Shadia Ikhamies · Jian Li · Carlos Mauricio Fontes Vieira · Jean Igor Margem · Fabio de Oliveira Braga
Editors

Green Materials Engineering
An EPD Symposium in Honor of Sergio Monteiro
Preface

Green engineering is the design, use of processes, and development of products that conserve natural resources, reduce pollution, and exert the smallest possible impact on the environment. Green engineering often promotes sustainability and minimizes risk to human health without incurring economic feasibility and efficiency. So, green engineering is not actually an engineering discipline in itself, but a comprehensive framework for all engineering disciplines. The Green Materials Engineering symposium is a TMS Extraction and Processing Division (EPD) symposium, sponsored by the Characterization of Minerals, Metals, and Materials and the Biomaterials Committees. This symposium is held in honor of Professor Sergio Monteiro from the Military Institute of Engineering, IME, Brazil. The symposium focuses on green materials including natural composites, bio-inspired armors, waste, clays added ceramics, lignocellulosic fibers, biodegradable polymers, and any type of natural material that could be related to engineering applications.

The Green Materials Engineering symposium held during the TMS 2019 Annual Meeting in San Antonio, Texas, USA, received 54 abstract submissions from different research groups, of which 34 were accepted as oral presentations and 20 accepted as posters. Of the presented papers, 33 are published in this book after being peer reviewed. These papers cover different fields including sustainable clays and ceramics, natural fiber composites, nano- and microgreen composites, properties and characterization of green materials, and biomass in armor composites. These materials are characterized using highly sophisticated techniques to examine their microstructure, mechanical, thermal, and functional properties.

This book will appeal to people from academia and industry who are interested in green engineering, sustainability, recycling, and environment, and it can help academia emphasize pollution prevention and incorporate risk into green engineering courses. It helps environmental and chemical engineers; postdoctoral, graduate and undergraduate students; people from industry; and environmental scientists to convert concepts of green engineering and sustainability to real designs, using the most valuable quantitative design tools and performance metrics.
The editors of this book express their genuine thanks and gratitude to TMS for giving the organizers and committee sponsors the opportunity to publish a stand-alone volume for this symposium. The editors also thank the publisher, Springer, who produced the book, and the authors, who are the basis of this scientific work.

Shadia Ikramayes
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Development of Silicate Glasses with Granite Waste

Michelle Pereira Babisk, Vinicius Rodrigues Gomes, Juraci Aparecido Sampaio, Monica Castoldi Borlini Gadioli, Francisco Wilson Hollanda Vidal and Carlos Mauricio Fonseca Vieira

Abstract: Granite is an igneous stone with high quartz (SiO₂), whose processing generates millions of tons of fine residue annually in Brazil. Among the various definitions of glass, the most widely used is that it is a physically homogeneous substance obtained by cooling a melting inorganic mass, which solidifies without crystallizing, therefore, glasses do not have a regular atomic arrangement and, hence, are called amorphous. The objective of this work was to characterize a granite chemically and morphologically and to use it as the main raw material for producing silicate glasses of the soda-lime and borosilicate types. The characterization of the granite waste revealed that the silica (SiO₂) is the major component, followed by the alumina (Al₂O₃), in grains of angular shapes, which favors the glass production process. The glasses produced were colored (green and amber), totally amorphous and with densities consistent with the values quoted in the literature, for each type of glass. The results show that this waste can be used as raw material in glassmaking, thus obtaining a correct destination for this waste.
Keywords Granite waste • Silicate glasses • Soda-lime glass • Borosilicate glass

Introduction

Stones are generally defined as natural solid bodies, formed by aggregates of one or more crystalline minerals. From the commercial point of view, ornamental and cladding stones are basically subdivided into two large groups, granites and marbles. As granites, they are generally made up of silica stones, while marbles, carbonates stones [1].

In the case of the production of ornamental stones, among other steps, the sawing of blocks is made to turn them into semifinished plates. The equipment used for the sawing process is called the loom, which consists of steel blades or diamond wire blades. In this phase, expressive amounts of waste are generated, according to surveys carried out by Vidal et al. (2013), the volume of fines generated, which corresponds to the volume of the cutting furrows, is equivalent, on average, to 26% of the initial volume of the block. In Brazil, it is estimated that approximately 2 Mt of fine waste is generated annually [2, 3].

According to Abiroehas (2018) granites made up more than 87% of Brazilian stone exports in 2017. Granite is an igneous stone, consisting mainly of feldspar, quartz, minerals with iron. The quartz has a crystalline structure composed of silica tetrahedra, silicon dioxide (SiO₂), and feldspar, which responds to the highest percentage concentration in the granite stone formation, have a crystallized silica structure. Feldspars are a series of aluminum silicates and alkaline or earth alkaline bases, both potassium and sodium feldspars are generally present. The micas are the minerals that present in smaller percentage in the composition belong to the group of aluminum silicates and other metals [4, 5].

Silica is a naturally occurring glass-forming oxide, and the addition of oxides imparts distinct characteristics. These oxides added to the silica may be either network modifying oxides or intermediate oxides. The network modifying oxides break the glass structure formed by silica, reducing the melting point and the viscosity of the fluid, and the intermediaries may act as modifiers or as network formers [6].

Since Zachariassen (1932) published and based his paper "The Atomic Arrangement in Glass" or X-ray diffraction results showing that the glasses differ from the crystals because they do not have a long-range symmetrical and periodic network except for their basic unity, different definitions of glass have appeared in the scientific literature, but several authors have maintained this dependence in their definitions [7-12].

ASTM (American Society for Testing and Materials) defines glass as an inorganic melt that has been cooled to a rigid condition without crystallization, and is therefore referred to as amorphous materials. A material is amorphous when it does not present a long-range order in the atomic arrangement, that is, when there is no regularity of its molecular constituents on a scale larger than a few times the size of these groups [6].
Development of Silicate Glasses with Granite Waste.

Industrially, the concept of glass can be restricted to the products resulting from the fusing of oxides or their derivatives and mixtures, generally having as main constituent the silica, for the common glasses. Within this scenario and context, the objective of this work is to characterize a fine granite waste and to use it as the main raw material to produce silicate glasses of the soda-lime and borosilicate types.

Experimental

In this work, we have used granite waste as silica source and commercial oxides to produce soda-lime and borosilicate glasses.

The granite residue was collected in a sawmill in Cachoeiro de Itapemirim/ES, Brazil. First, the waste was air dried to remove excessive moisture followed by later drying in an oven at ±110 °C for 24 h. The batch was disaggregated with mortar and pestle and sieved in 40 µm size.

For the addition of the other component oxides of the glasses, the following chemical reagents type A.R.: sodium (Na₂CO₃) and calcium (CaCO₃) carbonates, alumina (Al₂O₃) and boric acid (H₃BO₃) were used.

The characterization of the waste was done by chemical analysis by X-ray fluorescence (XRF) and morphological by scanning electron microscopy (SEM). The XRF was performed on a Paralytical Axios spectrometer (WDS-2), and the SEM micrographs were obtained on a MEV FEV Quanta 400 scanning electron microscope.

The glass compositions (Table 1) were based on a glass used in beverage packaging for soda-lime and Pyrex® glasses for borosilicate [6]. They were cast in a furnace Sentro Tech Corp. SF-1730C-445 at 1500 °C. The samples were subsequently annealed at 600 °C for 2 h.

The X-ray diffraction patterns of the glass samples were collected in a Bruker-D4 Endeavor equipment, under the following operating conditions: Co Ka (35 kV/40 mA), gonimeter velocity of 0.02°/s per step with counting time of 1 s per step and collected from 5 to 80° 2θ. The glass samples densities were obtained by the Archimedes method at 22 °C using water as immersion fluid.

<table>
<thead>
<tr>
<th>Table 1 Composition of glasses wt%</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>CaO</th>
<th>B₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda lime</td>
<td>72</td>
<td>2</td>
<td>13.5</td>
<td>12.5</td>
<td>–</td>
</tr>
<tr>
<td>Borosilicate</td>
<td>79</td>
<td>2</td>
<td>6</td>
<td>–</td>
<td>13</td>
</tr>
</tbody>
</table>
Results and Discussion

The main raw material for manufacturing silicate glasses is sand, which has the function of providing silica (SiO$_2$) to the glass [13]. As this research aimed to use the fine granite waste to replace the sand, the discussion of its characterization will be made in comparison of this raw material.

Industrially, the angular grains of the sand favor the process of production of the glass, because the fusion begins at the tips and edges of the grains. In the micrographs obtained by MEV of the fine quartzite residue, shown in Fig. 1, the morphology of the particles of the residue can be observed and that these have angular grains (Fig. 1b) [14].

In a non-focused heating on crystals, it is common for the melt to occur on the surface, since the melting kinetics favors the ends of the crystals, so fusion occurs "from the outside to the inside." Quartz, for example, can remain solid up to 300 °C above its natural melting temperature (1400 °C) in the regions of the center of the material because of this effect of melting kinetics [15].

Table 2 shows the chemical composition of the granite waste. It is possible to observe the majority presence of SiO$_2$ (69.9%), glass-forming oxide, which confirms its efficiency as a silica supplier for the production of silicate glasses, followed by Al$_2$O$_3$ (17%) intermediary oxide. Significant amounts of CaO, K$_2$O and Na$_2$O, network modifying oxides have also been identified. Content of 1.3% of Fe$_2$O$_3$ was identified; in this work, this oxide will play a fundamental role as it will act as a dye in the formulation of the glasses.

![Micrographs of fine granite waste: a 1000x and b 2000x](image)

**Fig. 1** Micrographs of fine granite waste: a 1000x and b 2000x

<table>
<thead>
<tr>
<th>Components</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>P$_2$O$_5$</th>
<th>TiO$_2$</th>
<th>Lol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>69.9</td>
<td>1.5</td>
<td>3.4</td>
<td>5.5</td>
<td>17</td>
<td>1.3</td>
<td>0.46</td>
<td>0.14</td>
<td>0.24</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Lol: Low loss on ignition
Fig. 2 Pictures of the glasses produced with granite waste: a Soda lime and b Borosilicate

<table>
<thead>
<tr>
<th>Table 3 Density of glasses produced with granite waste (g/cm³)</th>
<th>Glasses</th>
<th>Soda lime</th>
<th>Borosilicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>2.55</td>
<td>2.37</td>
<td></td>
</tr>
</tbody>
</table>

Due to the presence of iron oxide in the granite waste, the soda-lime glass showed a greenish color, while the borosilicate showed amber coloration.

In commercial terms, the color of glass can be very important in marketing matters as it can help in choosing the product. Besides the esthetic function, the color of the glass also has a utilitarian function. Depending on the element, it can filter the light, letting some rays pass and retarding others. That is why green and amber bottles are used for drinks and medicines, because these glasses prevent the passage of certain (ultraviolet) radiations, which deteriorate the products.

Figure 2 shows the images of the glasses produced where it is possible to visualize the text through the samples with approximately 2 mm of thickness, it can be observed that both the soda-lime glass and the borosilicate have good transmittance in the visible region.

The X-ray diffractograms of the glasses produced are shown in Fig. 3. It can be observed the absence of crystalline peaks, and the spectra represent a typical amorphous band around 27°, due to the majority presence of silica in the glasses. This result characterizes the glasses as amorphous, they do not present a long-range order in the atomic arrangement.

The densities of the glasses produced are presented in Table 3 and are close to the values in the literature. The densities of the soda-lime glasses are compatible with the increased density that alkali incorporation provides in the glass silica network, which leaves densities around 2.57 g/cm³, very close to the value found for the glass produced with the granite waste. The packing of the SiO₂ and B₂O₃ networks is similar, which maintains a similar oxygen atom packing and there is no significant variation in density between the glassy silica and the borosilicate glass, keeping the density in values around 2.22 g/cm³, the presence of the alkali oxides in the waste, thus adding more of these in the composition, may have influenced and a small increase in the density value of the borosilicate glass produced with the waste can be observed [16].
Fig. 3 X-ray diffractograms of the glasses produced with granite waste

Conclusions

It is justified the use of granite waste for the production of silicate glass, soda-lime and borosilicate types, its characterization proved the majority composition of silica (69.9%) and alumina (17%), as well as oxides alkaline and alkaline earths used in the composition of the glasses produced. The morphology of the waste in angular grains helps the fusion and, consequently, the productive process. The glasses produced were totally amorphous and colored (green and amber), due to the presence of iron oxide in the granite waste, the color of the glasses can be important in esthetic matters, and also useful, because these glasses block certain radiations. Despite the color, they presented good transmittance in the region of the visible and densities compatible with the respective types of glasses. The results show that this waste can be used as raw material in the manufacture of silicate glass, thus obtaining a correct destination for this waste generated in the order of millions of tons.

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