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CHARACTERIZATION OF CASTOR OIL POLYURETHANE COMPOSITES WITH GLASS POWDER WASTE FOR APPLICATION IN THERMAL INSULATIONS

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ABSTRACT

The production of PURM (rigid polyurethane foam from castor oil source) composites with glass powder (GP) waste is economical and renewable actions of fabrication of thermal insulating materials. Based on these aspects, the study aimed to characterize composites PURM with 5, 10, 20, 30, 40 and 50% of GP waste contents, by mass. It was observed the influence of the GP percentages in PURM matrix of the composites. The results of the characterizations of density, thermal conductivity, morphology by SEM and chemical microanalysis by EDS were introduced and discussed. In general, the structure of pure PURM showed the elongated, regular and large pores; while composites of PURM + GP presented the irregular, small and rounded pores with presence of deformed cells. By density analysis it was percept the proportional relationship between the thermal conductivity and the GP contents. However, thermal conductivities of the PURM-GP5 and PURM-GP10 composites indicated similarities with pure PURM. Therefore, the PURM composites can be used as thermal insulating material, including their environmental advantages, like reduction of raw material content, use of renewable source and of waste material.

KEYWORDS: PURM, GP, Composite, Thermal Conductivity, Insulating Material.

CARACTERIZAÇÃO DE COMPOSÍTOS DE POLIURETANO DE ÓLEO DE MAMONA COM PÓ DE VIDRO PARA APLICAÇÕES EM ISOLANTES TÉRMICOS

RESUMO

A produção de compósitos PURM (espuma rígida de poliuretano à base de óleo de mamona) com o resíduo do pó de vidro (GP) oriundo do processo de lapidação é uma ação econômica e renovável de fabricação de materiais isolantes térmicos. Com base nestes aspectos, o estudo teve como objetivo caracterizar os compósitos PURM com 5%, 10%, 20%, 30%, 40% e 50% em massa de GP, observando-se a influência destes porcentuais de GP na matriz dos compósitos PURM. Os resultados das caracterizações de massa específica, condutividade térmica, morfologia por MEV e microanálise química EDS foram apresentados e discutidos. De uma forma geral, a estrutura do PURM puro apresentou poros grandes, regulares e alongados, enquanto os compósitos de PURM + GP mostraram estruturas de poros irregulares, pequenos e arredondados com presença de células deformadas. A massa específica apresentou uma relação proporcional com a condutividade térmica e o percentual de GP destes compósitos de PURM. Entretanto, observaram-se semelhanças na condutividade térmica dos compósitos PURM-GP5 e PURM-GP10 e PURM puro. Portanto, estes compósitos podem ser aplicados como isolantes térmicos. Sendo assim, a aplicabilidade deste resíduo pode contribuir econômica e ambientalmente através redução proporcional do consumo de matéria-prima e do descarte de tais resíduos no meio ambiente.

PALAVRAS-CHAVE: PURM, GP, compósito, condutividade térmica, massa específica

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1 INTRODUCTION

The oil industry is one of the most polluting, in addition to being a non-renewable source of materials. Also, the natural degradation of their products is so slow. In addition to this problem, the disposal of garbage in landfills is another inconvenience that needs urgent solutions; since the increasing consumption of products promotes more garbage generation, as well as the need for more landfills for the deposit of this waste. The lapping and cutting processes of glass make considerable amount of glass powder, GP, and this waste is not recycled.

The rigid polyurethane foam derived from petroleum, PUR, is usually one of the most commercially used in the thermal insulation of several refrigeration systems. However, there is necessary to make products from renewable sources. PURM is rigid polyurethane foam made from vegetable source of castor oil. So, this material presents an environmental advantage in relation to the petroleum PUR foams.

As long as there is similarity between properties of PURM composites and pure PURM, these news composites can be apply like alternative thermal insulations. Obtain and characterization of PURM composites with GP can be a technical environmental solution to substitute the materials from non-renewable sources and also to reduce the amount of no discarded materials through its use. Therefore, present work aimed to obtain and to characterize the PURM + GP composites and to compare their thermophysical, morphological and chemical properties with of the pure PURM.

2 LITERATURE REVIEW

The PU foam is a thermoset material and its structure is composed of expanded closed cell (Mano & Mendes, 1999). According to Oertel (1985), this material has a low density (20 kg/m^3 at 30 kg/m^3). Motta (2011) explained that due to density and structure of PUR foam, its disposal is problematic, as the foam occupies a large volume. Because these characteristics, the polyurethane foam wastes are very difficult to decomposition in the natural conditions. Based to Review of Harini (2018), the natural degradation PU foams can appear after 20 at 30 years. However, the full degradation of PU foam can has a long decomposition time (about 150 years), like was referred by FISCHER (2002).

Based on study of Alves (2005), the polymerization of the rigid foam of polyurethane castor oil PURM occurs by the reaction of organic isocyanate resin (Reagent A) with polyol (Reagent B). The PURM is biodegradable by making it traditionally used a green alternative polymers (Cangemi, Santos & Claro Neto, 2010). According to Santos (2009), glass is the material that has the highest chemical stability and can bind chemically with any element from the periodic table. By studies of Galvão *et al.* (2013), the SiO_2 and CaO oxides are responsible, respectively, for the formation of the glass network and chemical stability, in addition to the white color.

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Thermal insulation is characterized by the low thermal conductivity values. Most of these materials has a porous structure and has small cavities with one type of low thermal conductivity gas confined in closed cells (Mendes, 2002). Martins & Pinto (2004) characterized the glass as a thermal insulating, whose thermal conductivity is between 0.72 and 0.86 W/m-K.

Thirumal *et al.* (2007) performed studies of the precipitates contents effects of SiO_2, CaC and GP added to PUR. The properties were compared to those of pure PUR. The specific weight was reduced with the addition of SiO_2, the same applies to the addition of $CaCO_3$ and GP, however, after a certain concentration, the density increased. Furthermore, they found that the reduction in isolation with increasing SiO_2 and $CaCO_3$ content was mainly due to the formation of structure of open and damaged cell; however, when the GP was used, the thermal conductivity decreases but afterward increases with the increase of its content of GP.

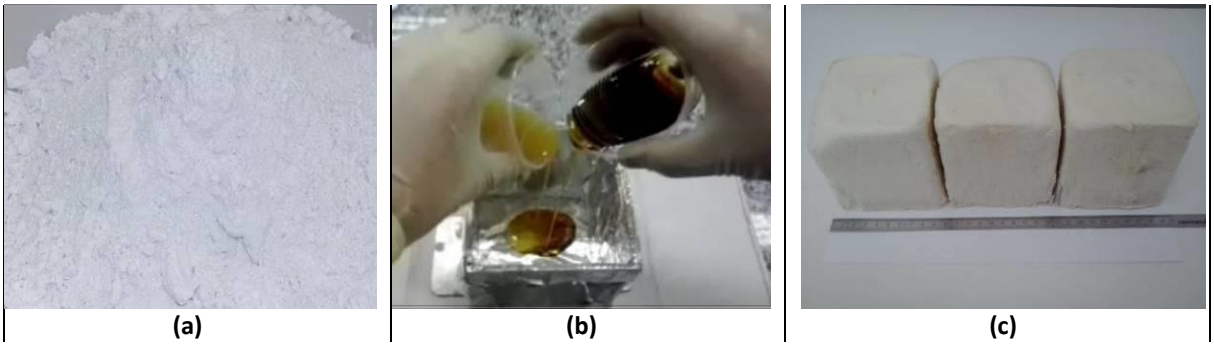
3 MATERIALS AND METHODS

The production of PURM and PURM + GP composites and the characterization methods adopted in this work are presented below.

3.1 Obtaining of the Composite of PURM + GP

The glass powder, Fig. 1a, obtained from the reject refining (grinding with mortar and pestle, grinding with a ball mill and mechanical sieving) to reduce the particle size had a mean diameter of 33 microns. From the mixture of the polymeric components A and B (Fig. 1b) in the proportions 1: 1.6 respectively, it was possible to obtain pure samples of PURM and their composites (Fig 1c.) with mass percentage of GP (5, 10, 20, 30, 40 and 50).

The main steps for obtaining the composites were: dried in an oven; weighing and adding the glass powder and the components A and B as stainless steel mold (1000 cm^3); stirring the mixture with a stirrer, foam expansion reaction and mold release of the bodies of the test piece after healing 20 minutes.



(a) (b) (c)

Figure 1: Manufacturing steps of composite PURM + GP: (a) particles of GP, (b) mixing the components A and B into the mold and (c) demolded test piece bodies.

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3.2 Determination of density and thermal conductivity

The density of the specimens used for test of pure PURM and PURM + GP was measured according to ABNT 11506, using a digital hydrometer DSL910 model of Gehaka, available in Fluid Mechanics Laboratory - NTI / UFRN. Its measurement was performed by weighing the bodies of the test piece of dry weight and wet weight (immersed in water).

KD2-Pro was used to perform the measurement of the thermal conductivity of the composites, which is available at LMF - NTI / UFRN. This equipment contains a SH-1 sensor (double thermal needles), which is inserted into the material, whose result is achieved after 2 minutes with temperature reading of 26 ± 1 °C and relative humidity of 32 ± 1%. Nine measurements were made on each surface, resulting in 54 measurements for each sample.

3.3 Morphological and chemistry characterization

The morphological and chemical analyzes of PURE and composites PURM + GP were performed through Scanning Electron Microscopy - SEM (Hitachi TM300) and Energy Dispersive Spectroscopy - EDS (Hitachi SwiftED 3000), available at the Materials Engineering Laboratory - DEMat / UFRN.

4 RESULTS AND DISCUSSION

The results of the characterization of PURM and PURM + GP composites are presented in terms of density, thermal conductivity, SEM and chemical microanalysis by EDS.

4.1 Density and Thermal Conductivity

In Fig. 2 graphs of density (kg/m^3 Fig. 2a) and thermal conductivity (W/m-K, Fig. 2b) of PURM + GP composites and pure PURM with the reference standard are shown. Due to the standardization of the sample size (1000 cm^3), it was necessary to decrease the amount of the components A and B (PURM formers) and increasing the amount of GP. With this, it was found that the bulk density increased with the addition of GP mass in composites, with the exception of PURM-GP5 and PURM-GP10, which had specific weight lower than that of pure PURM. Galvão et al. [8] reported that there is a proportional relationship of percentage of GP in the PUR matrix (derived from oil) with the specific weight of composite PUR + GP.

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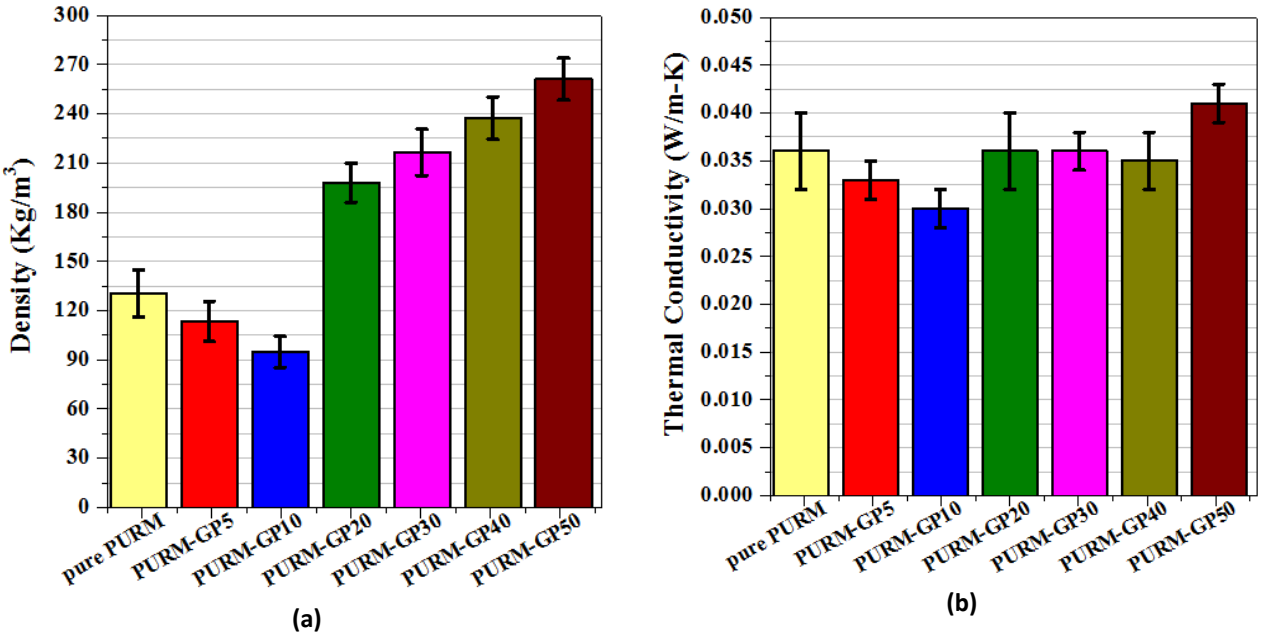

Figure 2: Graphs of (a) density and (b) thermal conductivity.

The values of thermal conductivity (W/m-K) of PURM + GP composites were compared with those of pure PURM and density. According to Borges (2009), materials with low density have low thermal conductivity; this is a key feature for a good thermal insulator. It could be perceived by the graphs of density (Fig. 2a) and thermal conductivity (Fig. 2b) that these magnitudes are correlated. It should be considered that the end of a foam thermal conductivity (k factor) is determined on the basis of contributions due to: convection, radiation, thermal conductivity of gas and polymer, and foam density.

However, it is noticed that 20% to 50% of contents in weight of GP, the conductivity has not kept a clear proportionality in relation to density, Fig. 2. Thirumal *et al*. (2007) found that the thermal conductivity of composite PUR + GP decreased in relation to pure PUR but then increased with higher percentages of the GP in matrix. This behavior was also observed in Fig. 2b. In the same study, Thirumal *et al.* (2007) also noticed an increase in thermal conductivity due to the increase of SiO_2 and $CaCO_3$ content, which resulted in the form of open and damaged cellular structure. Thus, it is also necessary to consider the influence of the size and number of pores in the foam PURM as well as the composition of GP and the location of the temperature sensors during the measurement.

4.2 Morphological characterization by SEM and chemical microanalysis by EDS

Figures 3 to 7 present microscopic and chemical analyzes of pure PURM and PURM + GP composite masses in percentages of 5, 10, 20, 30, 40 and 50%. The SEM and EDS of pure PURM were

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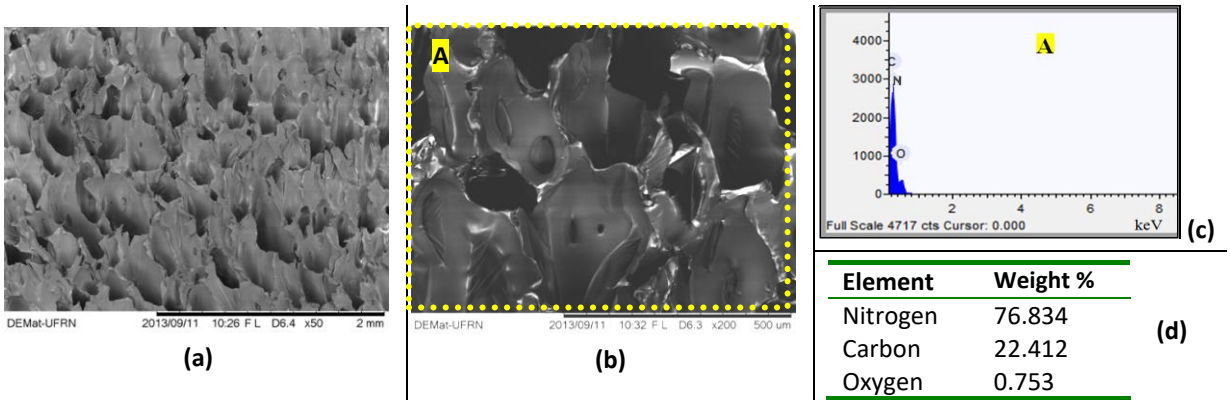
used as reference to evaluate the effects of adding GP composites. One particular area of pure PURM (Fig. 3) and points on the pure load micrographs of the composite PURM with GP (Figs. 5, 6 and 7) were identified for investigation using semi-quantitative EDS elemental chemical microanalysis.

In Fig. 3 (a) and (b) is observed that the cell structure of pure PURM presents formation of elongated cells (elliptic) with a regular pore size. The presence of the chemical elements C, N and O in the analysis by EDS characterizes the pure PURM matrix, Fig. 3 (c and d).



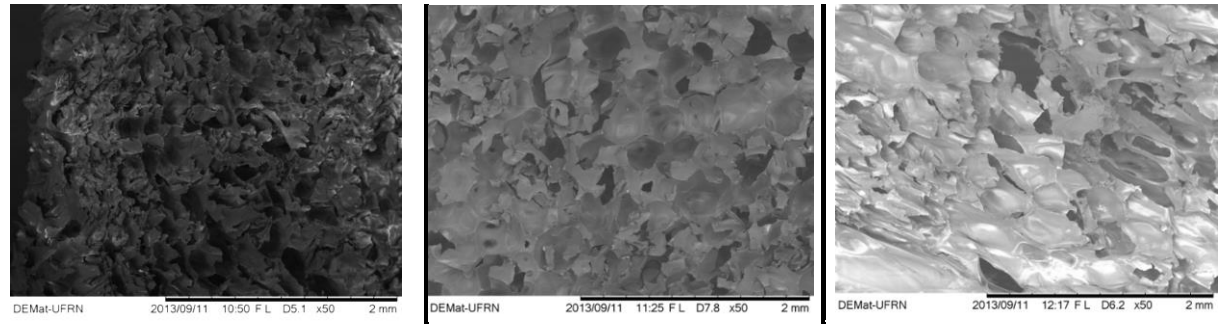
(a) (b) (c)

Element	Weight %
Nitrogen	76.834
Carbon	22.412
Oxygen	0.753

(d)

Figure 3: SEM and EDS of pure PURM: (a) 50x, (b) 200x, (c) spectrogram and (d) area A element percentages.

Fig. 4 shows different morphologies obtained for each composite. Note that, as the percentage of GP increases dispersed in the PURM matrix, there is a greater decrease agglomeration of pores, thickness of the structure and pore size and destruction of some structures but with a greater irregularity. This was probably due to barriers caused by expansion GP, requiring a change in flow of foam growth modifying its cell structure. These irregularities were more intense for the microstructures of PURM + GP50 composite.



(a) PURM-GP5 **(b) PURM-GP10** **(c) PURM-GP20**

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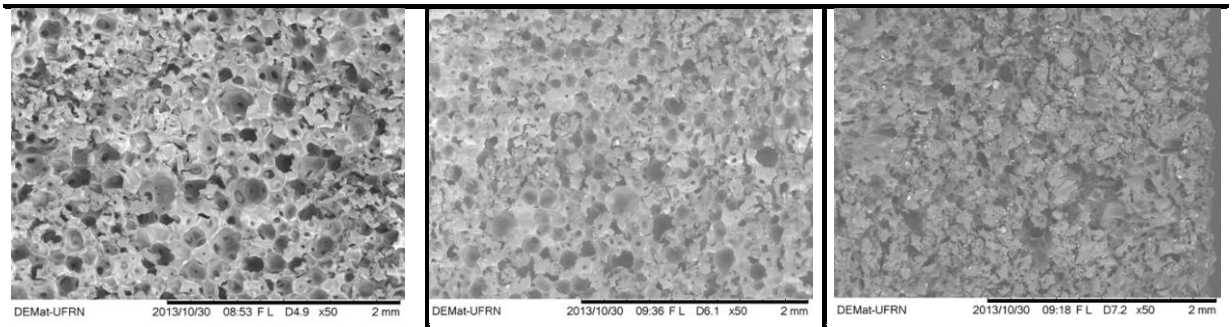
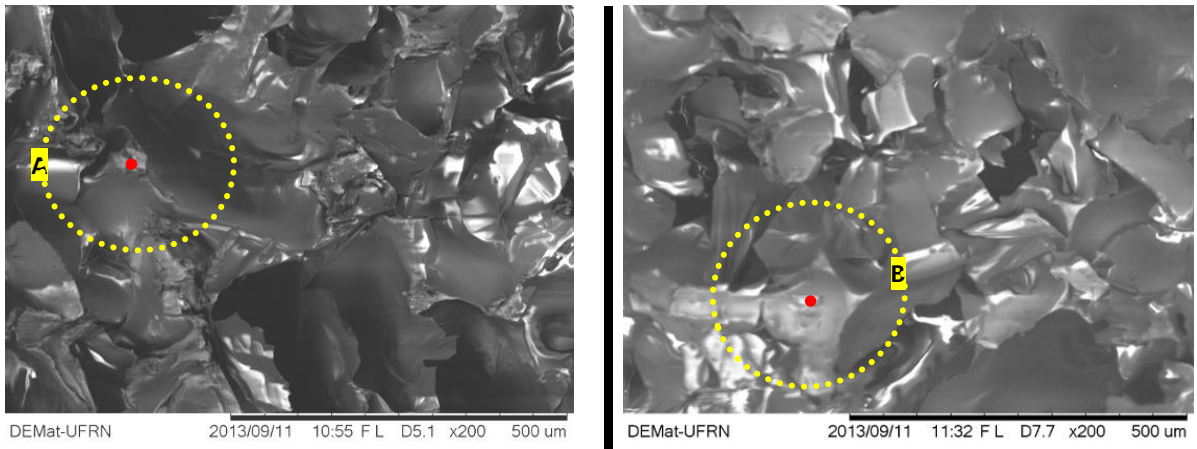
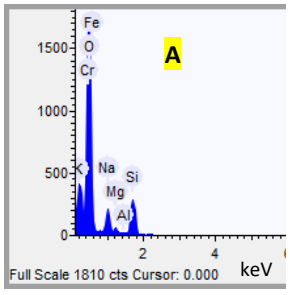


(d) PURM-GP30 (e) PURM-GP40 (f) PURM-GP50

Figure 4: SEM of the surface of composites PURM + GP, magnification of 50x.

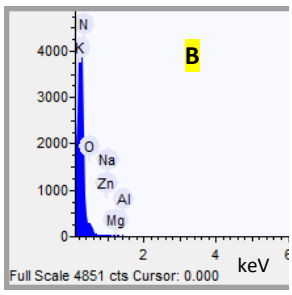


(a) PURM-GP5 (b) PURM-GP10



Element	Weight %
Sodium	44.005
Oxygen	40.725
Silicon	10.844
Chrome	1.448
Iron	1.592
Magnesium	0.942
Aluminium	0,243
Calcium	0.202

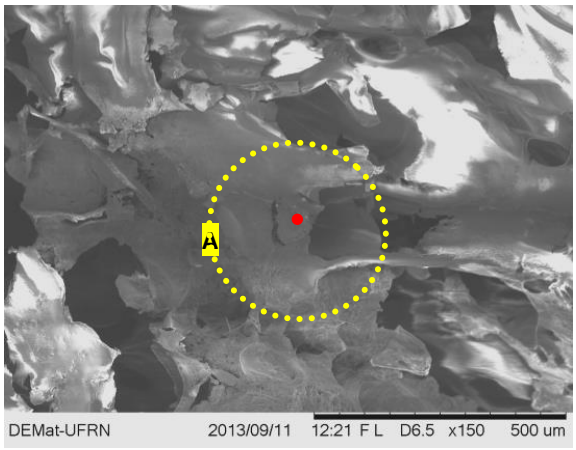
(c) PURM-GP5



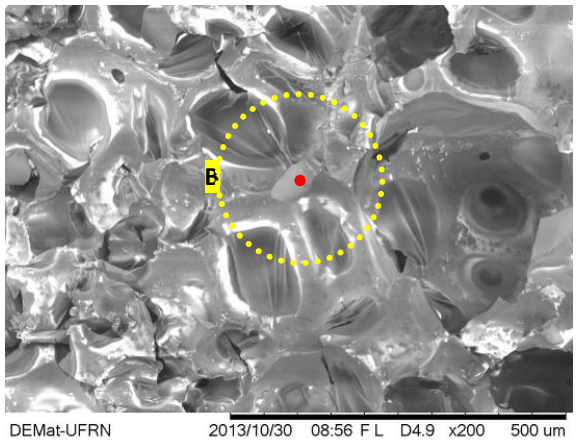
Element	Weight %
Oxygen	51.289
Nitrogen	39.238
Silicon	3.543
Zinc	2.153
Magnesium	1.516
Aluminium	1.369
Calcium	0.500
Sodium	0.392

(d) PURM-GP10

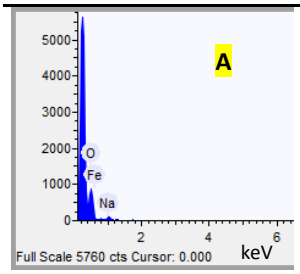
Figure 5: SEM with 200x magnitude of the composite (a) PURM-GP5 and (b) PURM-GP10 with identifying of the points contained in (c) A and (d) B by EDS.



(a) PURM-GP20

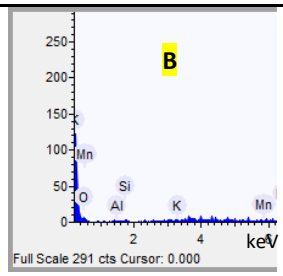


(b) PURM-GP30



Element	Weight%
Oxygen	81.209
Iron	11.167
Sodium	5.641
Silicon	1.657
Calcium	0.326

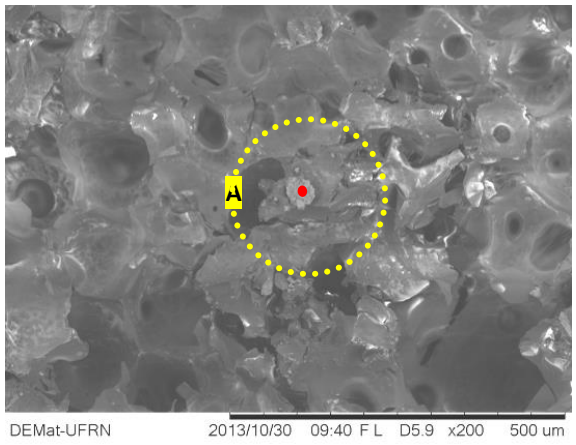
(c) PURM-GP20



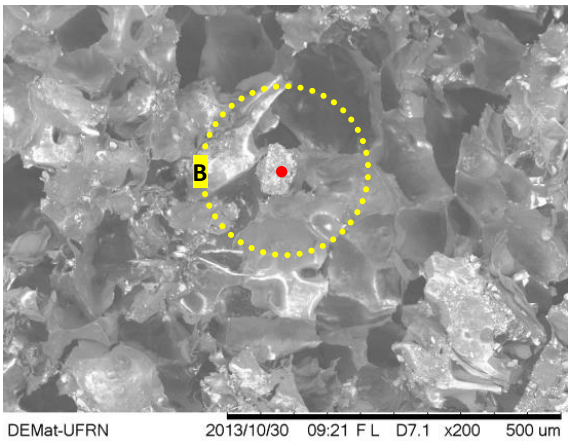
Element	Weight %
Oxygen	97.825
Manganese	0.686
Silicon	0.638
Calcium	0.624
Aluminium	0.226

(d) PURM-GP30

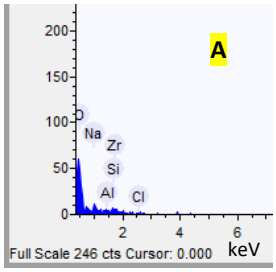
Figure 6: SEM with 200x magnitude of the composite (a) PURM-GP20 and (b) PURM-GP30 with identifying of the points contained in (c) A and (d) B by EDS.



(a) PURM-GP40

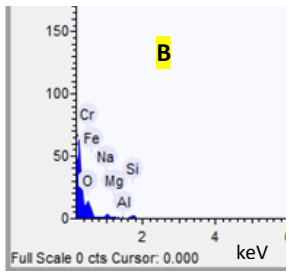


(b) PURM-GP50



Element	Weight %
Oxygen	50.720
Sodium	11.911
Silicon	16.666
Zirconium	9.193
Calcium	7.995
Aluminium	3.514

(c) PURM-GP40



Element	Weight %
Oxygen	60.035
Calcium	10.355
Iron	8.287
Silicon	6.289
Sodium	4.049
Aluminium	0.790
Magnesium	0.194

(d) PURM-GP50

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Figure 7: SEM with 200x magnitude of the composite (a) PURM-GP40 and (b) PURM-GP50 with identifying of the points contained in (c) A and (d) B by EDS.

Figures 5, 6 and 7 show surfaces of the composite PURM + GP at magnification of 200x, except PURM-GP20 (150x), where the elemental compositions are indicated by the spectrogram with the respective mass percentages of the selected points. So, were noticed intensities of the peaks corresponding to the elements that make up the GP (Si, O, Na, Ca).

In the Figures 3 to 7, observed the different types of interactions of GP particles with the cell structure of PURM in relation with the increase in the percentage of these mass and contributed to destroy the organized formation of the porous structure of the PURM foam.

All of this directly influences in the thermal conductivity, thus reducing the insulating capacity of PURM + GP composites in relation to PURM. It is observed that higher density contributed to increase the thermal conductivity of the composites to relation to PURM.

5 CONCLUSIONS

The work dealt with the obtaining and characterization of PURM composites with incorporation of GP from waste glass from lapping. Aiming their use as a cheap and environmentally friendly insulating material, thermo-physical, chemical and morphological characterizations were performed to compare these composites with pure PURM. The results are as follows:

The density and thermal conductivity showed proportional relation to each other as well as being directly proportional to the content of the GP in composites of PURM, except for composite containing 5 and 10% GP, which had the lowest specific gravity. It was also seen that the conductivity is equal and/or less than pure PURM and therefore suitable for the purpose.

The pure PURM contained in its structure large, regular and uniform elliptical pores, whereas in the composite, increasing the content of the GP in PURM matrix promoted decrease in the pores, causing collapse of the structure, as seen in PURM-GP50. EDS analysis confirmed the basic characteristics of the constituent particles of GP.

Microanalysis by EDS showed the increase in the amount of elements identified with the content of the GP added in the PURM. EDS also showed that in up to 30% of the GP there is an increase in oxygen content that can be associated at the oxides characteristic of this powder.

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