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Microstructure and mechanical properties of artificial marble

Carlos E. Gomes Ribeiro [a,b], Rubén J. Sanchez Rodriguez [a,*], Eduardo A. de Carvalho [a]

[a] North Fluminense State University, Laboratory of Advanced Materials, Polymer and Composites Section, Campos dos Goytacazes, RJ, Brazil
[b] Federal Institute of Espirito Santo, Mechanical Engineering Department, Cachoeiro de Itapemirim, ES, Brazil

HIGHLIGHTS

- Impact of microstructure on the properties of artificial marble (AAM).
- The regular interphase resin-residues improve the mechanical properties in AAM.
- The AAM produced from coarse waste cutting offers an alternative material to industry.

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ABSTRACT

Artificial marble (AAM) was manufactured from waste material from dolomitic marble slabs. Fragments of marble slabs (waste) were processed by resin transfer molding (RTM) and vacuum vibrocompression (VVC) technologies using unsaturated polyester resin (UPR) to obtain AAMs with different microstructures.

The AAM-RTM and AAM-VVC produced with 13 to 15%w/w UPR have different physical properties. The AAM-VVC had a higher density (2.38 $g.cm^{-3}$) and lower porosity (0.39 wt%) and exhibited a higher tan δ intensity peak in an oscillatory mechanical test, associated with interfacial friction that is characteristic of the microstructure observed in the fracture region of AAM-VVC samples. The AAM-VVC also exhibited a higher bending modulus (21.5 GPa) and compressive modulus (3.9 GPa), between that of natural dolomitic marble and UPR, which were characteristic of this more compact AAM. The less dense microstructure of AAM-RTM explains the smaller bending modulus (0.93 GPa) and compressive modulus (0.63 GPa) compared to AAM-VVC.

The AAM-RTM and AAM-VVC microstructures and associated properties enable various applications for these alternative materials in the construction industry, providing a means of reducing the amount of stone waste and providing an economic value to marble waste.

1. Introduction

It is estimated that the worldwide production of ornamental stone in 2012 was 123.5 million tons, with Brazil contributing 6.1% of this total, which makes it the fourth largest producer [1].

The manufacture of Brazilian ornamental stone is without a doubt a source of wealth and social development. Notwithstanding the benefits, the processing steps from stone extraction to finishing (mining, cutting, polishing and lapping) generate large amounts of industrial byproduct or waste. The amount of byproduct generated as a result of extraction is determined to be somewhere between 40% and 60% of the global production, and another 30–35% is generated as a result of cutting and lapping [2].

The costs involved in discarding the waste in accordance with recent, considerably stricter environmental laws has fueled the search for technological alternatives to handle these industrial waste streams. Roohbakhshan and Kalantari [3] report the use of stone waste as a component in brick mix, highway construction, urban landfill impermeabilization and concrete fine-aggregate replacement. Bilgin et al. [4] report that up to 10%wt of fine marble waste can be added to brick mix without affecting the product's final properties.

Using artificial or engineered stone in the housing and construction industry and in the restoration of stone elements in historic buildings is an effective, environmentally friendly alternative to use this waste in a value-added way [5].

The use of marble slabs waste to produce cheaper materials that imitate high-strength natural marble has increased in recent decades. The use of these alternative materials will continue growing for the foreseeable future with a predicted demand of

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* Corresponding author.
E-mail address: sanchez@uenf.br (R.J. Sanchez Rodriguez).

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6.7 million m^2 for the US market alone by 2016, representing an 8.2% growth over 2011 [6].

The application of alternative artificial marble (AAM) derived from waste marble in the building industry depends both on the physical and mechanical properties of the marble and on the formulation properties, which will be influenced by resin content and the microstructure of the AAM introduced in the manufacturing process.

The use of resin transfer molding (RTM) and vacuum vibrocompression (VVC) technologies, which are characterized by low labor requirements, good dimensional tolerance and relatively low cost, offer the possibility of studying how the microstructure of AAM is affected by the manufacturing process.

In the RTM process, resin is injected into a mold containing the particles. The resin distribution in the volume depends on the resin flow around the marble waste particles, controlled by the addition of solvent, which introduces voids in the AAM product [7,8].

In the VVC process, the resin impregnation of marble waste particles occurs before molding without a solvent, which means that the void formation is more controlled, it depends on the efficiency of air bubbles removal in pre-cured formulation promoted by the use of vacuum and vibration in the compaction steps [9,10]. Various reports discuss the correlations between the compositions of artificial marble and the physical and mechanical properties [9–12], but they did not discuss the effect of the AAM microstructure when equal compositions and similar contents are used in AAM formulations, and the reports do not describe artificial marble's potential in specific applications in the building industry.

The aims of this study were to produce alternative materials from dolomite marble waste employing RTM and VVC manufacturing techniques and to evaluate the impact of their microstructure on the physical and mechanical behavior of these AAMs.

2. Materials and methods

2.1. Coarse cutting waste

Marble slabs waste strip-shaped was collected in a disposal area of Polita Marble Company that produces raw slabs of marble and lapped products, located in Cachoeiro de Itapemirim, Espirito Santo State, Brazil. After collection it was crushed to pass in 10 mesh sieve. To the AAM-RTM formulations was collected fraction with particles between 10 and 230 mesh to improved mold filling.

2.2. Unsaturated polyester component

Orthophthalic unsaturated polyester resin (UPR) with a medium viscosity, 1.23 $g.cm^{-3}$ density at 25 °C, and a gel time of 12–15 min at 25–35 °C, was used to formulate the artificial marbles. To AAM produced by RTM (AAM-RTM) was used 10% w/w (relative to UPR weight) of a thinner solvent for improved mold filling. To AAM produced by VVC (AAM-VVC) not was used thinner solvent. As initiator was used methyl ethyl ketone peroxide (MEKP) (1% w) to RTM and VVC processes.

2.3. Artificial marble

The marble slab waste were previously crushed and classified. These particles were dried at 80 °C for 2 h to remove humidity because it may reduce the cure process efficiency and adhesion between resin and waste [13].

2.3.1. AAM-RTM formulation

The hot slab marble waste particles were placed in a mold (150 × 150 mm), closed. It was vibrated and press (15-ton) at 60 °C after that was applied vacuum for 5 min. After air removal to resin was injected by a screw actuated piston.

After resin injection, the vacuum and vibration system was activated again for 10 min, and was applied 5 MPa compressive stress for 30 min. The AAM-RTM slab was removed to the final cure at 90 °C (4 h).

2.3.2. AAM-VVC formulation

The particles, after dry process, were placed into a vacuum mixer and after that the resin was added by vacuum suction. The marble waste and resin were mixed and added in a 605 × 300 mm mold. It was spread and submitted to vibration. Afterwards with vibration and vacuum condition was applied 1.7 MPa compressive stress on the formulation contents in the mold for 30 min. The AAM-VVC slab was removed and submitted to final cure at 90 °C (4 h). A final heat treatment was conducted in both system to remove the residual solvent and complete the unsaturated polyester cure [14,15].

The main difference between AAM-RTM and AAM-VVC processes is in the wetting of marble particles by unsaturated polyester. To AAM-RTM, the UPR is injected in the mold and needs to flow between marble particles, while to AAM-VVC, marble particles and UPR are mixed before molding, which enhances wetting of the particles.

2.4. Chemical and mineralogical composition of waste

Quantitative mineralogical composition of the marble slabs waste was obtained by means of X-ray diffractometry (XRD) performed on powdered samples. XRD analysis was performed using a SHIMADZU XRD-7000 diffractometer operating using Copper Kα radiation and 2θ ranging from 3° to 90°. Chemical composition was determined by X-ray fluorescence using a Philips PX2400 spectrometer (elements are presented in oxide form).

2.5. Thermal behavior of AAMs and waste contents

The thermogravimetric analyses (TGA) were carried out in TGA 5000ir TA Instruments. About 12 mg of samples were heated from 25 to 1000 °C using a heating rate of 10 °C/min under dynamic air atmosphere (100 mL/min) in platinum pans. The compositions and homogeneity of artificial marbles (AAM-RTM and AAM-VVC) were determined using 3 samples from different regions of the specimen.

2.6. Water Absorption, density and apparent porosity

The water absorption, density and apparent porosity from natural marble and artificial marble were determined by the ASTM C373-16 item 5.3 [16]. The soak time was modified to 3 h as suggested in Brazilian stand. Five cubic samples with lattices of approximately 25 mm in length were evaluated to each material.

2.7. Slab surface and microstructure of AAMs

The microstructure observation was performed using a JEOL JSM 6460 LV scanning electron microscope (SEM) operating at 20 kV on gold-plated samples. From the SEM images were observed 400 points and then evaluated existence of voids and cracks. The percentage of these defect detected were 37,8% (a) and 12,2% per m^2 (b) .

2.8. Young's modulus and ultimate strength

Three-point bending and compression tests were performed using the INSTRON 5582 Universal Testing Machine. Compression test specimens were based on the EN 14617-15 standard [17]. The cube lattices were approximately 25 mm in length.

For the produced artificial stone, three layers were glued together with polyester resin to reach the desired length. The load application speed was 0.5 mm/min until final failure was reached. Bending specimens were cut from plates with 70 × 20 × 10 mm loaded at the center and tested at 0.5 mm/min.

2.9. Dynamic mechanical behavior

Dynamic mechanical analysis was carried out using a Q 800 DMA TA Instruments and dual cantilever clamp. The specimens with 60 × 12 × 5 mm were heated at 3 °C/min operating at frequency 1 Hz from 20 to 175 °C. Specimen dimensions were 60 × 12 × 5 mm.

3. Results and discussion

3.1. Chemical and mineralogical composition of Polita marble waste

Polita marble slabs waste is predominantly composed of dolomite ($CaCO_3MgCO_3$) and diopside ($CaMgSi_2O_6$), as shown by the X-ray diffractogram in Fig. 1.

Karaca et al. [18] present a study in which dolomites ($MgO \geq 10\%wt$) and dolomitic marbles ($4\% \leq MgO < 10\%wt$) were shown to have higher mechanical resistance compared with calcitic marbles. The authors report a compressive S_{UT} approximately 118 MPa for dolomites with 20 and 13% MgO, while for calcitic marbles, the compressive S_{UT} is in the 22 to 58 MPa range. Moreover, less abrasion loss was observed for dolomites and dolomitic marbles, which is attributed to the higher hardness of dolomite (4 Mohs) compared to that of calcite (3 Mohs).