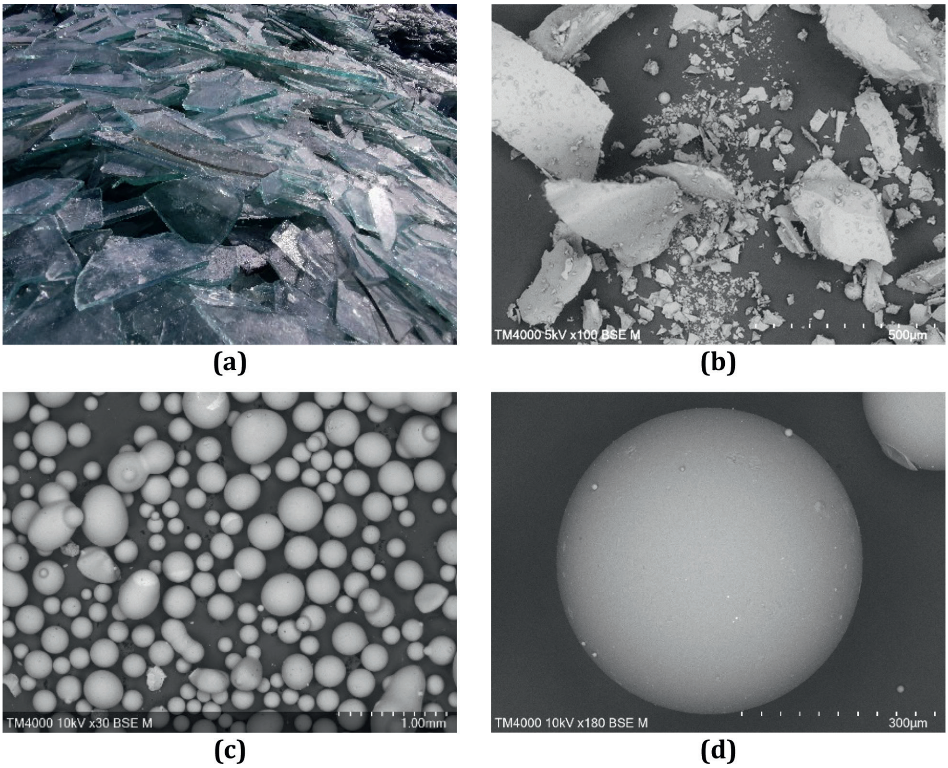


Figure 1.
"Standard" glass beads—from recycled float glass to finished product. (a) Broken pieces of float glass; (b) glass granulate before sieving, fraction <1.00 mm; (c) produced GB, fraction 0.20–0.85 mm; (d) GB with diameter circa 0.35 mm, with visible surface defects and contamination with pendant mini-beads.

be used as one of the raw materials for the virgin melts. It is noteworthy that not all glass compositions can be easily converted into beads. The production process from virgin glass melt is almost exclusively utilized for GB with RI >1.5 and for GB with RI 1.5 in diameters ≥0.60 mm. Although preparation of GB with RI 1.5 in diameters <0.60 mm from virgin glass melts is also possible, for the described industrial applications, it is seldom practiced: Besides being currently less economical, bead formation is often more difficult. The manufacture processes from virgin raw materials are proprietary; descriptions in the literature or in patents are scarce and do not seem to represent the actually employed commercial methods. A great advantage of forming GB from virgin glass melts is their significantly higher quality; excellent roundness and almost complete absence of defects are typical for the commercial products. High roundness and smooth surface are desired in many applications because better functional properties can be obtained. Because production from virgin glass melt can be done in an electric oven, without the natural gas as energy source, the environmental footprint is different.

Basic properties of the GB discussed herein and their typical composition are shown in **Table 1**. Their division to various types was based on their utilization in RM; it is subjective but consistent with other author's work. Interestingly, GB with RI 1.7–1.9 are not known to be broadly manufactured or used; only recently, first commercial trials in RM seemed to have been made, but literature reports are not available yet. Similar spherical crystalline materials, with RI reaching even 2.4, not glassy but in some high-end RM playing the same role as GB [14, 15], shall not be discussed herein.

Type of GB	"Standard"	"Large"	"Premium"	"High index"
Refractive index	1.5	1.5	1.6–1.7	1.9
Raw material	Recycled float glass (glass granulate)	Virgin glass melt	Virgin glass melt	Virgin glass melt
SiO_2	70–75%	60–75%	30–50%	10–25%
MgO	1–5%	1–10%	10–15%	<2%
CaO	5–15%	5–20%	20–30%	1–10%
Na_2O	10–15%	10–20%	<2%	<2%
TiO_2	<1%	<1%	10–15%	25–35%
Al_2O_3	<2%	1–5%	10–20%	<2%
BaO	<1%	<1%	<1%	40–55%
Density [g/cm^3]	2.4	2.4	3.2	4.6
Typical usage	RM, blasting, peening, filtration, filler, other	RM, filtration, other	RM, other	RM, other

Table 1.
Types of GB for commercial applications and their basic properties, including typical composition.

Global warming potential (GWP), that is, carbon footprint, to evaluate the environmental impact of processes and products can be assessed. In **Table 2**, GWP caused by the production of various types of GB is provided, based on calculations done for environmental product declarations [16]. The data are for a modern plant located in Europe and specific production processes utilized there; hence, these values are likely to be different elsewhere (sometimes to a significant extent). This variable belongs to known inadequacies of life cycle assessments [17]. The data are for cradle-to-gate life stages; analysis for cradle-to-grave has not been done so far and is unlikely to be reliable because of various end usage and fates. Nonetheless, since GB are benign, the main environmental impacts are associated with their production. Based on the professional knowledge, there are current efforts in the industry to minimize the GWP and simultaneously to increase the quality of the produced GB; however, no related patents or literature reports on this topic can be found. In the case of "Standard" GB, the process efficiency optimization can bring some benefits; elimination or limiting of natural gas usage would be advantageous, but the need to achieve high temperature is an obstacle. The production from virgin melts can also benefit from the utilization of alternative energy sources.

Typically, GB are coated with an organosilane to assure their adhesion to the polymeric matrix, to promote free flow, to protect the surface, and to provide other desired effects. The coating quantity is miniscule (loss-on-ignition can be estimated at $<0.05\%$) and, unlike sizing of fiberglass [18], contains no polymeric ingredients.

GB type	"Standard"	"Large"	"Premium"	"High index"
GWP [kg CO_2 eq.]	1.1	1.7	1.5	2.6

Table 2.
GWP for manufacture of 1.0 kg of GB.

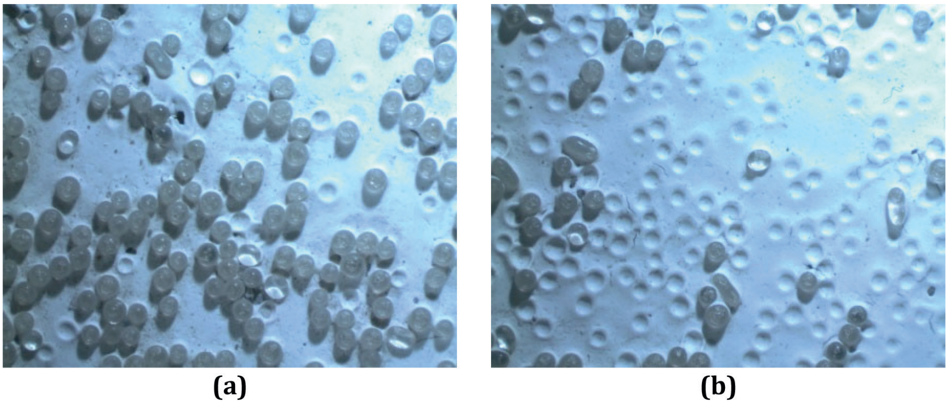


Figure 2.
Effect of organosilane coating on adhesion of GB to RM (12 h of abrasive testing in laboratory). (a) Good adhesion, with few GB extracted from the film; (b) Poor adhesion, with the majority of GB lost.

No published research results on this interesting topic were found; the only published results related to RM reported unrealistic coating quantity and procedures [19]. The selection of organosilane depends on the target matrix and the desired properties [20, 21]. The effect of selection of organosilane coating for GB on their adhesion to RM is illustrated in **Figure 2** (unpublished results from a laboratory experiment with GB purposefully improperly embedded in RM to evaluate adhesion due to chemical bonding).

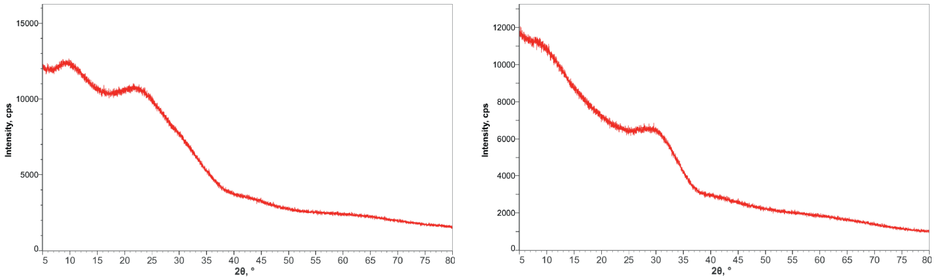
2.2 Harmful ingredients

It is of utmost importance that GB are free from toxic elements that could leach to the environment or negatively affect the health of people working with them. For this reason, maximum concentrations were set in various norms and GB are routinely spectroscopically analyzed. The maxima permitted in Australian and European standards (the same requirements are also in the United States, Korea, Brazil, and other countries) and the results of tests recently performed on exemplary GB from European manufacturers are provided in **Table 3**. Laboratory analyses done in the past on several batches of GB showed that in no case the set maxima were exceeded [24, 25]. Low contents of these harmful elements were also confirmed in samples collected in the field [26]. Hence, prior reports of contaminated GB imported to the United States [27, 28] and to Brazil [29] were describing only a local issue that appears to have been successfully alleviated.

An important issue that recently surfaced was the alleged presence of crystalline silica in GB, particularly those prepared from virgin glass melts that contain cristobalite-rich quartz sand as one of the ingredients. Such claim contradicted industrial knowledge; indeed, analyses done with X-ray diffraction (XRD) on 11 samples of different GB from several manufacturers worldwide demonstrated that only fully annealed amorphous glass was present, so no toxicological risk existed [25]. Exemplary XRD spectra, showing a large hump characteristic for amorphous substances, are provided in **Figure 3**. Importantly, the absence of crystalline silica was also reported from an occupational safety assessment of GB used for abrasive cleaning [30].

Element	Cr	Cr(VI)	As	Cd	Sb	Hg	Pb
Maximum permitted per EN 1423, Class 1 [22]	—	—	200	—	200	—	200
Maximum permitted per AP-S0042 [23]	—(a)	10	50	10	50	10	50
Glass granulate	7.5	<0.25	0.4	<0.1	2.2	<0.1	6.3
"Standard"	8.1	<0.25	0.18	<0.2	0.16	<0.1	1.5
"Large"	3.4	<0.25	<0.25	<0.1	2.8	<0.1	7.3
"Premium"	2.8	<0.25	<0.2	<0.1	<0.1	<0.05	0.9
"High index"	2.1	<0.25	2.8	0.13	10.9	<0.1	4.7

Table 3.
Limits and contents of harmful elements [mg/kg] in various types of GB. (a) When chromium content exceeds 10 mg/kg, test for Cr(VI) must be performed.



(a) (b)

Figure 3.
XRD spectra of exemplary GB [25]. (a) "Standard" GB prepared from recycled float glass; (b) "Premium" GB prepared from virgin raw materials.

3. Road markings

3.1 Materials and principles

The usage of GB in RM is a well-established procedure since the 1950s [31]. Most often, GB with diameters 0.20–0.80 mm are used, but range 0.06–2.00 mm is possible. The specific size ranges depend on the desired properties and local considerations. Nonetheless, particularly in North America, gradations and RI are fixed in standards and adjustment to obtain the desired properties are effectively not allowed (equally detailed specifications exist for the paint layer of RM) [32, 33]; hence, reports of new developments from that region are scarce. Before the role of GB in RM is described, one must understand that all RM are speciality industrial maintenance coating systems comprising two layers: the bottom paint (color) layer and the upper drop-on GB (retroreflective) layer. These layers must cooperate to yield the final functional product—visible for road users (pedestrians, drivers, and machine vision equipment) and simultaneously durable [34]. Two key roles are furnished by the drop-on GB: They protect the underlaying paint layer from abrasion and concurrently deliver retroreflectivity—the phenomenon of reflecting the light from car's headlights back toward the driver [4, 35]. It is achieved through embedment of the GB in the paint; usually to circa 50–60%, but the optimum varies depending on the RI of the GB [35, 36]. Retroreflectivity is measured through coefficient of retroreflected luminance (R_L) and expressed in the unit of mcd/m^2/lx. Critical role among paint ingredients plays the white pigment, TiO_2, with RI 2.6 and the ability to scatter light instead of absorbing it [37, 38]; its presence in the paint layer of RM permits for creation of an efficient diffusion cone; thus retroreflection can be obtained. Without TiO_2, it is necessary to use GB with RI >1.5 to achieve meaningful R_L. Note that TiO_2 nanoparticles or anatase TiO_2 are not known to be commercially utilized in any RM because they seem to be incapable of forming efficient surface for retroreflection.

The GB are applied through drop-on process, immediately after the paint layer is laid on the road surface; typical spreading rates are 0.3–0.5 kg/m^2. GB of the same type and dimension ranges can also be intermixed with the paint (in the industry called 'premix' beads), where they play a role of a modifier of rheological properties and a coarse filler; typically, their content is 20–30% of the applied mass. In case of thermoplastic RM, the premix GB also deliver retroreflectivity as they are being exposed while the thermoplastic material wears-off [39]. This design feature of wearing-off is unique to thermoplastic RM: It assures prolonged visibility of RM through R_L, but at the cost of increased particulate emissions. Anti-skid particles (hard coarse inorganic fillers with irregular shapes) do not deliver R_L but are often intermixed with the GB (both the premix and the drop-on); they protect the paint layer from abrasion and deliver skid resistance. Like GB, they should be coated with properly selected organosilane to maximize adhesion and thus functional properties of RM. A cross section through RM that includes both drop-on and premix GB and premixed coarse fillers that act as anti-skid particles is shown in **Figure 4**.

When assessing RM, one must keep in mind the profound distinction between their *functional* and *physical* service life [40]. Before usage, all RM should be homologated to assure that all of the functional parameters are met throughout their designed *functional* service life period [41, 42]. The *functional* service life is the period when RM meets the functional parameters, especially retroreflectivity (typically the first parameter to fail because the drop-on GB are exposed to the vehicles encroaching on the RM). Upon wear and tear, functional properties of RM fail and they enter their

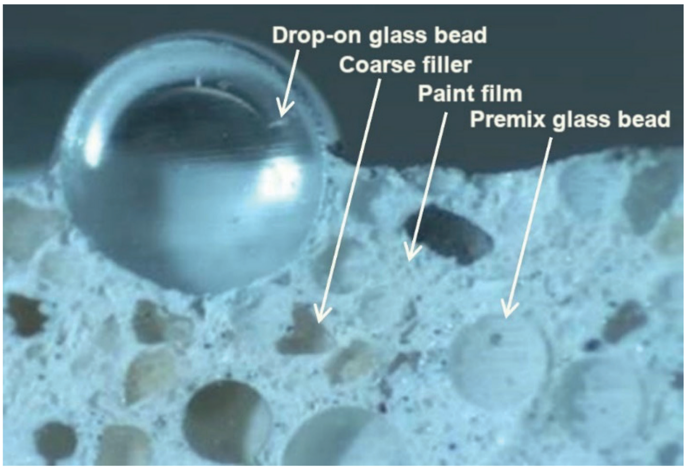


Figure 4.
Cross section through a thick layer RM.

physical service life period, when they still remain on the roadway and are visible, but slowly undergo abrasion until becoming fully eroded. It must be emphasized that functional service life of RM may end upon either extraction of the GB from the film or upon their physical damage [43]. The period, during which the GB (either drop-on or premix) and the coarse fillers premixed within the paint protect the RM from erosion can be very long. Average annual abrasion of thick layer RM at German test field in Harz mountains was estimated at <5% [44]. Hence, the protective role of GB cannot be underestimated. The majority of the RM after usage are mechanically removed and disposed in a landfill and/or recycled together with the asphalt [45]; their abrasion and release to the environment is only a rare event [40].

The presence of GB in the environment was suggested as a proxy for the abrasion of RM [26, 46–48]. It is correct approach, but one must keep in mind that such contamination can occur only after the RM are utilized past their designed and intended *functional* service life. At the same time, one must observe that the sole presence of GB in the environment is insufficient indicator—the same types of GB that are used for RM are also utilized for other industrial purposes, during application of RM there is always an overspray of the GB, and while some of the GB may be extracted from the paint, other can still protect it from wear [39]; a confirmation from other indicators is necessary for unequivocal assignment.

3.2 New types of glass beads for improved visibility

Whereas for many years, "Standard" GB were used in RM, in 2010 the first successful commercial trials with "Premium" GB were conducted. These new GB were developed to alleviate the issue of low R_L achieved under wet conditions and also to increase R_L on dry roads while simultaneously increasing scratch resistance as compared to "High index" GB. The use of the "Large" GB, through facilitating moisture drainage, alleviates the issue of inadequate visibility under wet conditions to only a minor extend, but their RI cannot change the optical properties of wet surface. Because water has RI 1.3, its layer on GB with RI 1.5 leads to diminishing R_L to almost nil. Hence, the advantage of using GB with RI >1.5, [14, 15]. Typical maximum R_L achieved in white RM in the field with various types of GB is shown in **Table 4**, based on author's evaluation.

Based on studies of drivers' needs, maintaining R_L > 150 mcd/m^2/lx has been proposed [49, 50]. Nonetheless, in the majority of cases, the road administrators accept R_L of 100 mcd/m^2/lx as the minimum under dry conditions in used RM (there are no requirements for wet conditions). Because visibility is related to contrast and edge detection, during daytime and in artificial lighting, RM are visible due to their color contrasting from the roadway surface; however, at night time, R_L augments the visibility [51].

The difference in visibility for drivers of RM with varying R_L has been studied, with consistently reported longer preview distances and easier detection with higher R_L and wider RM [52, 53]. Quite strong positive correlation between R_L and road

Type of GB	"Standard"	"Large"	"Premium"	"High index"
Diameters [mm] typically utilized in RM	0.06–0.85	0.60–2.00	0.30–1.00	0.30–1.00
R_L (dry) [mcd/m^2/lx]	350	450	1000	1800
R_L (wet) [mcd/m^2/lx]	60	100	200	400

Table 4.
Typical maximum R_L under dry and wet conditions obtained with various GB in white flat RM.

safety had been found based on single vehicle collision datasets [53–55]; the effect is most likely occurring because the drivers are able to better and earlier see RM with higher R_L. Importantly, RM of Type II (i.e., designed for improved visibility under wet conditions) were found to be better visible and were preferred by drivers [56, 57]. The profound difference in visibility of Type I and Type II RM at night under wet conditions is illustrated in **Figure 5** [58]; these and other dissimilarities were also quantified using contrast ratio [58, 59]. A combination of high R_L and Type II characteristics appears to be the optimum solution.

Yellow (sometimes also orange) RM are commonly utilized throughout the world, mostly to separate the directions of traffic, as temporary markings within road work zones, and for other signalization. Since such colored RM contain only miniscule quantity of TiO_2 in the paint, to obtain meaningful R_L one needs to use GB with RI >1.5. Field studies done in Switzerland [60] and later in Texas [32] confirmed that high R_L under both dry and wet conditions could be obtained in yellow RM with the "Premium" GB and that the effects were long lasting; the difference between the achieved visibilities is illustrated in **Figure 6**. The utility of GB with RI >1.5 is also exploited in preparation of RM with simultaneously high skid resistance and high R_L [61, 62]. Whereas no detailed cost-benefit analysis for such RM is currently available, one should note that preliminary calculations indicated lower long-term costs due to less frequent needs of renewals [60].

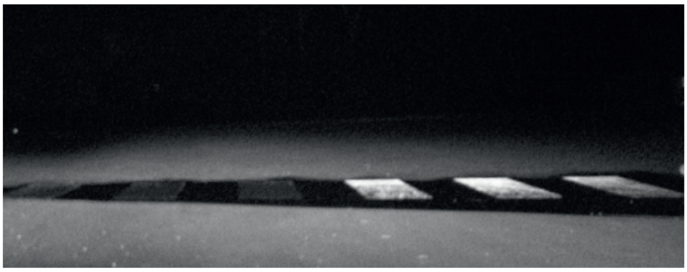


Figure 5.
RM of Type I (on the left) and Type II (on the right) at night under wet conditions in headlights' illumination [58].

Figure 6.
Yellow pedestrian crossing in Switzerland; "zebra" stripes on the left reflectorized with GB characterized by RI 1.6–1.7 ("Premium") and on the right with RI 1.5 ("Standard").

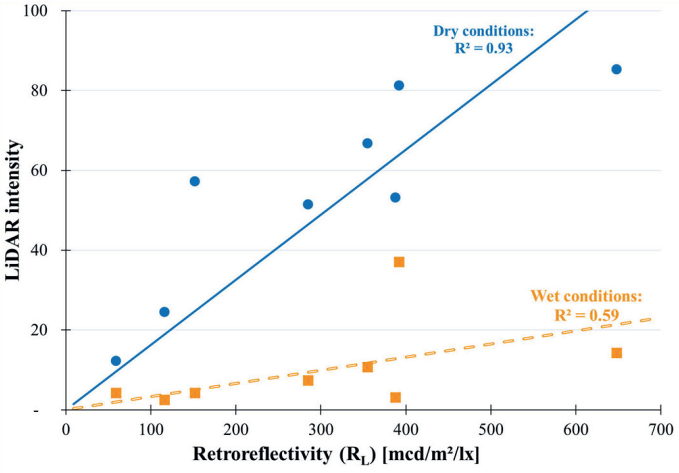
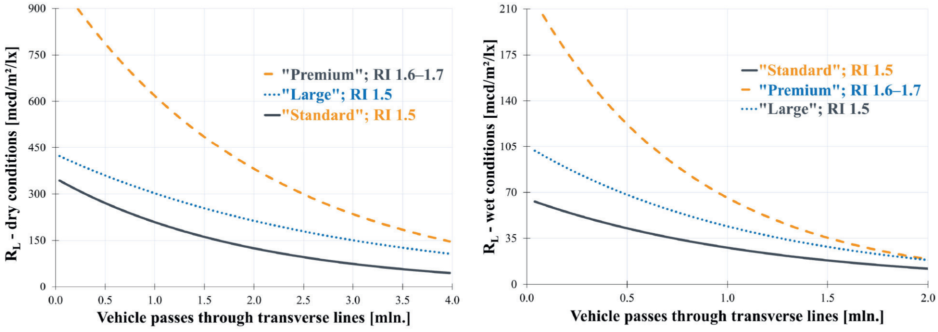


Figure 7.
Correlation between R_L of RM and lidar response, based on study under laboratory conditions [59].

A straight correlation between R_L of RM and lidar response, as shown in **Figure 7**, is well established [59, 63, 64]. This emphasizes the need to maximize R_L also for the machine vision equipment utilized in driver assistance systems.

Side-by-side field evaluation of RM comprising various paints and drop-on GB was performed [65]. The results indicated that the choice of paint controlled the functional service life of RM, but the selection of the type of GB played equally profound role. A summary of the results related to the GB is shown in **Figure 8**—consistently, the use of "Premium" GB resulted in higher initial R_L and longer functional service life than the use of other types of GB. Even though the rate of R_L decay with the "Premium" GB was higher than with the "Standard" GB, much higher initial R_L allowed for prolonging of the functional service life of the tested RM [65].

Very importantly, the prolonged service life achieved with the "Premium" GB was reported as lowering the overall long-term carbon footprint of the RM despite



(a) (b)

Figure 8.
The effect of GB selection on retroreflectivity decay of RM [65]. (a) Dry conditions; (b) Wet conditions.

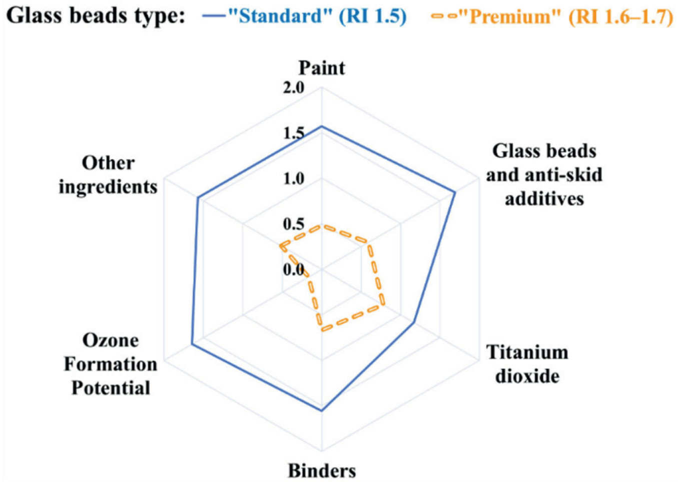


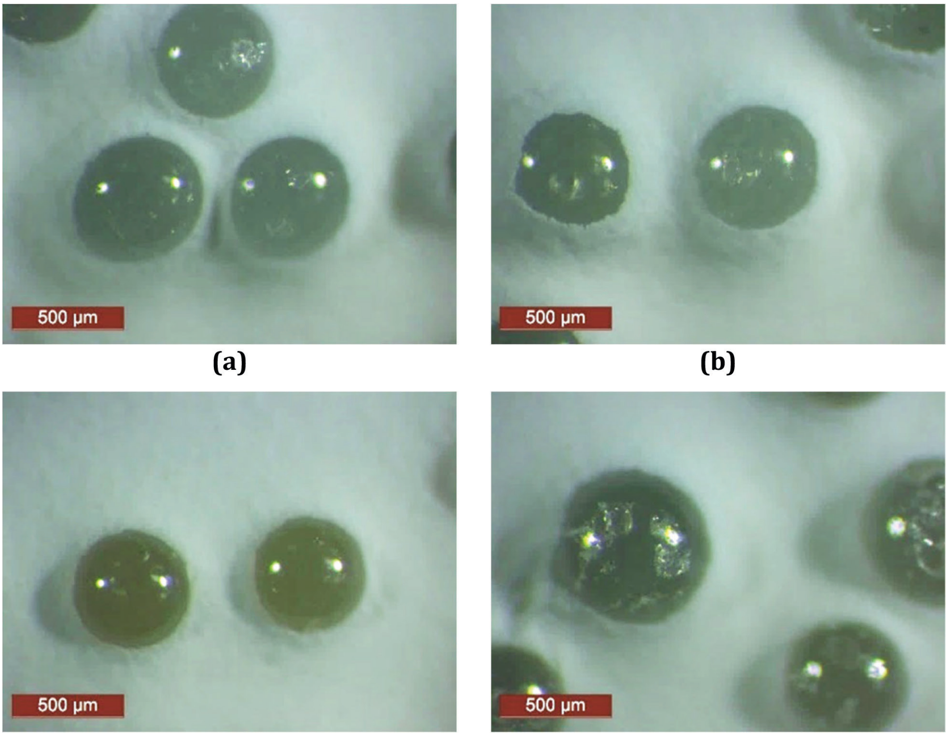
Figure 9.
Long-term usage of ingredients for RM as a function of GB selection (relative quantities, average from several types of paints) to maintain R_L > 150 mcd/m²/lx (i.e., functional service life) with series of renewals for 20 years.

higher initial environmental expense [65]; results of exemplary calculations of materials usage and emissions, done based on the outcome from the aforementioned side-by-side field study, are provided in **Figure 9**. Furthermore, despite the increased unit cost of such materials, the long-term financial expenses were not expected to increase; less frequent renewals would bring this advantage [66].

In addition to protecting the paint layer from abrasion and providing R_L, GB also contribute to the increase in skid resistance of RM; this weakly studied issue is of profound importance. Field studies demonstrated that while the surface of paint without the retroreflective layer can be dangerously slippery, skid resistance of the same paint with the drop-on GB was comparable to measured at asphalt surface [67, 68]. Glass granulate, which is the raw material for the production of the "Standard" GB, can also be utilized to increase skid resistance of RM; however, despite very high initial effectiveness, it undergoes polishing and skid resistance quickly decreases [68].

3.3 Scratch resistance of glass beads

The increase in RI of GB, achieved through modification of composition, caused a decrease in their scratch resistance, which leads to decreased durability. During a laboratory study in a drum filled with abrasive material, profoundly different extent of the physical damage to GB has been observed, as shown in **Figure 10** [69]. Hence, the decay rate of R_L and thus the period of functional service life of RM were affected; it is a valid explanation of the reported high initial properties and their quick decay [70, 71]. It is one of the reasons that "High index" GB are utilized mainly in airfield markings, where different visibility geometry and the necessity of providing excellent conspicuousness of markings are more important than the length of functional service life and cost [72, 73].



(a) (b)

(c) (d)

Figure 10.
Microscope images of GB (diameter 0.6–0.8 mm) after laboratory abrasion testing. (a) "Standard"; (b) "Large"; (c) "Premium"; (d) "High index" [69].

4. Other industrial uses of glass beads

4.1 Composites

Numerous aspects of using GB as fillers for plastic composites have been thoroughly reviewed in the past, so reiterating the prior descriptions is unnecessary [21, 74, 75]. The GB used as fillers and reinforcement materials in composites usually have diameters 0.02–0.07 mm (broad range 0.001–0.10 mm). Typically used loading of filler beads in plastic composites is 10–30% (with the known range 5–50%) by weight. The theories for the GB reinforcing action include interfacial adhesion, crystallization reinforcing, filler frame reinforcing, and synergistic reinforcing; however, none of them alone can correctly explain the mechanisms as too many parameters play a role [76]. During compounding, the filler GB become quite randomly distributed throughout the polymer matrix, as shown in **Figure 11**.

The GB are not simply fillers. Their incorporation in various plastic composites was reported to affects their density, flow properties, viscosity, rheological properties, shrinkage, impact strength, stiffness, tensile strength, sliding, and hardness [77]. A unique property of filler beads with larger diameters is their tendency to redistribute within a composite to the extent that the near-wall region becomes depleted of them [78], which affects the flow during compounding. The interactions between the polymer and the GB are quite strong, but they decrease as the filling content

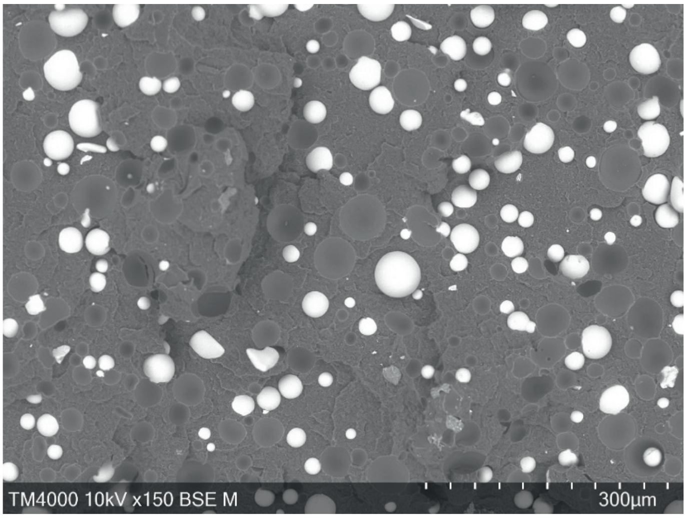


Figure 11.
Cross section of a polypropylene composite filled with 30% of GB with diameters 0.02–0.07 mm.

increases, which could be explained through coalescence of the beads [79]. Since failure of composites was reported as originating from debonding between the bead and the polymer matrix due to stress-strain behavior [80, 81], appropriate compatibilizers and coating of the GB are critical [20, 21, 82]. Removal of impurities from the surface of GB was reported to increase properties of the composites [83]. The use of recycled GB in preparation of composite panels for sound control has also been reported [84]. The use of filler beads in adhesives is also known [85]. Recycling and reuse of filler beads from composites remain essentially unknown because of the heterogeneity of the materials [86]; however, the filled plastic composites can be used as cheap fillers for other composites.

4.2 Other industrial uses

The use of GB as filtration media is well-known since the 1970s [5]. Typically, GB with diameters 0.02–2.0 mm are used for this purpose, with exact diameters and their ranges differing depending on the specific needs [87]. To explain their efficiency, theory based on the method of isolated fibers concept has been proposed [88], but other theories and mechanisms of filtration have also been explored [5, 89]. The surface roughness of the filtration media was reported as playing significant role, with the moderately rough GB shown as being the most efficient [90, 91]. The efficacy of GB in removing up to 99% of suspended solids has been demonstrated [92, 93].

The use of GB for abrasive cleaning of surfaces (blasting) is a well-established commonly used protocol [6, 94, 95]. Similarly, GB are used for peening of metal surfaces where they are one of the most efficient media [96]. Peening—mechanical working of metal surfaces—is used to improve the properties of metal surfaces, typically to introduce compressive residual stress that improves fatigue strength; during peening, hardness, surface topography, and porosity are simultaneously modified. GB with dimensions 0.02–1.00 mm are being utilized, typically within narrow size distribution range. Selection of the dimensions of the blasting beads, the nozzle configuration [97], and control of the pressure permit for fine-tuning to achieve the desired effect [98]. The advantage of using GB for this purpose is the possibility of obtaining exquisitely smooth finish and delicate action. Successful cleaning of soft surfaces, such as gypsum, from old paint has been reported [99]. The accuracy of the blasting procedure with GB can be illustrated by their utilization for cleaning of a root canal during a dental surgery under solely microscope control [100]. From occupational safety and environmental perspective, very important is the minimization of dust and the absence of crystalline silica as compared to other blasting media, especially sand [30, 101]. During the usage, the blasting GB are suffering damage, so they can be reused only a few times [102].

The retroreflective properties of embedded GB are commonly used in safety vests [103]; the use of GB with RI >1.5 is advantageous. Interesting emerging usage of GB, also associated with their retroreflective capabilities, is in creation of heat reflecting sheeting for building façades [8]; an advantage of GB with RI >1.5 was measured [104]. Aging of such coatings in the environment, which results in the loss of effectiveness, was reported as one of major issues; a study has shown that GB diameter played a role, and the optimum was obtained with 0.20–0.30 mm, applied at 0.2–0.3 kg/m^2 [105].

5. Conclusions

The described solid sphere GB are commonly used for several industrial applications that include reflectorization of RM, abrasive cleaning or peening of surfaces, filtration, filling and reinforcing of plastic composites, and other. Those GB provide unique properties that make them irreplaceable at present. Advantages of such GB include their high stability, good mechanical properties, low surface area due to spherical shape and smoothness of the surface, high resistance to etching and fragmentation, and chemical inertness; because of being made from fully annealed amorphous glass devoid of harmful elements, they remain excellent choice also from environmental and occupational safety perspectives. The utilization of GB for abrasive cleaning or peening allows for precise control of the surface quality. As fillers in plastic composites, GB modify the properties in a manner not achievable with alternate fillers. In their main application—reflectorization of RM—they play crucial role in protecting the paint from abrasion and in delivering retroreflectivity. The reflective properties of GB are also employed for creating heat reflecting sheets.

Most of such GB are manufactured from crushed recycled float glass, which set practical limits related to their dimensions, surface quality, external appearance, and RI; carbon footprint of their production is significantly lowered because of the use of a recycled raw material. GB with increased RI are manufactured from virgin glass melts; their exquisite surface quality along with the higher RI was reported as furnishing better properties in RM, particularly augmenting visibility under wet conditions. Notwithstanding higher environmental impact of the production from raw materials, the overall carbon footprint of RM reflectorized with such “Premium” GB remains relatively unchanged because of prolonged functional service life; simultaneously, increased visibility for drivers translates to improved road safety and easier driving for additional meaningful but unquantified social advantages.

The field of solid-sphere GB seem to be quite mature, mostly price-driven, and proprietary to the manufacturers; hence, literature and patents remain scarce; more current attention is given to hollow sphere and porous GB, which were not discussed herein. There are efforts to minimize carbon footprint associated with the production of GB; nonetheless, the necessity to obtain high temperature to melt the glass is the limiting factor. Recycling and reuse of the described GB are almost unknown; after use, they are permitted to enter the environment where they undergo slow decomposition (since they are benign, this does not constitute any issue).

Conflict of interest

The author of this chapter is employed by a manufacturer of glass beads that were described. His employer played no role in the selection of references and the presented research results.

Author details

Tomasz E. Burghardt
M. Swarovski GmbH, Neufurth, Austria

*Address all correspondence to: tomasz.burghardt@swarco.com

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