

COMPARATIVE INVESTIGATION OF EGGSHELL'S PARTICLE SIZE DISTRIBUTION AS FOAMING AGENT FOR MANUFACTURING GLASS FOAM

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Abstract: Various waste materials have been repurposed as secondary raw materials for producing environmentally friendly building products. One type is glass foam which is a thermal insulation material. To produce glass foams, glass powder is mixed with a foaming agent and treated at temperatures higher than 600 °C to inflict gas formation. An essential step in preparing the raw materials is grinding them to an optimal particle size range. Eggshells, due to their high calcium carbonate content, can serve as a foaming agent. However, their plate-like structure makes it challenging to accurately determine size parameters. This study presents a comparison of two different analytical methods—laser diffraction (LD) and dynamic image analysis (DIA). The results show that as grinding time increases, particle size decreases and sphericity improves. Particle breakage begins after 16 minutes, achieving optimal size at 30 minutes. Consistency is observed between the measurement methods at 60 minutes of grinding as particles become more compact and spherical.

Keywords: *eggshell, grinding, recycling as foaming agent, ball milling, glass foam*

1. INTRODUCTION

With increasing urbanization, the consumption of non-renewable raw materials continues to rise, leading to significant environmental issues if not disposed of properly (Cheng et al., 2016; Liu et al., 2019; Shelby, 2017). Effective waste management is essential for promoting sustainable development.

Glass foams are environmentally friendly materials if made from secondary raw materials (Fóris and Mucsi, 2023a; Scarinci et al., 2005; Souza et al. 2017; Assefi et al., 2021; Cengizler et al., 2021). They can be used as aggregate, heat insulation, or

filler because of their many positive features like being lightweight, highly porous, chemically neutral, non-flammable, and frost-resistant. With relatively low thermal conductivity, glass foams effectively prevent heat transfer (Goltsman and Yatsenko, 2023). Those foams open new opportunities for waste materials such as glass and eggshell powder to make a high-value product that easily fits into the circular economy concept. A key disadvantage of glass foams is the production cost, which is attributed to high raw material expenses (using SiC as a foaming agent) and energy-intensive processes, like milling and thermal treatment.

To produce glass foams, foaming agents are necessary to create pores (Da Costa et al., 2020). The foaming agents release gas in the molten glass during decomposition. Carbonates are cost-effective types of foaming agents (Thulasikanth and Padmanabhan, 2023). One example of this is eggshell (Fóris and Mucsi, 2023b) due to its high calcium carbonate content. Eggshells (ES) are one of the most abundant food wastes through everyday egg consumption. 50,000 tons of ES waste are generated approximately every year worldwide (Das et al., 2022). Eggshells' main constituent is calcium carbonate (94–96%) or more specifically calcite in crystalline form (Baláz, 2018). It is suitable for forming a porous structure in glass foams because CO₂ is generated during the thermal decomposition of calcium carbonate at high temperatures (700–900 °C) (Souza et al., 2017; Osfour and Simon., 2022).

An essential step in glass foam production is grinding the raw materials to the optimal size. Generally, raw materials need to be ground to less than 100 µm for effective foaming (Guo et al., 2023; Bueno et al., 2020). The particle size of the foaming agent directly influences the pore size and foaming behavior. If the particle size of the foaming agent is uniform, the resulting glass foam structure is homogeneous, which is advantageous regarding its material specification (Spence and Kultermann, 2016).

The primary challenge with eggshells lies in their plate-like particle shape, making it difficult to accurately determine the particle size distribution. To accurately characterize the particle size and morphology of raw materials such as eggshell powder, advanced measurement techniques are required. Conventional sieving often fails to capture fine fractions and irregular particle geometries. Among the widely used techniques, laser diffraction and dynamic image analysis provide complementary information. In the following, LD will be used to refer to laser diffraction, and DIA to dynamic image analysis.

LD is based on the principle that particles scatter light at angles inversely proportional to their size, allowing rapid determination of particle size distribution over a wide range. LD is advantageous due to its speed, reproducibility, and ability to measure large sample volumes, but it assumes spherical particle geometry. This limitation can lead to inaccuracies when analyzing materials such as eggshells, which often have irregular, plate-like morphologies.

DIA, on the other hand, directly captures two dimensional images of particles in motion, enabling simultaneous evaluation of both size and shape descriptors (e.g., aspect ratio, sphericity, convexity). Although DIA provides detailed morphological

information, it generally requires longer measurement times, careful sample dispersion, and larger datasets for statistical reliability.

This study aimed to examine the effects of grinding on the particle size distribution and shape parameters of eggshells using two different methods: laser diffraction and dynamic image analysis.

2. MATERIALS AND METHODS

The raw material consisted of chicken eggshell waste, which was subjected to ball milling for varying durations ranging from 1 to 60 minutes (Figure 1). A general overview of the physical characteristics of the chicken eggshell is presented in Figure 2. This figure illustrates the layered structure of an ES, showcasing its unique hierarchical architecture. Starting from the outermost layer, the eggshell consists of a cuticle colloid layer and a surface layer, which provide a protective coating. Below this lies the palisade layer, composed of tightly packed materials that add strength and support. The mammillary layer follows, featuring structures that connect to the underlying fiber membrane. Notably, the structure contains gas pores and bubble pores that enable gas exchange, which are essential for biological processes. Additionally, sub-layers like the sub-micro-sphere layer and nano-line layer contribute to the eggshell's strength and rigidity, while the outer and inner membranes form a barrier that further reinforces the structure (Hincke et al., 2012).

Before milling, ES waste was heat-treated in boiling water for 30 minutes to remove the organic content. Then the material was dried at 105 °C for 2 hours until mass consistency. Before milling, the ES was kept in a desiccator at room temperature (25 °C). The eggshell's thickness was measured with a digital gauge. The average thickness was $401 \pm 28.29 \mu\text{m}$.

The grinding process utilized a planetary mill with stainless steel balls of 10 and 20 mm diameter as the grinding media. Throughout the experiment, eggshell is referred to as ES.

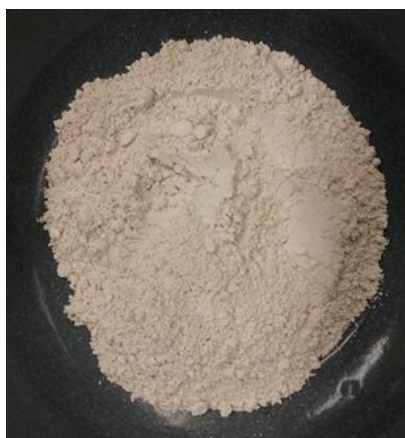


Figure 1
ES powder after 60 minutes grinding

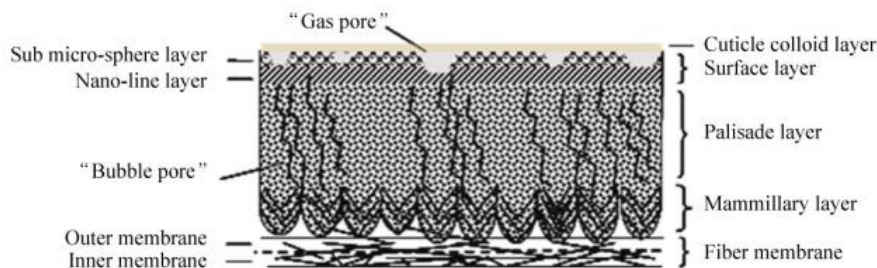


Figure 2
Description of ES (chicken ES) (Zhou et al., 2011)

2.1. Methods for raw material characterization

The chemical compositions of eggshells were measured by a Rigaku Supermini 200-type wave-length X-ray fluorescence spectroscopy (XRF). The loss of ignition (LOI) was measured at 950 °C with 90 min heating rate, and 60 min holding time in a static furnace. The XRF and LOI experiments were carried out from the original sample (before ES was heat-treated in boiling water). Table 1 shows the results of XRF and LOI measurements. The primary component of the eggshell is CaO, comprising 54.5% of the total mass, reflecting the high calcium carbonate content of the eggshells. The LOI content is relatively high at 45.7%, indicating a significant amount of volatile material during thermal treatment. These values highlight the suitability of eggshells as a potential source of calcium carbonate for applications such as foaming agents in glass foam production.

Table 1
Chemical composition and
loss of ignition of ES

	(m/m%)
SiO₂	0.3
Al₂O₃	0
MgO	0.62
CaO	54.4
Na₂O	0.13
K₂O	0.13
Fe₂O₃	0.03
MnO	0.001
TiO₂	0.002
P₂O₅	0.499
S	0.21
F	<0.3
LOI	45.71

2.2. Methods for ES powder characterization

The ground powders were analyzed with two different methods. For the first method LD, a Horiba LA-950 V2 laser diffraction particle size analyzer was used in wet conditions using distilled water as dispersing media, applying the Fraunhofer theory. For the second method DIA, Retsch Camsizer XT dynamic image analyzer was used in dry conditions. To evaluate the influence of milling on the shape properties, the parameter sphericity (surface rounding of grains) SPHT was selected

$$\text{SPHT} = 4 \pi (\text{particle area}) / (\text{particle perimeter})^2 \quad (1)$$

For the sphericity, the mean value, and the confidence interval of a 95 % level of confidence were calculated as

$$\alpha_{\text{bottom}} = \bar{X} - t_{0,95} * \frac{S_n^*}{\sqrt{n}} \quad (2)$$

$$\alpha_{\text{top}} = \bar{X} + t_{0,95} * \frac{S_n^*}{\sqrt{n}} \quad (3)$$

$$\alpha_{\text{top}} - \alpha_{\text{bottom}} \quad (4)$$

where \bar{x} is the mean, $t_{0,95}$ is the t-distribution value at 95 % confidence level, S_n^* is standard deviation, n is the number of values, α_{bottom} is the lower limit of the 95% confidence interval, α_{top} is the upper limit of the 95% confidence interval.

3. RESULTS AND DISCUSSION

Particle size distributions are provided in Figures 3 and 4 in volume distribution (Q_3) with the two different devices (Horiba LA-950 V2 and Retsch Camsizer X2).

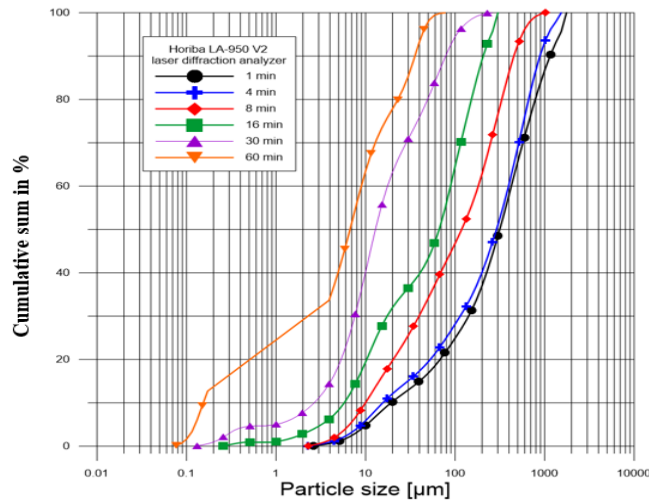


Figure 3

Particle size distribution curves at different grinding times (laser diffraction analyzer Horiba LA-950 V2)

In Figure 3 the LD results showed no major size reduction before 4 min of grinding. At 8 minutes, the particle size starts to decrease significantly. At 30 minutes, the particle size distribution is much finer with the majority (97.88%) of the particles falling below 100 μm , indicating sufficient grinding. The curve suggests that grinding at this stage reaches an optimal balance for producing finer particles. By 60 minutes, the particle size distribution shifts even further, with a 55% of particles being less than 10 μm in size. This demonstrates that with prolonged grinding, the particle sizes become even smaller and more homogeneous, as the curve becomes steeper, suggesting more uniform particle sizes. The 30-minute grinding represents a good trade-off between size reduction and energy input, as particles below 100 μm are achieved, which is typically suitable for applications in glass foam production.

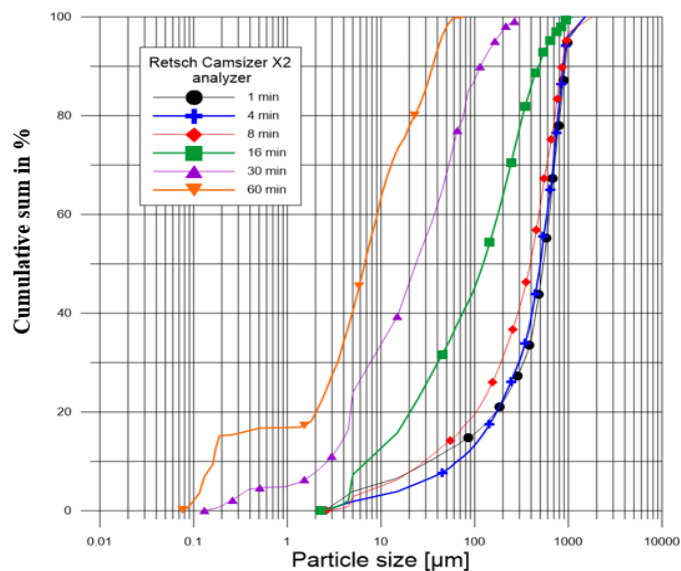


Figure 4
*Particle size distribution curves at different grinding times
(dynamic image analyzer Retsch Camsizer X2)*

During the DIA method with Retsch Camsizer X2 the diameter of circumference was used to evaluate the particle size distribution. Similar to the previous graph, short grinding times (1–8 minutes) show no significant size reduction. By 16 minutes, approximately 85% of the particles fall within the 1–100 μm range, although the distribution is still relatively broad. After 30 minutes of grinding, 85% of the particles have shifted to a smaller size range, with most particles below 100 μm . The distribution becomes narrower, indicating more uniform particle sizes. Comparing the two methods, the major size reduction starts after 8 minutes of processing. With the increasing grinding time, the particle size reduces respectively, this trend can be seen in the case of both methods. However, slight fluctuations between the methods can be observed at shorter grinding times, as shown in Figure 5.

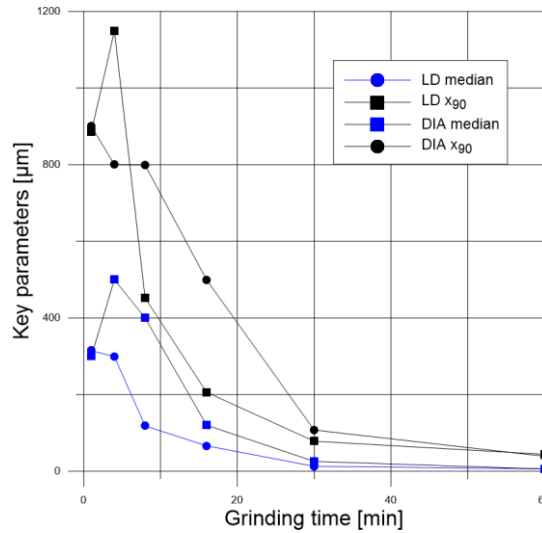


Figure 5

Key parameters measured by Camsizer (DIA) and Horiba LA-950 V2 laser diffraction analyzer (LD)

In Figure 5, it can be noticed that the key parameters of the PSD (median and x_{90}) decrease with increasing grinding time. An increase of the upper particle size x_{90} can be observed from 1 to 4 minutes of grinding, which can be an artefact due to particle shape. This artefact in particle size distribution is due to the anisotropic shape of the particles, which causes inconsistent measurements depending on their orientation during analysis. Both LD and DIA show a clear trend of particle size reduction with increasing grinding time. The particle size distribution stabilizes after around 30 minutes of grinding, where the differences between the two methods become minimal. For early grinding times, DIA may be more sensitive to larger, irregularly shaped particles like the plate-like structure of eggshells, whereas LD seems to show slightly smaller particle sizes initially. The reason for this is DIA measures the longest axis of irregular particles, it records larger sizes for plate-like eggshell fragments, while LD assumes spherical equivalents and therefore reports slightly smaller particle sizes at early grinding times. Both methods are effective in tracking particle size reduction over time, and after 30 minutes, both converge to show a similar particle size distribution, indicating more homogeneous particles.

In Figure 6, the SPHT values indicate that the sphericity of the particles increases with prolonged grinding time. As grinding progresses, the particles become more compact, gradually losing the plate-like structure of ES. A steady rise in sphericity is observed as grinding time extends with minimal changes detected before 8 minutes. This observation aligns with the particle size distribution measured by DIA, which also shows little variation in the early stages of grinding. However, by 60 minutes, a substantial improvement in sphericity is evident compared to the 1-minute grinding.

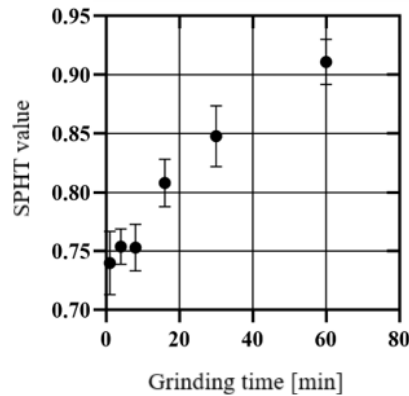


Figure 6
Sphericity results measured by Camsizer (DIA) analyzer at different grinding times

This tendency correlates with the two different methods. Laser diffraction makes the convenient assumption that every particle is a sphere, so where the SPHT values are close to 1, the LD and DIA methods show similar results. This similarity in results is apparent after 30 and 60 minutes of grinding. However, at shorter grinding times (1–8 minutes), notable discrepancies are observed. Laser diffraction indicates a significantly larger fraction of particles below 100 μm compared to image analysis, which still records most particles in the coarser size range. During the initial grinding phase (up to 8 minutes), the particles retain much of their original size and shape. Only after 16 minutes do the particles begin to break down at the plate edges and decrease in size. Concurrently, a major increase in sphericity is observed, reflecting the loss of their plate-like structure and a shift toward a more spherical shape.

The experimental results highlight the significant influence of grinding time on eggshell particle size and morphology, as well as the suitability of different analytical methods for particle characterization. Particle breakage was observed to occur mainly after 16 minutes of grinding, with an optimal fraction of particles smaller than 100 μm being achieved after 30 minutes. These findings are consistent with the observations of Baláz (2018), who reviewed ball milling of eggshells and reported that extended grinding enhances fineness and reactivity, although the efficiency of the process is strongly influenced by the original morphology of the material (Baláz, 2018). Similarly, Guo et al. (2023) demonstrated that the fineness of glass-based aggregates has a direct effect on the performance of lightweight concretes, reinforcing the need to optimize grinding conditions to obtain desirable particle properties (Guo et al., 2023).

The results also showed that longer grinding time increases particle sphericity, as particles gradually become more compact and rounded. This is in line with the descriptions by Zhou et al. (2011) and Hincke et al. (2012), who reported that the hierarchical, plate-like structure of eggshells presents challenges for comminution

(Zhou et al., 2011, Hincke et al., 2012). These structural characteristics explain why short grinding times do not yield strong correlations between particle size and shape.

The results indicate that DIA provides more reliable measurements at shorter grinding times, when particles retain their plate-like geometry, since it records particle dimensions directly from images. However, with extended grinding (60 minutes), the results from DIA and LD converge due to the particles' increasing sphericity, leading to a high level of agreement between the two methods. This dual applicability of LD and DIA highlights the importance of combining complementary techniques for accurate characterization. While Spence and Kultermann (2016) noted that uniform particle size enhances the homogeneity of construction materials, studies have not explicitly compared LD and DIA in the context of waste-derived powders.

In summary, this study confirms that systematic grinding is essential to overcome the plate-like morphology of eggshells, with particle size reduction and sphericity improvement directly influencing the effectiveness of eggshells as a foaming agent. Furthermore, the complementary use of LD and DIA provides a more complete characterization of particle properties, offering methodological guidance for future investigations.

4. CONCLUSIONS

During the experiments, systematic grinding tests were carried out and particle size distribution and particle shape distribution were investigated. The following conclusions were observed from the measurements:

- The breakage of the particles occurs at 16 minutes. Before that, the size and shape parameters do not change a lot (1–8 minutes),
- As the grinding time increases, a gradual decrease in particle size can be seen with an optimal size fraction of $<100\ \mu\text{m}$ being achieved after 30 minutes of grinding,
- With increasing grinding time, the particle size decreases and the particles' sphericity value increases because of more compact particles,
- At shorter grinding times, the two results do not correlate because of the plate-like shape of the particles. More energy and longer grinding are required to break these particles down. DIA measures an average of the longest, medium, and shortest physical dimensions of the plate-like particles, therefore bigger particles are measured compared to LD method,
- At the 60-minute grinding interval, the particle size distributions obtained by the two evaluation methods exhibit a high degree of agreement, primarily due to the particles' sphericity values approaching unity. Due to the plate-like nature of eggshells at shorter grinding times, DIA method is suggested to investigate particle size distribution, but at longer grinding times (60 minutes of grinding) LD analyses can give reliable results because the particles become more compact and spherical the effect of grinding.

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