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Road Marking Glass Microspheres Fabricated from Rice Husk Ash

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In this work, it is reported a comparison between solid microspheres produced from glass having conventional industrial sand (IS) and glasses made with rice husk ashes (RHA) as a source of silica. The same composition was used to fabricate both glasses. The focused was the production of glass microspheres for road horizontal marking, which would attend the type classification called Premix. The microspheres were obtained by the horizontal flame method. The results showed that characteristics such as production yield, morphology, granulometry and, mainly, retroreflectivity measurements are not altered when rice husk ash is present in the glass composition, showing that this can be a sustainable alternative material for this important application.

Keywords: *Sustainability, rice husk ash, microspheres, horizontal road signaling, industrial sand.*

1. Introduction

With the advancement of society, several industrial segments have been producing a significant amount of waste, which, if disposed incorrectly, causes an environmental imbalance. In this sense, the 2030 Agenda consists of a global action plan that brings together 17 sustainable development goals, established by the General Assembly of the United Nations[1]. In these objectives, it can be observed a concern to generate innovation considering sustainable means, and with the preservation of nature. Thus, it becomes fundamental to use renewable materials and to develop methodologies and technologies for the manufacture of products, generating added value for materials otherwise discarded. Moreover, many products that could use sustainable materials in their manufacture continue to be produced with raw materials that degrade the environment. The glass industry, for example, uses a large part of natural reserves of industrial sand, since the silica found in the sand is the main glass component. However, the extraction of these natural reserves entails and contributes significantly to the degradation of the environment, harming from the removal of native vegetation to the erosion and silting of watercourses[2]. More than that, recent studies indicate that the global demand for sand could increase in 45% up to 2060, from 3.2 billion metric tons a year in 2020 to 4.6 billion metric tons, which could result in a shortage of this material[3,4]. In this way, a sustainable alternative material with a high silica content could contribute for this global demand, in addition to minimizing environmental impacts and reinforcing environmental preservation. Among the alternative materials for glass production, the rice husks ashes (RHA) can be considered a potential substitute for silica from industrial sand since, in addition to being a sustainable material, it is possible to extract around 90% of pure silica from RHA depending on the purification steps adopted[2,5,6].

According to United States Department of Agriculture (USDA), in 2021, around 500 million metric tons of rice were produced in the world, a production approximately constant in recent years[7]. Brazil, for example, produces an average of 11 million metric tons of rice annually[8]. The rice husk is equivalent to approximately 20% of the grain weight and, if it is burned to produce energy, around 20% of the husk becomes ash[9,10]. Thus, approximately 20 million metric tons of RHA have been produced in the world in 2021; this is a reasonable amount, that could be used to satisfy a good part of the demand for silicate glasses, either as a percentage of this material with IS or even as a total replacement. The use of this solid residue would open the possibility of commercial valuation of this residue, in addition to minimizing environmental impacts and closing the production cycle of the rice chain.

Among the various uses of vitreous materials, the production of microspheres is of great interest since they have large range of applications, in different segments such as energy applications, passing through the medicine until their use in road signaling[11-13].

For the specific case of solid microspheres, the main application is in the road marking segment, since the microspheres exhibit the retroreflectivity effect[13-16]. For the case of a vehicle on the road, retroreflectivity refers to the amount of light emitted by the headlights that is reflected by the demarcations with microspheres back into the driver's eyes. During daylight, the driver can discern road markings simply by the contrast between their colors and the pavement surface. However, at night, visibility becomes a function of the luminous contrast between the road markings and the pavement surface. This contrast is amplified when there is retroreflectivity in the demarcations, bringing more security to the drivers[16]. According to Zhang et al.[17], demarcations without glass microspheres are, at night, far from having adequate visibility when illuminated by external sources.

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There are several parameters that impact the retroreflectivity values of the microspheres, such as: the refractive index of the glass, the percentage of anchorage, the density, the type of glass microsphere, the granulometry, shape and imperfections, number of spheres present and exposed to the light, microsphere application forms, weather conditions and characteristics of the binder used in the asphalt mix[16-19]. In Brazil, the normative standard that regulates this application is the NBR 16184 - Horizontal Road Markings - Glass Spheres and Microspheres - Requirements and Test Methods[20]. Microspheres are classified into types according to their granulometry. For example, Type-IB microspheres (also called Premix) are those incorporated into the paint, allowing retroreflection only after the surface of the applied film wears with time, exposing them[20]. These microspheres, in their largest percentage, must have a diameter between 75 and 180 μm[20]. Type-IIA microspheres (also called Drop-on), as another example, are those applied by spraying together with paint or thermoplastic, so that they remain on the surface of the applied film, allowing immediate retroreflection[20]. The Drop-on type has to present diameters greater than 300 μm. It is estimated that in Brazil more than 30 thousand metric tons of microspheres are used every year. Considering that Brazil generates around 400 thousand metric tons of RHA per year, and that approximately 1 metric ton of RHA generates 1 metric ton of microspheres, the Brazilian domestic market for microspheres could be completely served by considering rice husk ash as a source of silica instead of industrial sand (IS) in the microsphere glass production.

For these reasons, this work aims to produce solid microspheres, made from glass with IS or RHA. The microspheres were compared and characterized in terms of morphology, granulometric distribution and retroreflectivity measurements, in order to see if they met the current standard and regulation for road marking. The success of this work can open the possibility to introduce a more sustainable material for this important application in road safety.

2. Materials and Methods

2.1. Bulk glass fabrication

For the glass production, IS and RHA were considered as the only a source of silica. The characterization of the IS and RHA composition was done by X-Ray Fluorescence (XRF) measurements. The glass composition was defined considering the following mole fractions (mol %) of oxides:

$$(40.00 - \mathbf{x})\mathbf{SiO_2} : (22.00)\mathbf{Na_2O} : (3.00)\mathbf{CaO} : (35.00)\mathbf{B_2O_3} : (x)\mathbf{Sb_2O_3} \tag{1}$$

where Boron trioxide was inserted in the composition in order to lower the melting temperature of the glass[21]. Antimony trioxide was added in the amount of 0.01 mol% in order to produce colorless glasses, just in the case of rice husk ash as source of silica[21]. The mixture was homogenized, with the aid of a pestle and mortar, and placed in a 30 ml gold/platinum crucible. Soon after, the crucible was taken to a muffle furnace at a temperature of 1200 °C for 3 hours for the melting process. Once the melting was done, the resulting liquid was poured into preheated rectangular stainless-steel molds at a temperature of 400 °C, in order to reduce the surface tensions of the produced glasses. The molds were kept at a temperature of 400 °C for 1 h. Finally, the glass was naturally cooled to room temperature. More details of the glass fabrication process can be seen in reference [21]. In the case of UV-Vis analysis, the samples were cut, sanded and polished using a metallographic polisher up to a thickness of 3 mm. After that, the transmittance of the samples was characterized in the visible range of the electromagnetic spectrum (400 - 700 nm).

2.2. Microspheres production

For the microspheres production, the glasses were ground by a pestle and mortar and sieved using granulometric sieves. To ensure that the microspheres were formed in the chosen diameter range, the ground glass shards were sieved, selecting the shards passing through the 250 μm sieve and retained on the 75 μm sieve. The materials retained in the sieve with an opening of 250 μm were subjected again to the milling process, in order to reduce its size. To generate microspheres, different methods can be used, such as: gravitational fall, powder flotation, plasma-spraying and horizontal flame[22-24]. Regardless of the method used, the principles for producing the microspheres are the same: Shelby[25] explains that due to the fact that molten glass behaves as a liquid, if these droplets of molten glass freely fall from a sufficient distance, they will assume a spherical shape as a result of the action of the surface tension. For the horizontal flame method, the glass powder is dispersed over the flame, which simultaneously raises the temperature of the powder and displaces it horizontally, as a result of the flame pressure, forming the microspheres. In this work, a *lab-made* apparatus was built that uses the horizontal flame method for the production of microspheres. The setup consists of a rectangular plywood box, in which refractory bricks are accommodated on its bottom and side walls. The bricks are also covered by a single sheet of galvanized steel, which covers both the bottom and the side walls of the apparatus. The box is closed at the top by a galvanized steel sheet in order to avoid the loss of the produced microspheres. The shards are poured directly into the flame, using a glass funnel, and they are projected to the other end, where the spheroidization process occurs. To produce the flame, a 13 kg liquefied petroleum gas (LPG) cylinder and a 1 m^3 oxygen (O_2) cylinder were used, in a 1:2 pressure ratio (kgf/cm^2), respectively.

2.3. Particle size distribution, morphology and retroreflectivity measurements

The granulometry quantification as well as the produced microspheres morphology (spheres, shards, ovoids, twinned) were made from optical microscopy images. More specifically, the images were analyzed using the ISCapture software[26], considering around 2000 counts of the elements generated after the spheroidization process. For the granulometry measurements, only the elements that became spherical were considered, and the diameter of each of these spheres was measured. To carry out the retroreflectivity measurements, the Easylux horizontal retroreflectometer (model classic) was used.

This equipment allows to quantify the nocturnal retroreflectivity for two different geometries, 15 m and 30 m, which correspond to the distance that the hypothetical vehicle would be from the point where the measurement is being carried out[27]. In addition, the equipment complies with all international road marking standards[28-30]. In this work, the data analyses were collected for both geometries. The measuring area of this instrument is 34 cm x 10 cm. In this sense, MDF plates were built in these dimensions, which allowed reproducing the analysis region of the horizontal road markings. On the MDF plates, ethylene vinyl acetate (EVA) plates of the same dimensions as the MDF were glued, which were painted with white solvent-based acrylic paint, simulating the road painting. The EVA plates were painted with a roller and the thickness was analyzed by a caliper. Immediately after painting, the microspheres were deposited by free fall at a height of 15 cm on the painted plate, considering a density of 100 g/m^2. All experiments were done in triplicate and, considering that the plates can be rotated 180º and measured again, a total of 6 measurements were made. As a reference for retroreflectivity measurements, EVA plates were used only with white acrylic paint, without microspheres.

3. Results and Discussion

In Table 1 are reported the most abundant elements found in the FRX analysis of the RHA and IS. In the case of IS, it is observed that it is basically composed of SiO_2, with minimum percentages of other oxides. For RHA, it is observed that, in addition to the presence of a high silica content, which makes it a suitable material for the production of silica-based glasses, other oxides are present. In particular, it was observed in another work that small amounts of manganese ions can cause an absorption around 480 nm, leaving the glass with a reddish color[21,31]. Actually, the absorbance at 480nm is an effect of the manganese 3+ oxidation state[21]. According to the literature, antimony trioxide can react with the metallic ions of manganese at high temperatures, by the following redox reaction[32]: $Sb^{3+} + 2Mn^{3+} \rightarrow 2Mn^{2+} + Sb^{5+}$, reducing Mn^{3+} to Mn^{2+} inside the glass matrix, enabling to obtain transparent glasses in the visible region. Thus, the addition of a low percentage (0.01%) in moles of antimony oxide (Sb_2O_3) allowed to obtain colorless glasses.

Figure 1 shows images of the produced glasses where: (a) glass from the conventional IS and (b) glass from RHA in the composition. As it can be seen, there are no significant differences in terms of color for both compositions. This statement is more evident in Figure 1(c), where the UV-Vis transmittance spectrum of the samples (a) and (b) can be observed. The optical behavior in the visible region of the electromagnetic spectrum is very similar, meaning that the source of silica for the glass microsphere production do not alter the light transmission in this medium.

According to the methodology, the glasses were ground, sieved and taken to produce the microspheres using the horizontal flame method. Figure 2 shows images, by optical microscopy, of the produced microspheres from RHA glass. In particular, Figure 2(a) reports only the products with perfect spherical morphology, while in Figure 2(b) it is possible to see other typical morphology that can be generated in the spheroidization processes, such as spheres, shards, ovoids and twinned.

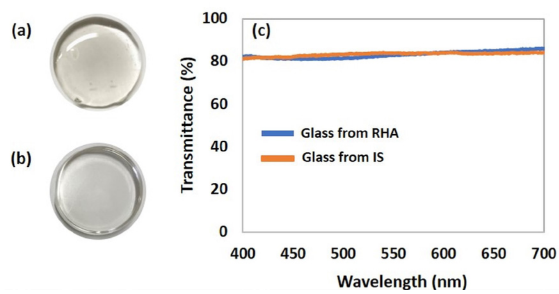

Figure 1. Images of the glasses produced considering as a source of silica: (a) IS and (b) RHA; (c) UV-Vis spectrum of samples (a) and (b).

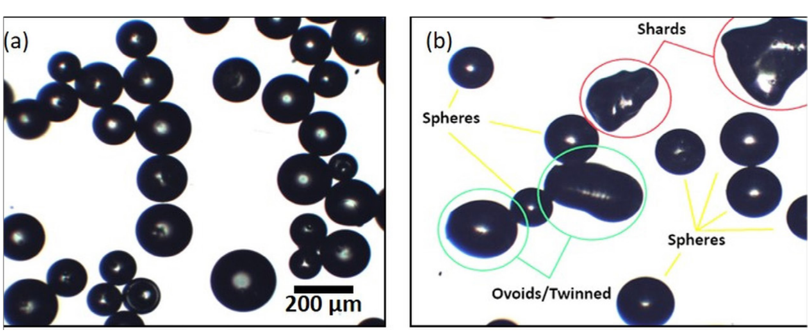

Figure 2. Images of the produced microspheres from RHA glass: (a) microspheres and, (b) other typical generated morphologies.

Table 1. XRF results of RHA and IS.

	SiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	K_2O	P_2O5
IS	99.997		0.001	0.002				
RHA	90.413	1.927	0.051		0.361	0.736	2.109	0.727

Ideal glass microspheres shape for road markings must be a perfect sphere. If the shape of the microspheres is elongated, angulated, or if they present an irregular shape, the light retroreflectivity values are highly reduced[33,34]. Generally, norms define the minimum percentages of spherical and random shapes particles that can be accepted for pavement markings. For comparison purposes, the Brazilian standard NBR 16184 was used as a reference. Table 2 shows the percentage of different elements generated after the spheroidization process using the horizontal flame method, comparing to the minimum limits for the number of spheres and the maximum limits for ovoids and shards[20]. This percentage was based on a count, via ISCapture software, of 2010 elements. As it can be seen, the percentages of the different geometric shapes, for both compositions, are in accordance with the Brazilian standard. Still, no significant morphologic differences are observed between the microspheres considering RHA and IS in the glass composition. More than that, the high percentage of spheres shows that the horizontal flame production process is suitable for the manufacture of microspheres for application in road markings.

During the morphology evaluation, the diameter of the generated microspheres was also measured. Figure 3 reports the results obtained in terms of microsphere percentage of the diameter of the microspheres, obtained by optical microscopy, which meet the granulometric range for glass microspheres by NBR 16184. The dashed black lines, in fact, represent the limits established by the Brazilian standard for Premix-type microspheres (Type-IB)[20]. No significant differences are observed between microspheres from IS and RHA: for microsphere produced with IS, 100% is smaller that 300µm, 94.5% would pass through the 212µm sieve, and 28.3% is smaller than 150µm, but larger than 63µm. Similarly, for microsphere produced with RHA, 100% is smaller that 300µm, 92.1% would pass through the 212µm sieve, and 32.8% is smaller than 150µm, but larger than 63µm. As it can be seen, the granulometry of both types of samples is contained within the established limits, and the manufactured samples are in accordance and can be classified as Premix-type.

In Brazil, according to the National Road Department (DNER), for Premix-type microspheres, it is recommended to use a density of 200g to 250g for each liter of paint[35]. Considering that the average paint thickness was 0.5 mm, the density of 200g/l is equivalent to a surface density of 100 g/m^2. Therefore, this minimum density was considered for the retroreflectivity measurements. In Brazil, the NBR 14723/2013 standard[28] provides the methods and criteria for evaluating the retroreflectivity, for the 15 m geometry. However, this standard does not define minimum limits for retroreflectivity values. Such minimum limits are usually set by federal and state autonomous entities, which are responsible for regulating and supervising the roads. As an example of minimum retroreflectivity limits of Brazilian regulatory agencies, the National Transport Infrastructure Department (DNIT)[36] requires a minimum of 100 mcd/m^2/lux for the white color paint on the roads under its jurisdiction; on the other hand, the Autonomous Roads Department (DAER)[37] requires a minimum of 130 mcd/ m^2/lux for white and yellow colors. For both agencies, as already described, the geometry of 15m is considered. In contrast, outside Brazil, regulatory agencies normally require measurements for the 30m geometry. The English standard[30] sets as a minimum value for road safety with a retroreflectivity of 100 mcd/m^2/lux, while for the American agency FHWA[38], the minimum value is 150 mcd/m^2/lux. In a recent study, it was showed that the road macrotexture affects the retroreflectivity, with higher retroreflecvity values for smaller mean texture depth[16]. Here, the EVA simulates a uniform pavement surface road, with very small mean texture depth.

Figure 4 shows the retroreflectivity measurements of the produced samples for the 15 m and 30 m geometries, considering EVA plates painted with white acrylic paint.

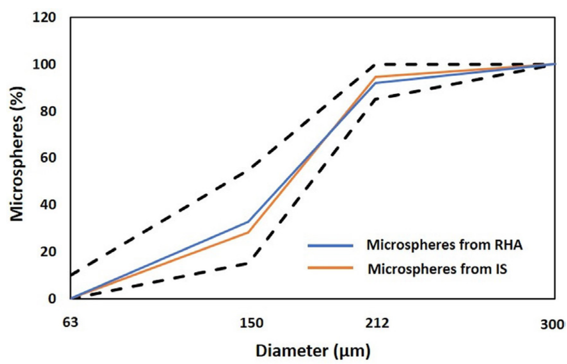

Figure 3. Evaluation of the diameter of the microspheres compared to the limits of the Brazilian standard (black lines) for Premix-type microspheres.

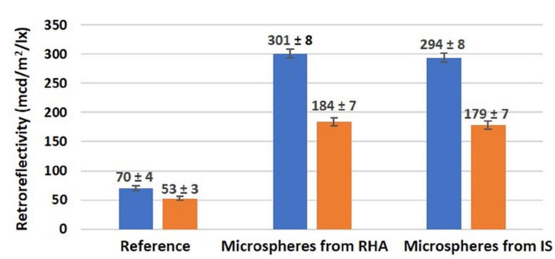

Figure 4. Retroreflectivity measurements for the 15 m (blue) and 30 m (orange) geometries in plates without microspheres, with microspheres from RHA e with microspheres from IS.

Table 2. Percentage of different elements generated after the spheroidization process and Brazilian standard as reference.

Sample	Spheres		Ovoids/twinned		Shards	
	Counts	%	Counts	%	Counts	%
IS Glass	1686	83.9	274	13.6	50	2.5
RHA Glass	1730	86.1	250	12.4	30	1.5
NBR 16184	-	77	-	20	-	3

As already described, an EVA plate painted only with paint was used as reference, without the deposition of microspheres. As it can be seen, the retroreflectivity measurements are greatly amplified when the microspheres are present on the substrate. It is also observed that the retroreflectivity measurements are always greater for the 15 m geometry, when compared to the 30 m geometry, in agreement with the results shown by Salles et al.[39]. This results in an increased visibility of road horizontal marking for the driver, especially at night.

More than that, the results show that the produced samples meet the retroreflectivity criteria for Brazilian agencies, but also for American and European standards. More in details, the measured retroreflectivity values are well above the minimum limits imposed by the Brazilian regulatory agencies, being around 3 times, the minimum determined by the DNIT and 2.3 times the threshold determined by the DAER. As for the English standard BS EN 1436, the results showed a retroreflectivity around 1.8 times greater than the minimum, while for the American agency FHWA, the retroreflectivity was around 1.2 times greater than the established threshold. Comparing the samples produced with RHA and IS, no significant changes were observed for the retroreflectivity measurements, for both geometries (15m and 30m). This suggests that microspheres with RHA in the glass composition can replace the microspheres produced in the traditional way, opening up another possibility of using this industrial residue, helping to close the rice production cycle and avoiding the IS use.

4. Conclusion

Microspheres from glasses made with rice husk ash and conventional industrial sand were successfully produced using the horizontal flame method. The produced microspheres, according to their granulometric distribution, were classified as Type-IB, in consonance to Brazilian standard NBR 16184. The production yield as well as the morphology meet the NBR 16184 standard. The results of the retroreflectivity measurements included the minimum values required by international standards. With regard to Brazilian agencies, the retroreflectivity results reached three times the established minimum. From the material point of view, the retroreflectivity results for IS and RHA are similar, so that glass made from rice husk ash can be applied to horizontal road marking, adding value to this agricultural residue and helping to avoid the industrial sand supply imminent crisis.

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