Manufacturing of porous refractories from Iraqi Kaolin by adding expanded polystyrene waste

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Abstract

Fabrication of porous clay refractory insulating specimens from Iraqi kaolin with different percentage of Expanded Polystyrene (EPS) waste crumbs additions were investigated. After mixing and forming by hand molding, the specimens was dried and fired at 1300 °C. The structural, physical, mechanical and thermal properties of the refractory insulating products were measured. Maximum addition of EPS (1.25 wt%) lead to reduce the linear shrinkage to less than 1.7% and increased apparent porosity up to 50 %. As well as, the density, Modulus of rupture and thermal conductivity were reduced to 1.39 g/cm³, 4.1 MPa and 0.21 W/m.K, respectively. The final outcome, addition of EPS showed good results in the formation of pores without distorting the dimensions of specimens and without any cracks. In addition, it is possible to use these thermal insulators at temperatures up to 1300 °C.

Introduction

Insulating refractories are one of the refractory types which are most commonly used for heating insulation in industrial applications today [1]. Clay refractories that have a highly porous structure display low thermal conductivity values [2]. Porosity is usually created by adding a combustible materials to the raw material mixture. During firing, the combustible material burns out, and leaves a large fraction of pores within the fired body [3]. In this research, Expanded Polystyrene (EPS) was used as a combustible material. EPS is a thermoplastic polymer with a closed cellular structure [4], and used extensively in construction, packaging, medical and food service applications.
Foamed polystyrene contains 2% polymerized polystyrene and 98% air [6]. Annually, large quantities of EPS waste are thrown or recycled in modern processes and convert them into other useful materials [7].

Kaolin is a clay raw material that has a wide use in industries depending on its purity. Kaolinite is a clay mineral with formula $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$, it is the major mineral component of kaolin with other oxides [8]. The refractories manufactured from kaolin are the most common commercial refractories because it has advantage to be easily accessible and not expansive [9].

Porosity is one microstructural variable that must be controlled to produce a suitable refractory brick. Strength, load-bearing capacity, thermal conductivity, and resistance to attack by corrosive materials, all increase with porosity reduction. Porosity is deleterious to the flexural strength for two reasons: (1) pores reduce the cross-sectional area across which a load is applied, and (2) they also act as stress concentrators for an isolated spherical pore. Experimentally it has been shown that the flexural strength ($\sigma_{fs}$) decreases exponentially with volume fraction porosity (P) as:

$$\sigma_{fs} = \sigma_o \exp (-n.P) \quad (1)$$

where: $\sigma_o$ is flexural strength of the material without porosity and n is constant.

The thermal conductivity of a porous refractories ($k_{ref}$) can be calculated by using Eq. (2):

$$k_{ref} = k_c \left( \frac{1 - P}{1 + P} \right) \quad (2)$$

where: $k_c$ is the thermal conductivity of the material without porosity [10,11].

The aim of the research is to eliminating the large quantities of EPS waste by add it to Iraqi kaolin to manufacture thermal insulations products.

**Experimental**

1. **Materials and sample preparation**

The Iraqi kaolin was used as a base raw materials for preparation of refractory mixtures. Chemical analysis of kaolin components are list in Table 1. Crushing, grinding and sieving processes was performed for kaolin to obtain particle size less than 150 µm. Some of kaolin powder was fired at 1100 °C to be converted to grog in order to reduce the shrinkage caused by the burning of plastic clay. EPS wastes were obtained from wastes of packaging of electrical equipment. A sharp metal tool was used to fragmenting the EPS into small pieces (Crumbs) with diameter < 5 mm, as shown in Fig.1.

!Table 1: Chemical analysis of kaolin*

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>CaO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Loss on ignition %</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.34</td>
<td>36.37</td>
<td>0.63</td>
<td>2.2</td>
<td>0.12</td>
<td>0.08</td>
<td>0.31</td>
<td>0.53</td>
<td>12.42</td>
</tr>
</tbody>
</table>

* Wadi Al-Hussainiat, Western Desert-Iraq
The general characteristics of the EPS employed are shown in Table 2, according to ASTM C578 [12], the test results showed that the EPS type II.

**Table 2: Specifications of EPS.**

<table>
<thead>
<tr>
<th>Classification</th>
<th>Results</th>
<th>Standard Specification ASTM C578-Type II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive resistance (kPa)</td>
<td>115</td>
<td>Min. 104</td>
</tr>
<tr>
<td>Flexural strength (kPa)</td>
<td>253</td>
<td>Min. 240</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>2.4</td>
<td>Max. 3</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.0243</td>
<td>Min. 22</td>
</tr>
</tbody>
</table>

The refractory mixture consisted of 20 wt% plastic clay and 55 wt% grog with 20 wt% of distilled water and 5 wt% of waterglass or sodium silicate Na₂SiO₃ (density 1.25 g/cm³). After several experiments of different EPS additives, various weights percentages were selected, as shown in Table 3.

**Table 3: Mix compositions.**

<table>
<thead>
<tr>
<th>Mix</th>
<th>Refractory Mixture wt%</th>
<th>EPS wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>99.75</td>
<td>0.25</td>
</tr>
<tr>
<td>C</td>
<td>99.5</td>
<td>0.5</td>
</tr>
<tr>
<td>D</td>
<td>99.25</td>
<td>0.75</td>
</tr>
<tr>
<td>E</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>F</td>
<td>98.75</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Good and homogeneous refractory paste mix was obtained for all mixtures, then the hand molding was done by using different size of metal molds. Different dimensions of specimens according to the requirements of the laboratory tests were prepared. The specimens was very slowly dried for (24 hours at room temperature) to prevent cracking during rapid evaporation, then fired at 1300 °C for 3 h as soaking time to get hard refractory bodies.

2. Test methods

The X-ray diffraction equipment type: SHIMADZU-XRD-6000 was used to characterize the crystalline structure of kaolin before and after firing. Linear firing shrinkage (L.S) was calculated by using the relation (3) according to ASTM C326 [13]:

\[
L.S = \frac{L_o - L}{L_o} \times 100 \%
\]  

(3)
where $L_0$ and $L$ are the plastic and fired length of test specimen before and after firing respectively.

The Apparent Porosity (A.P) and Bulk Density (B.D) were calculated by using the following relations according to ASTM C20 [14]:

\[
A.P = \frac{W_s - W_d}{W_s - W_i} \times 100\% \quad (4)
\]

\[
B.D = \frac{W_d}{W_s - W_i} \left( \frac{g}{cm^3} \right) \quad (5)
\]

where $W_d$, $W_s$ and $W_i$ are the masses of the specimen when they are dried, Saturated with water and immersed in water, respectively.

Cold crushing strength ($\sigma_c$) and modulus of rupture were tested according to ASTM C133 by using laboratory hydraulic universal test equipment, type JIANQIAO using the relation:

\[
\sigma_c = \frac{F_{\text{max}}}{A} \quad (6)
\]

(for cylindrical specimens with radius $5\pm0.1$ cm).

where: $F_{\text{max}}$ is maximum load indicated by the testing machine (N) and $A$ is an average of the areas of the top and bottom of the specimen perpendicular to the line of application of the load ($mm^2$). Also, the modulus of rupture has been measured in 3-point bending test using the relation:

\[
MOR = \frac{3P_1}{2bd} \quad (7)
\]

(for cuboid specimens $80\times40\times20$ mm).

where: $P$ is maximum applied force (N), $l$ is span between supports (mm) and $b,d$ are breadth and depth of specimen (mm) [15].

The coefficient of thermal conductivity ($k$) was measured by using Lee's Disk type Griffin and George LTD-Germany. The shape of specimens are disks with diameter 4 cm and 0.5 cm in thickness [16, 17].

**Results and discussion**

The X-ray diffraction results of the Iraqi kaolin before and after burning are illustrated in Fig. 2. It is clear that the main minerals of kaolin before burning are kaolinite and quartz with a small amount of other minerals formed by other oxides. When kaolin is burned at a temperature of 1300 °C, it is converted to Mullite ($3Al_2O_3.2SiO_2$) which is the primary refractory compound, with excess of silica ($SiO_2$) in the cristobalite phase as shown in Fig. 2(b). It was also noticed that a limited quantity of silica remains in the quartz phase and can be converted to cristobalite phase if its burned at temperatures higher than 1300 °C [18].

![X-ray diffraction patterns of the kaolin](image)

**Fig. 2: X-ray diffraction patterns of the kaolin, (a) before, (b) After burning at 1300 °C.**
Linear shrinkage was decreased with increase the percentage of EPS which may be due to increase the voids between the clay grains then reducing the amount of clay per unit volume as shown in Fig. 3. The decline of shrinkage is severe, in comparison between two cases; without and without 1.25 wt% of EPS additions, where the values decreased from 9% to 1.7% as shown in Fig. 4. Generally, low shrinkage values were due to the addition of non-plastic clay (Grog) to the mixture. Also, the EPS crumbs act to inhibit early shrinkage due to loss of lattice water in kaolinite during firing process and transform it to Meta-kaolin [19]. These observations differ from results of other researchers such as (C. Sadik et al., 2013) who concluded that the shrinkage was increasing with porosity increases when adding sawdust to kaolin. This difference can be explained by sublimation of sawdust, while the EPS crumbs is melted and then evaporated during firing [20].

Fig. 3: Illustration of the variation of pore size of specimens containing kaolin and different EPS additions: (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1, (f) 1.25 wt%.

Fig. 4: Linear Shrinkage of kaolin specimens depending on EPS additions.
Porosity is one of the most important physical factors affecting the determination of other properties of refractories, such as mechanical and thermal properties, in addition to determining the range of possible applications as refractory insulations. Fig. 5 shows that the porosity was increased with increases the percentage of EPS, so that the value of porosity reaches 50% when adding 1.25 wt% EPS. These results are very consistent with the expected values of porosity, when theoretically computed from the relationship between volume and density of EPS using Table 2.

![Graph](image1)

**Fig. 5: Variation of apparent porosity with EPS additives.**

The surface morphology of specimens is shown in the Fig. 3, it is clear that the increase of the voids on the surface with EPS additions increases, so that, the shape of the pores takes the same form of EPS crumbs.

The bulk density was determined for the grouping of insulating firebrick according to ASTM C155. Fig. 6 shows the bulk density decreased with EPS additions increase. While the density decreased from the maximum value without EPS addition (2.02 g/cm³) to (1.39 g/cm³) when adding 1.25 wt% of EPS.

![Graph](image2)

**Fig. 6: Bulk density dependent on the EPS additions.**
Flexural strength or modulus of rupture (MOR) of specimens is shown in Fig. 7. Depending on the increase in the EPS addition and porosity content, cold modulus of rupture of the samples progressively decreased from 11.3 to 4.1 MPa. The strength of samples was almost compatible with ASTM C133. The chemical composition of kaolin played an important role in increasing the mechanical strength, where some of flux oxides make glass phase at high temperature. The experimental relationship between modulus of rupture and porosity is shown in Fig. 6, and when comparing with relationship (1), it is possible to calculate the constant value \( n=0.03 \) and the MOR at zero apparent porosity is 18.6 MPa.

![Fig. 7: The modulus of rupture depends on porosity.](image)

Fig. 7: The modulus of rupture depends on porosity.

Fig. 8 shows that the thermal conductivity values decrease rapidly with increase in porosity from 0.61 to 0.21 W/m.K. The effect of porosity is important to keep in mind. When the thermal conductivity of air is negligible compared to the solid phases, the addition of large (>25 percent) volume fractions of pores can dramatically reduce thermal conductivity. This approach is used in the fabrication of insulation refractories. Briefly, the large amount of porosity leads to improved thermal shock resistance of refractory insulating bricks [21].

![Fig. 8: Relation between porosity and thermal conductivity.](image)

Fig. 8: Relation between porosity and thermal conductivity.
Conclusion
EPS polymer waste addition to kaolin has achieved important goals, such as obtaining porous thermal insulation products withstand 1300 °C as well as elimination of EPS waste. Small amount of EPS (1.25 wt%) achieved excellent results for porosity (50 %), with good mechanical strength and low thermal conductivity. The inverse relationship between the shrinkage and the percentage of EPS added was useful in controlling over the dimensions of products, in addition to the importance of adding grog to reduce shrinkage. All the phase transformations due to firing of kaolin were completed at 1300 °C, especially quartz conversion to stable cristobalite phase, this happened with support of the thermal energy emitted from EPS burning.

References
