Incorporation of unserviceable tire waste in red ceramic

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A spent tire without the legal possibility of running is classified as unserviceable tire waste. In this work, incorporation of rubber tire waste (RTW) in clay ceramics used in the production of bricks and roofing tiles was for the first time evaluated. The raw materials were initially characterized in terms of its mineralogical and chemical composition by X-ray diffraction (XRD) and X-ray fluorescence (XRF), respectively. Physical and mechanical properties of RTW incorporated ceramics such as bulk density, water absorption, linear shrinkage, flexural and compressive strength were determined. Besides, thermal analyses by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out in the plain RTW. Different ceramic compositions were prepared with amounts of 0.5; 1; 1.5 and 2 wt% RTW incorporated into the clay ceramic. Prismatic specimens were prepared by uniaxial pressing and then sintered at 850 and 950 °C. The results indicate that the investigated waste contributes to a saving in energy during the ceramic sintering due to its high amount of carbon. An increase in the ceramic porosity above 1.5 wt% of RTW was responsible for increasing the water absorption. Within standard deviations, both the shrinkage and strength were not impaired. The clay ceramic with 1 wt% of RTW sintered at 950 °C was the most suitable condition observed. Hence, these results showed a viable alternative to RTW, turning it into an environmentally friendly by-product for civil construction materials.

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1. Introduction

The steady population growth is currently associated with a considerable increase in the consumption of industrialized products. Most of these products are designed to have short lifetimes and then might often be inadequately disposed. A well-known example is that of unserviceable tires, which
is becoming a global problem, as their growth of disposal is steady increasing [1]. Unservicable tires are considered non-biodegradable with indeterminate decomposition time. According to the Brazilian Institute of the Environment and Renewable Natural Resources (IBAMA), in 2016 the number of unserviceable tires disposed in Brazil was close to 500 thousand tonnes [2]. This is a worrisome fact since such value tends to increase exponentially. Moreover, improper solid wastes disposal in the environment, like unserviceable tires, increases the pollution of soil and contributes to public health problems. In particular, unserviceable tires disposal also causes the proliferation of insects and diseases due to the accumulation of water inside the tire curved shape [3,4].

Several studies have investigated the incorporation of industrial wastes in clay ceramics for civil construction such as structural blocks and red bricks [5–11]. The ceramic industry has the great advantage of a high volume production, which enables consumption of large quantities of waste. Indeed, the world production of ceramic bricks is over 1 trillion units and counting [11]. The volume of consumption combined with the physical and chemical characteristics of ceramic raw materials and the peculiarities of the ceramic processing make the ceramic industrial sector one of the most important options for recycling solid wastes [9–13]. In a recent review article, Al-Fakhri et al [14] mentioned several kinds of waste materials used to produce masonry bricks. The authors classified the studies on two methods: burnt and unburnt bricks. Although the last method does not require sintering temperature to produce bricks, i.e., does not have the shortcoming of high-energy consumption, in general, the high amount of waste material incorporated results in low compressive strength. However, it is noteworthy that it is possible to use some waste materials in brick manufacturing as a sustainable alternative without impairing significantly the properties of the brick [14]. Indeed, the incorporation of industrial waste in ceramic matrices has relevant advantages, such as saving of non-renewable raw materials, development of environmentally friendly products and reduction in energy consumption. In particular, the incorporation of unserviceable tire waste in products for civil construction has been investigated [1,15]. It was found that the incorporation of rubber tire waste (RTW) contributes significantly to the industrial process and to preserve the environment. In addition, the high calorific value around 9200 kcal/kg of the rubber enables significant energy savings during the sintering process [13]. On the other hand, materials with high amounts of carbonaceous and/or organic substances, such as hydrocarbon-based rubber, tend to increase the ceramic porosity after sintering. Therefore, the incorporation of small amounts is recommended [13–15]. Mohammed et al [3] investigated geopolymer interlocking brick incorporating crumb rubber in unfired brick. The results indicated that is possible to use this as non-load bearing material since the average compressive strength was 3.98 MPa. The author also recommended the adding of nano-silica to enhance the brick [3]. Even though wastes such as RTW and incorporated products for civil construction might not be classified as advanced materials, their modern processing requires special physical and chemical techniques in order to obtain the best possible properties. General example of modern physical and chemical preparation procedures to develop advanced materials may be found in the works [16–24] of the research group of M. Salavat-Niasari, involving sonochemical synthesis, photocatalysis and grafting of nanoparticles in nanodimensional microreactors.

The novelty aim of the present work was to incorporate RTW in clay ceramics sintered at 850 and 950 °C. The influence of weight fraction, up to 2%, of incorporated RTW in the physical and mechanical properties of clay ceramic was evaluated using updated diffraction tecniques and electron microscopy techniques.

2. Experimental procedure

The materials used in this investigation were a clay body and a rubber tire waste (RTW). The clay body, a mix of kaolinitic weak and strong clays [25], is used to produce roof tile and bricks in the city of Campos dos Goytacazes, Brazil. The RTW from the retreading process was provided in powder form by the IDEA Clinic Institute, located in the city of Magé, Brazil. The clay ceramic was milled and dried at 110 °C in an air oven for 24 h. Then, it was sieved to 20 mesh size (840 μm) for the preparation of different ceramic compositions. The RTW was used in its as-received condition. Chemical composition and microstructure of the raw materials were evaluated by scanning electron microscopy (SEM), optical microscopy (OM), X-ray diffraction (XRD) and X-ray fluorescence (XRF). The XRD analysis was carried out in a Shimadzu XRD 7000 diffractometer using CuKα radiation with 2θ range from 5° to 100°. The XRF was conducted in a Shimadzu EDX 700 model and loss of ignition of the raw materials was calculated according to Eq. 1.

\[
\text{LOI} = \frac{M_d - M_r}{M_d} \times 100
\]

where LOI is the loss on ignition (%), \(M_d\) is the dry sample mass at 110 °C (g), and \(M_r\) is the calcined sample mass at 1000 °C for 1 h (g).

In addition, the thermal behavior of RTW was characterized by differential scanning calorimetry (DSC) and thermogravimetric (TG/DTG) analyses. These analyses were simultaneously carried out in a model SDT 2960 TA Instrument operating under an argon atmosphere (100 mL/min) and a heating rate of 10 °C/min up to 1,100 °C.

The particle size distribution for both materials was evaluated by sieving and sedimentation methods according to the Brazilian standard [26]. These procedures consist of classifying the particle size that is retained in the coarse sieve (up to 20 mesh), and fine sieve (20, 40, 60, 100–200 mesh). The sedimentation technique was performed by dispersing 70 g of the sample in 125 mL of water with the addition of 5.71 g of sodium hexametaphosphate buffered and 1 g of sodium carbonate to disaggregate the particles. The solution is stirred for 15 min and placed in test tubes. The equivalent spherical diameter of the sample particles was calculated by Stokes law, where the sedimentation rate depends on the particle size and fluid viscosity.

Five ceramic compositions (0, 0.5, 1, 1.5 and 2 wt% of RTW), all with 8% of moisture, were prepared and identified as shown.
in Table 1. The clay ceramic was oven-dried at 110 °C and disaggregated in a ball mill, as well as the rubber powder, both sieved to 40 mesh size (0.425 mm).

Pristic specimens with dimensions of 114.0 × 25.0 × 11.0 mm were prepared by uniaxial pressing under pressure of 20 MPa and then dried in an air oven to a constant weight at 110 °C.

These samples were sintering at 850 and 950 °C for 2 h with a heating rate of 2 °C/min. Physical properties, of bulk density, water absorption, and linear shrinkage were determined as per ASTM C373 standard [27]. The mechanical properties were determined by three-points bend test and compressive strength test. Both mechanical tests were conducted in a universal testing machine Instron 5582 under ASTM C674 [28] and ASTM C62 [29] standard, respectively. The cross-head speed of 0.1 mm/min was used in the mechanical tests. The fracture surface of the sintered samples was analyzed by scanning electron microscopy (SEM) in a model SS500-50 Shimadzu microscope.

3. Results and discussion

The chemical composition of the clay ceramic is shown in Table 2. In this table, it should be noticed the predominance of silica (SiO₂) and alumina (Al₂O₃) that, by combining, are forming aluminosilicates, such as kaolinite and muscovite mica [30]. In addition, the presence of quartz and gibbsite was observed. In this table, a high amount of color enhanced oxides is also verified, mostly Fe₂O₃, which is the main source of red color after the sintering [31]. By contrast, the percentage of fluxing components (alkaline and alkaline earth oxides) is low and the loss on ignition value is relatively high, which contribute to increase the porosity of the ceramic material [32]. It is worth mentioning that the LoI parameter is related not only to the loss of volatile elements but also, the organic material as well as the dehydroxylation of kaolinite and gibbsite [33–36].

Table 3 shows the chemical analysis of the RTW. The occurrence of heavy metals, such as Pb, Cr, and Cd was verified, although they are not in significant values. Moreover, a high concentration of carbon was found as well as considerable concentrations of S, Fe, Zn, P, Mg, Al, K, Ca, Ba and Tl. These results are in accordance with the high amount of C, Zn and Fe observed by Canova et al. [37], which investigated the incorporation of tires waste in a mortar.

Fig. 1 shows the XRD pattern diffractogram of the clay body. In this figure, the main peaks verified are from kaolinite (Al₂O₃·2SiO₂·2H₂O), quartz (SiO₂), gibbsite (Al₂O₃·3H₂O), muscovite (K₂O·3Al₂O₃·6SiO₂·2H₂O) and minor peaks from montmorillonite [Ca, Na]₀·₃Al₂(Si, Al)₂O₁₀·2(H₂O) and sepiolite [(Mg,Fe)₄Si₆O₁₅·(OH)₂·6H₂O]. Quartz, or free silica (SiO₂), is a mineral found naturally in clays and soil and is considered an impurity, because it acts as an inert material [30], reducing the material’s plasticity. Besides that, the quartz may cause harmful effects due to its polymorphic transformations at high temperatures. The muscovite with reduced particle size can act as a fluxing component as a result of the presence of alkaline oxides. However, it is also a mineral with lamellar behavior being able to cause defects in ceramic products [34].

The XRD performed on the powder RTW is shown in Fig. 2. In the diffractogram, it is observed a characteristic halo at 2θ from 13 to 30° (Fig. 2), which is related to the amorphous behavior of the polymeric material. This result corroborates the high amount of carbon obtained in Table 3. In Fig. 2 it is also possible to observe the presence of naphthen (C₁₀H₈). According to the literature [35], the 1,5 diisocyanate naphthen is used in hot-molded solid elastomers with high performance, such as tires. The diffractogram also presents other crystalline phases, with non-identified compositions. The existence of these phases is confirmed by identification of the elements in Table 3.

Fig. 3 shows the DSC and TG/DTG curves of the RTW. Some thermal events are worth discussing. The first exothermic peak at 258.58 °C in the DSC curve with a TG weight loss of 14.7% is assigned to the release of adsorbed water. The second exothermic event occurred from 400 to 650 °C with a significant weight loss of 78.8%.

Two points should be emphasized regarding the exothermic peaks in Fig. 3. First, the sintering of organic compounds promotes the appearance of porosity, which impairs the technical properties [35–37]. Second, the heat flow due to the organic compounds combustion of 2.97 kJ is an advantage in reducing the fuel consumption during the sintering of a clay ceramic. It is noteworthy that 1.11 kJ are necessary to sinter 1 kg of clay ceramic [13]. As such, there should be about 2.7% of the energy economy for each 1 wt% of added sewage sludge.

Figs. 4 and 5 show the optical microscopy images of the ceramic with 0 (M0) and 0.5 wt% (M0.5) incorporated RTW, respectively. In Fig. 4 it is observed the presence of quartz and mica particles. It is worth mentioning that the dark region might be an indication of the presence of ferromagnesian minerals in the clay ceramic (Fig. 4). The presence of dark dots observed in Fig. 5 corresponds to the rubber particles in the specimen M0.5. Quartz particles are also indicated in this figure.

Fig. 6 presents the water absorption of all ceramic compositions, sintered at 850 and 950 °C. In this figure, it is noticeable that even considering the statistical errors, the RTW incorporation changed the water absorption of the samples, which increased for both sintering temperatures. The reducing in the water absorption for the higher sintering temperature (950 °C) is also observed, which evidences the formation of a higher amount of liquid phase and closure of open porosity of the ceramic [36]. In fact, this property is strongly related to the material porosity, indicating that the incorporation of RTW causes an increase in the porosity of sintered ceramic. Amounts higher than 1.5 wt% of incorporated RTW showed a water absorption value above the recommended by the Brazilian standard [38]. At 950 °C, the clay ceramic compositions below 1 wt% of RTW showed a water absorption of approxi-
Fig. 1 – X-ray diffraction of clay ceramic.

Fig. 2 – X-ray diffraction of RTW.
Table 2 – Chemical composition of ceramic clay.

<table>
<thead>
<tr>
<th>Oxide content</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>P₂O₅</th>
<th>MnO</th>
<th>Na₂O</th>
<th>LOI*</th>
</tr>
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<tbody>
<tr>
<td>(% mass)</td>
<td>45.52</td>
<td>28.67</td>
<td>8.05</td>
<td>1.35</td>
<td>1.47</td>
<td>0.24</td>
<td>0.87</td>
<td>0.15</td>
<td>&lt;0.05</td>
<td>0.35</td>
<td>13.07</td>
</tr>
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</table>

* LOI, loss on ignition.

Table 3 – Chemical composition of RTW.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Al</th>
<th>Ba</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
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<tbody>
<tr>
<td>Concentration (%)</td>
<td>396.15</td>
<td>493.40</td>
<td>214.43</td>
<td>267.71</td>
<td>327.39</td>
<td>259.94</td>
<td>257.61</td>
<td>231.60</td>
<td>220.35</td>
</tr>
<tr>
<td>Standard (%)</td>
<td>8.00</td>
<td>2.50</td>
<td>0.09</td>
<td>0.80</td>
<td>2.40</td>
<td>28.00</td>
<td>2.60</td>
<td>0.70</td>
<td>2.40</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ti</th>
<th>V</th>
<th>Zn</th>
<th>P</th>
<th>S</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (%)</td>
<td>336.12</td>
<td>311.07</td>
<td>213.85</td>
<td>214.91</td>
<td>181.97</td>
<td>317.93</td>
<td>769.89</td>
<td>279.55</td>
<td>589.59</td>
</tr>
<tr>
<td>Standard (%)</td>
<td>1.60</td>
<td>0.40</td>
<td>18.20</td>
<td>8.80</td>
<td>41.00</td>
<td>3.00</td>
<td>3.40</td>
<td>8.00</td>
<td>6.20</td>
</tr>
</tbody>
</table>

Total carbon: 75.80%

Fig. 3 – DSC/TGA curves of RTW.

The linear shrinkage of the different ceramic compositions, sintered at 850 and 950 °C, is shown in Fig. 9. In general, it is possible to verify that the linear shrinkage of the sintered ceramics barely changes for all RTW incorporations at 850 °C. A small increase in linear shrinkage occurs above 0.5 wt% of RTW incorporation fired at 950 °C. For RTW incorporation above 1 wt%, there is no change in linear shrinkage.

Fig. 10 shows the flexural strength for all ceramic compositions at 850 and 950 °C. According to this figure, it is possible to observe that the mechanical strength of the ceramic is influenced by the amount of incorporated RTW [35,37] since it directly affects the material porosity (Fig. 9). In this figure, it was observed that the flexural rupture strength of the ceramic samples increases with the temperature. It was also verified that all formulations sintered at 850 and 950 °C reach approximately 25%, which is recommended value for the manufacture of the bulky bricks [39].

Fig. 7 shows the bulk density of all formulations. It is possible to note that the particle density is kept the same for the incorporation up to 0.5 wt% of RTW in the ceramic clay. For incorporations above 1 wt%, the particle density decreases, indicating that the incorporation of RTW changed the packaging of the ceramic mass during samples conformation. This may cause some shortcomings, such as cracks in the ceramic.

The open porosity of all ceramic samples sintered at 850 and 950 °C is shown in Fig. 8. According to these results, it was observed that the incorporation is affected according to the firing temperature. At 950 °C, the pore concentration is higher for all condition, in particular for the samples with 1.5 and 2 wt% of RTW.
Fig. 4 – Micrographs of M0 formulation obtained in confocal microscope under magnification: (a) 216×; and (b) 430×.

Fig. 5 – Micrographs of M0.5 formulation obtained in confocal microscope under magnification: (a) 216×; and (b) 430×.

Fig. 6 – Water absorption of compositions sintered at 850 and 950 °C.

Fig. 7 – Bulk density of the different ceramic compositions.

the value of 2.0 MPa, which is specified in the standard for the manufacture of solid bricks. It is worth mention that only the formulation M0.5 approaches the value of 5.5 MPa specified for ceramic blocks [38]. It can be noticed that the porosity increases for the formulation M1.5 sintered at 950 °C (Fig. 9), which may have contributed to a slight reduction in the mechanical strength.
Fig. 8 – Open porosity of different compositions sintered at 850 and 950 °C.

Fig. 9 – Linear shrinkage compositions sintered at 850 and 950 °C.

Scanning electron microscopy (SEM) images of sample M0, sintered at 850 and 950 °C, are shown in Fig. 11. A rough texture is observed in samples sintered at 850 °C and a high value of open porosity is verified (Fig. 11a). After sintering at 950 °C, a more dense microstructure is formed (Fig. 11b). Moreover, in

Fig. 10 – Flexural strength of compositions sintered at 850 and 950 °C.

Fig. 12 it is observed the presence of a high amount of pores and cracks, a fact that increases gradually with the incorporation of RTW. These defects might be attributed to the coarse granulometry of rubber powder particles, which provides a low packing density of these particles. The size and pore frequency increase with the RTW incorporation. The occurrence of various pores can be verified for the formulations M1.5 and M2, in both temperatures (Fig. 12). This fact might be assigned to the high amount of carbon in the RTW, which increases the porosity due to the combustion of the organic and/or carbonaceous existing substances [13].

Sieve analysis was performed and the grading curve of rubber tire waste (RTW) is shown in Fig. 13. It is observed that almost 95% of the RTW is between 0.1 and 1 mm, which was also identified by Segre and Joekes [40] and Oda and Fernandez Jr [41] in cement and asphalt cement incorporated with the tire waste, respectively. This granulometric fraction is in the range sand fraction (>20 μm), which according to Melchiades et al [42], can reduce the flexural strength of the ceramic.

Fig. 14 shows the compressive strength of the five ceramic compositions sintered at 850 and 950 °C. In this figure is verified a sharp decline in compressive strength for the samples sintered at 850 °C with the incorporation of RTW up to 1.5 wt%. At 950 °C, it is also observed a decrease in compressive

Fig. 11 – SEM images of M0 samples sintered at: (a) 850 °C; and (b) 950 °C.
strength with higher amounts of RTW in comparison to the ceramic without incorporation of RTW, but less pronounced for the clay ceramic with up to 1 wt% RTW. Therefore, taking into account the other results, the incorporation of 1 wt% RTW and sintering at 950 °C it is the condition recommended.

A comparison between the best condition obtain in the present work (ceramic with 1 wt% RTW sintered at 950 °C) and the unfired brick incorporated with crumb rubber studied by Mohammed et al [3] is shown in Table 4. In this table is possible to note the difference in properties, as they depend on the process and material composition. However, these results

<table>
<thead>
<tr>
<th>Properties</th>
<th>Red ceramic/1 wt%RTW (950 °C) PW*</th>
<th>Rubberized interlocking bricks (unburnt) [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength (MPa)</td>
<td>17.29</td>
<td>3.98</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>4.72</td>
<td>0.258</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>24.80</td>
<td>25.23</td>
</tr>
</tbody>
</table>

* Present work.
indicate the possibility of other applications for the rubber waste [3].

4. Conclusion

- The incorporation of rubber tire waste (RTW) changed the technological properties of the sintered red ceramic at 850 and 950 °C. The clay ceramics with amounts above 1.5 wt% of RTW showed an increase in water absorption and porosity for both sintering temperatures. These results might be attributed to the decreasing of clay packing and high concentration of carbon, which is volatilized at high temperatures resulting in pores.
- The clay ceramic with up to 1 wt% RTW and sintered at 850 and 950 °C did not modify significantly the water absorption, linear retraction, and flexural strength.
- It was also noticed through the bend test that the mechanical strength is affected with the increasing amount of waste incorporation, although all the formulations sintered at 850 and 950 °C reached values of the mechanical resistance specified for the solid brick manufacturing standard (2.0 MPa). This result corroborates the benefits of the rubber tire waste incorporation into red ceramic.
- It is worth mention that the ceramic incorporated with 1 wt% of RTW and sintered at 950 °C was the most suitable condition observed since it exhibited the best result for both compressive and bend tests.
- Therefore, the incorporation of RTW in red ceramic is a viable procedure, which turns the RTW in an environmentally friendly by-product.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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