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# Reaction of Activated Geopolymers in Acid Medium and Application of Polyaniline as a Conductor of Electricity

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**Abstract:** In 1972, the French chemist Joseph Davidovits named a new class of inorganic polymers, the geopolymers. This was due to his search for flame-resistant materials that were harmless to the environment and human health. These materials were produced by reacting aluminosilicates in alkaline solution. However, over time, it was discovered that it was possible to produce the same material via an acidic route, using phosphoric acid. In this sense, this work aimed the production of geopolymers in acid medium and the insertion of 10%, 25% and 50% of conductive charge to produce a geopolymer capable of conducting electric charge. To verify the conductive capacity of the material, the resistivity test, and Thermogravimetric Analysis (TGA) were performed to investigate the loss of mass as a function of temperature. The tests were performed in triplicates and the data obtained were analyzed by ANOVA and Tukey method and the results showed that the values were different from each other, indicating the domination of resistivity with increasing polyaniline concentration.

**Keywords:** Geopolymers, acid route, polyaniline, metakaolin, conductivity, phosphoric acid.

**Adherence to the BJEDIS' scope:** The article presented here has relevant results regarding the use and application of ANOVA statistical analysis and Tukey's method, which made it possible to identify the differences between each composite in conducting electricity. These showed that they are statistically different from each other.

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## 1. INTRODUÇÃO

Conductive polymers were discovered in 1976 and are defined as materials that can conduct electrical energy. They are, in general, easy to produce and have a high percolation threshold, and it is necessary to modify some structural properties to obtain a stable material for the desired application. Currently the best-known conductive polymers are: polyacetylene, polypyrrole, polythiophene, poly(p-phenylene), poly (p-phenylene vinylene), and polyaniline (1).

Polyaniline is a polymer that has gained prominence due to its ease of production, low cost, higher electrical conductivity than some known metals, good chemical, and environmental stability. It is obtained from the activation of aniline in acid medium (2). Its industrial application is wide and can be used in molecular sensors, rechargeable batteries, transistors, electrochromic windows, shielding for electromagnetic interference, optical devices, light emitting diodes, among others. With its wide range of applications, polyaniline is widely used in composites, such as supercapacitors (3) and field effect transistors (4). Given the ability of polyaniline to be used to produce composites, this enables its insertion in different matrices.

A new class of polymeric materials of inorganic origin appeared in 1976, those discovered by the French chemist Joseph Davidovits, who named them geopolymers. According to Davidovits, geopolymers are defined as inorganic polymers obtained from aluminosilicates (metakaolin, fly ash, glass powder, red mud, among others) (5) with the addition of an alkaline solution (usually sodium or potassium) or acid (usually hydrochloric, sulfuric, or phosphoric acid). Its applications are varied, and can be in the manufacture of bricks, ceramics, encapsulation for protection against toxic and radioactive waste, fire-resistant composites, sealants for industry, fire protection (with or without the addition of fiber composites), cement and concrete with low $CO_2$ emissions, and tools for aeronautics (6). Liu and co-workers compare the use of phosphoric acid-based and alkaline solution-based geopolymers. The authors identified that, alkaline solution geopolymers show lower compressive strength due to the ability of the alkaline solution to dissolve the aluminosilicates of the raw material. While geopolymers activated by phosphoric acid provide the balancing of the positive charges of the acid with the negative charges of the aluminosilicates, which allows neutrality and facilitates the chemical reaction (7).

Therefore, the geopolymers can be used as a matrix to insert fillers that can ensure good properties. For example, some geopolimeric composites were produced with the main objective to increase durability, using $TiO_2$ and Epoxy resin (8). Others were produced to increase the strength using hybrid fibers (9). But there is the production more sophisticated using geopolymers, such as Lithium-ions composites to used lithium-ions batteries, modification of polyimide fiber with carbon nanotubes to increase mechanical enhancement (10).

Using research in Google Scholar to find papers about the use of geopolymer applications, in the period 2018 at 2021, were found 5.420 papers about geopolymer resistance at the fire and increase of mechanical properties, but only 908 papers were of geopolymer produced with phosphoric acid and 395 were papers of the geopolymer conductor. This research showed there are few studies on the theme of conductive geopolymer and this opens the door for further research on the conductive property of geopolymers. many possibilities to use the geopolymer as a polymeric conductor (11–13).

Therefore, the objective of the work is the geopolymerization in acid medium and addiction of polyaniline to observe the capacity of electrical conductivity. In addition, verify by means of calculations using ANOVA and Tukey if the results are statistically relevant, to understand the influence of the filler on the geopolymer matrix.

## 2. MATERIALS AND METHOD

### 2.1. Production of the geopolymeric composites

To production the geopolimeric composites were prepared a solution at 6 M using phosphoric acid and with the aid of a mechanical stirrer was left stirring at 300 rpm for 5 minutes. From this solution 1 ml was collected and reserved, to be used to dissolve the ammonium persulfate for polyaniline production.

The preparation of the polyaniline in-situ was carried out as follows: on the acid solutions was inserted 4 g of metakaolin and performed the mechanical stirring at 300 rpm for 10 minutes, after this time, was added 0,256 ml of aniline and it was left stirring at 300 rpm until the aniline dissolved completely. Meanwhile on the 1 ml of acid solution collected was dissolved 1,28 g of ammonium persulfate and added a reaction with metakaolin and aniline. After addition was possible observed the color change of reaction. This methodology was used to produce geopolymers with 10% of polyaniline.

To produced composites with 25% and 50% was performed the previous methodology but using 0,640 ml of aniline and 3,20 g of ammonium persulfate, 1,28 ml of aniline and 3,20 g of ammonium persulfate, respectively. After all the productions, the samples were placed in an oven at 80°C for the curing process to take place.

### 2.2. Characterizations

#### 2.2.1. Thermogravimetric Analysis

The samples were analyzed by thermogravimetry using Perkin Elmer equipment with nitrogen atmosphere. Heating from 30°C to 200°C and heating rate of 20°C.min$^{-1}$.

#### 2.2.2. Resistance Analysis

Resistance analysis was measured, using a Keithley 6517B electrometer with a current of 20 mA and 100 volts. The average diameter was equal to 0.3 mm (14). The data were obtained after an electrification sweep of 120 s. The tests were carried out in triplicate.

#### 2.2.3. Resistivity

Resistivity was measured using the formula already described in the literature [11].

$$\rho = \frac{(R * \pi * r)^2}{e} \qquad (1)$$

Where:

ρ = resistivity (Ω.cm$^{-1}$)

R= resistance (Ω)

r= radius (cm)

e= sample thickness (cm)

### 2.3 Statistical Analysis

The average values of the variables obtained in the treatments were compared using Tukey's test at 5% probability using the Sigma Plot 12.5 program (15, 16)

## 3. RESULTS AND DISCUSSION

The images of the composites produced were registered by camera of smartphone and edited using the PhotoScape program, of the geopolymers without filler and polyaniline. The samples showed the color change after the addition of polyaniline. The samples were showed in Figure 1.

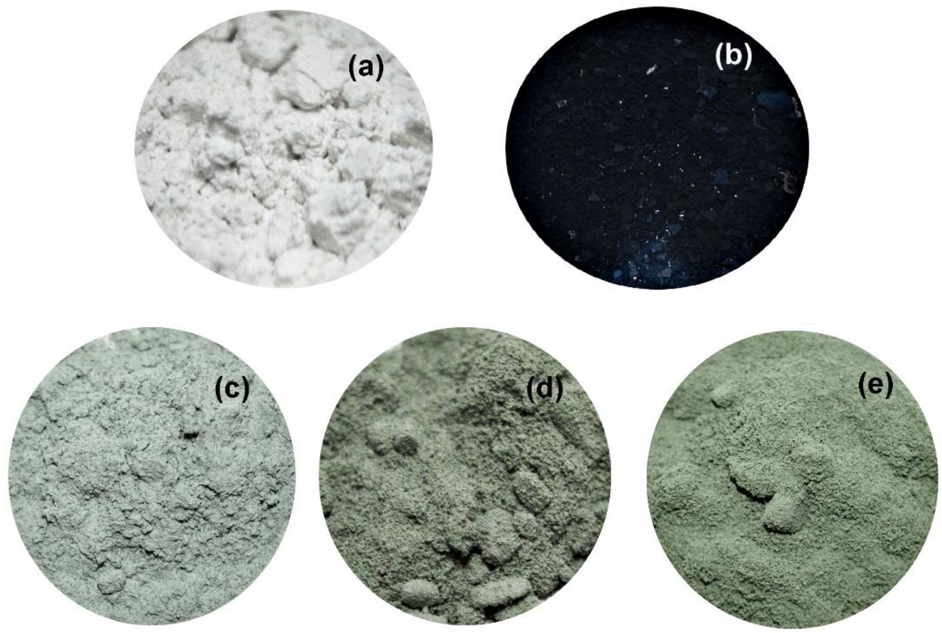


**Figure 1.** Geopolymer synthesized from 6 M phosphoric acid solution (a), polyaniline activated with 1 M phosphoric acid (b), and composites with 10% (c), 25% (d), and 50% (d) of polyaniline.

The samples were previously analyzed by thermogravimetric analysis, with the objective of identifying the loss of material mass as a function of temperature, as shown in Figure 2. In this case, degradation temperatures of the hydroxyls present in the materials are observed. Thus, it was possible to identify the evaporation of free water in the geopolymer (GeoB) at 113°C and for the composites it was observed the decrease of water evaporation temperature at 82°C, this can be attributed to endothermic events in which, the composites are absorbing heat and thus, performing the evaporation process. In this sense, increasing the amount of polyaniline in the matrix decreases the amount of water available in the reaction medium. Because an in situ polymerization is performed, the amount of reactants gradually increases, and the available water participates in the reaction (9).

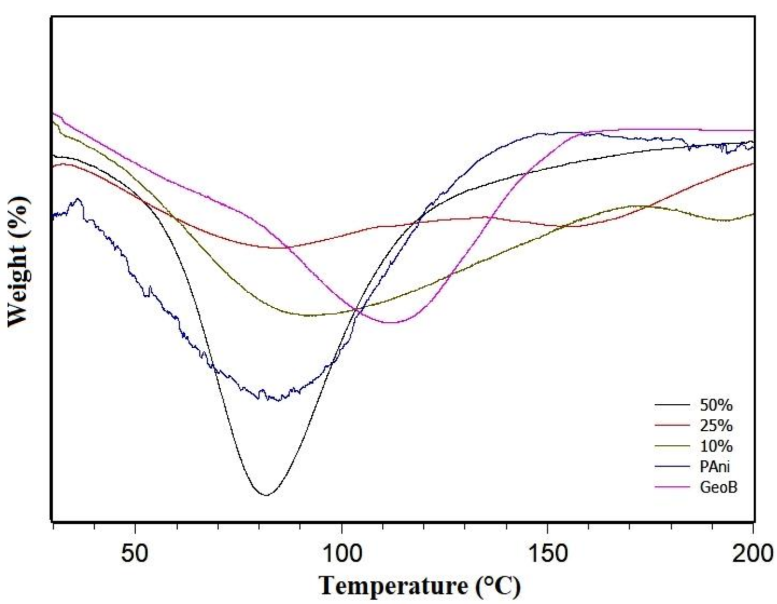


**Figure 2.** Thermogravimetric Analyses of the samples.

The samples obtained were submitted to Resistivity analysis, to evaluate the influence of the amount of Polyaniline on the electrical resistance of the material.

In general, geopolymers are resistive materials, as shown in Figure 3 (a). But because they can receive conductive charges, they can have this resistivity decreased. In the case presented here, the decrease in resistivity with increasing polyaniline concentration in the geopolymer matrix is noticeable. This happens because polyaniline is a conducting polymer, but its resistivity is increased due to its activation in phosphoric acid, an acid considered weak that allows the conversion into the salt base is partial, being the resistivity $8.55x10^6 \pm 3.70x10^5$ (17). When compared to the literature, the geopolymers presented here have high resistivity. Geopolymeric composites produced with graphene oxide, which are the most widely used, have a resistivity of $1.5x10^3$ (18). However, graphene oxide is a charge that is considered difficult to produce, due to the complexity of the chemical reaction and the parameters involved(19). While polyaniline is a polymer that is easy to obtain and low cost (20). These results are encouraging, since it allows observing the influence of polyaniline in decreasing the resistivity of geopolymers, opening room for modifications that allow a greater decrease in resistivity.

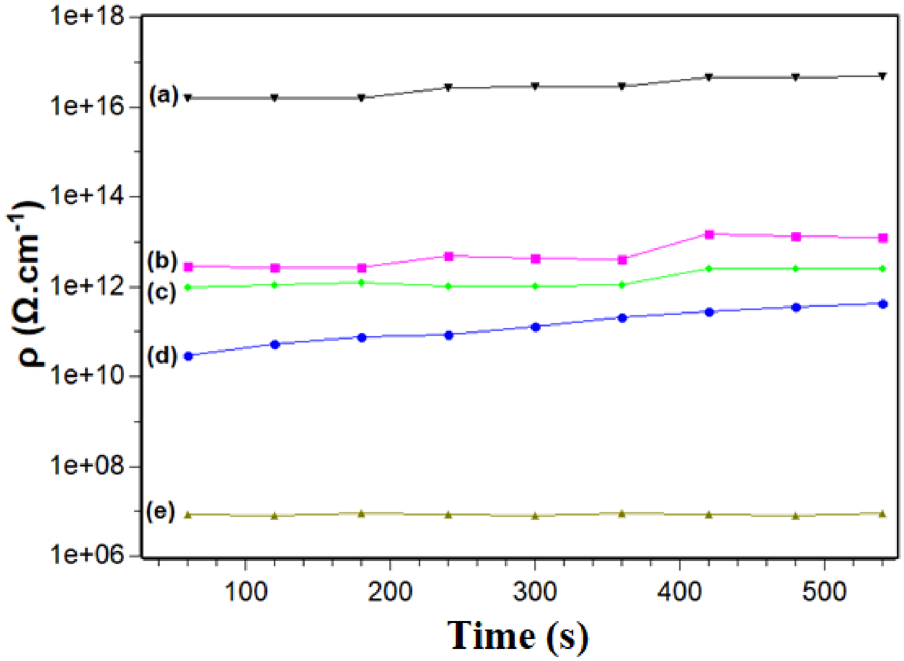


**Figure 3**. Resistivity of geopolymer and composites loaded with Polyaniline in situ (a) geopolymer; (b) 10% PAni; (c) 25% PAni; (d) 50% PAni and (e) PAni.

Table 1 shows the decrease in resistivity as a function of the amount of charge in the matrix, and the variations in resistivity and the confidence limit proved that the samples are different from each other, as well as the ability to conduct electricity. The results obtained to ANOVA and Tukey's method prove that the samples were different with the values at probability 5% (15, 16).

**Table 1.** Resistivity values of the geopolymer and the composites.

| **Samples** | **ρ (Ω.cm-1)**<br>**average values** |
|---|---|
| GeoB | $2,97x10^{16} \pm 1,01x10^{16}$ **a** |
| PAni | $8,55x10^{6} \pm 3,70x10^{5}$ **b** |
| 10% | $1,54x10^{12} \pm 5,46x10^{11}$ **c** |
| 25% | $6,83x10^{12} \pm 3,89x10^{12}$ **d** |
| 50% | $1,8x10^{11} \pm 1,08x10^{11}$ **e** |

## 4. CONCLUSION

From the results obtained it was possible to conclude that, the production of the geopolymers and the composites were accomplished. The Thermogravimetric Analysis showed that the presence of polyaniline in the matrix influenced the evaporation temperature of free hydroxyls, which showed its presence in the matrix. The resistivity analysis proved the effect of polyaniline in decreasing the resistivity of the material, due to its conductive characteristic. This work presented a high potential, because it was possible to identify a material capable of conducting electrical energy, but there is still the need for some adjustments, so that they are able to generate enough electrical energy in order to be used as a model of renewable energy.

## LIST OF ABBREVIATIONS

PAni: Polyaniline

TGA: Thermogravimetric Analysis

P.A.: For Analysis

Geo: Geopolymer

GeoB: Geopolymer used as blank in sample.

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### *Sample CRediT author statement*

**Fabíola da Silveira Maranhão:** Conceptualization, Methodology, Data analysis, and Writing-Original draft preparation. **Fernando G. de Souza Junior:** Conceptualization, Supervision, Reviewing and Editing. **Nathália da Silva do Carmo dos Santos:** Data analyses and Reviewing, **Cintia Patrícia Santos da Paixão:** Reviewing, **Sérgio Thode Filho:** Conceptualization, Supervision, Reviewing and Editing, **Diganta B. Das:** Reviewing, Editing and Validation.

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