

EFFECT OF PRODUCTION CONDITIONS ON MECHANICAL PROPERTIES OF BAUXITE REFRACTORY MATERIALS

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Compressive strength of bauxite refractories with phenol-formaldehyde resin as binder, used as lining in high temperature furnaces, was investigated in this study. Mechanical properties are used to determine the material's mechanical resistance and thus they represent the life time of the refractory. Different bauxite grain size, resin content and molding pressure were selected for the preparation of the specimens. The stress - strain data of compression test were modeled using parameters with physical meaning such as maximum stress (σ_{max}), maximum strain (e_{max}), elasticity parameter (E), and viscoelastic parameter (p). In addition, simple mathematical models were developed to correlate the maximum stress and corresponding strain to producing conditions and raw materials' characteristics. After data processing it was noticed that when increasing molding pressure maximum stress and maximum strain increased, while the viscoelastic parameter decreased. As far as elasticity parameter is concerned, at first it decreases with grain size and beyond a critical value of molding pressure, between 100 and 200MPa, it increases. Higher resin content led to higher compressive strength, due to higher cohesion and bonding strength. On the other hand, increased bauxite grain size leads to samples with degraded mechanical properties as larger granules hinder sintering between the granule boundaries.

INTRODUCTION

Refractories are currently widely used in the iron and steel industry (using over 65 % of world production) but also in the glass, aluminium, ceramics industry [1, 2], as lining in ladles, soaking pits, and furnaces. Amongst aluminosilicate refractories such as mullite, corundum, sillimanite and andalusite, bauxite refractories were selected to be investigated since they indicate high bulk density and therefore high compressive strength [3].

One of the most well-known techniques for the production of refractories and ceramics is the mixing of several components in the form of powder, formation of the mixture to the final shape and firing to the suitable temperature, where desired properties are attained. During firing recrystallization, crystal growth and sintering occurs [3], which leads to mechanical resistance and densification of the articles.

Resin bonded refractories were first used in the 60 's [4-6], while pitch and coal tar with the addition of anthracene oil were used to produce the resins. A major disadvantage of the coal-tar pitches is the content of carcinogenic aromatics, especially the benzopyrene [7]. In the past decades the most commonly used resins are phenol-formaldehyde resins which are divided into two

major categories, novolak and resol type resins, according to their molecular ratio of phenol per formaldehyde [8]. Resol resins are thermosetting, while novolak are thermoplastics [7, 9]. The role of the binder is essential in the production of refractories since it determines the moldability of the product [10] and it eases the transfer of the product from the production line to the kiln, where sintering occurs [3]. In addition, properties such as porosity pore size distribution, mechanical properties and chemical and mechanical corrosion depend on the resin type and content.

Lattice mechanisms of deformation and boundary mechanisms of deformation are the main mechanisms responsible for material failure [11]. Defects in the microstructure, resulting either from manufacturing process or nucleation under a macroscopic loading, lead also to a damage mechanism of deformation. Under compressive stresses, any vitreous phase that is present is forced between the facets of grains and flows towards voids or lower stressed regions. The critical wear process actually involves the nucleation and propagation of grain boundary microcracks. A microcrack is nucleated and travels at a characteristic velocity along a low energy grain face until a multi-boundary junction is encountered, when development of the crack is temporarily inhibited [12].

The crack thus causes the local loss of material, through grain detachment, and consequently leads to break point. The mechanical properties in room temperature, such as compressive strength and elastic modulus, are essential when selecting refractories and designing refractory components. Therefore, many authors have already examined the mechanical properties of refractories [3, 13-16].

The innovative aspect of this paper is the fact that apart from comparing the materials' properties, a mathematical model with physical parameters was used in order to correlate the experimental data with molding pressure. In addition, all production conditions were investigated thoroughly. Four different resin contents were selected to be mixed with shaft kiln bauxite and the effect of molding pressure on their mechanical properties was investigated. A number of mathematical models was examined in order to select the most suitable and simple, according to the experimental data [17-19]. The mathematical model involves parameter with physical meaning, such as maximum stress (σ_{max}), maximum strain (ϵ_{max}), elasticity parameter (E), and viscoelastic exponent (p). The influence of molding pressure on these parameters was investigated and shown in correlation models.

EXPERIMENTAL

Materials

Samples were prepared, using shaft kiln bauxite with particle size from 90 to 315 μm and phenol-formaldehyde

novolak type resin content varying from 0 to 10%. Figure 1 indicates the XRD analysis of raw bauxite, where it is shown that the primary and the secondary phase is $\alpha\text{-Al}_2\text{O}_3$ and mullite respectively. The mixing of the raw materials was conducted using a Heidolph RZR 2041 mixer, which ensures the uniform mixing of materials. Cylindrical specimens 13 mm in diameter and 16 mm in height were molded applying 60-400 MPa pressure, using a Specac manually operated hydraulic press (25tn). The specimens were fired at 1200°C in a Nüve muffle furnace (MF 120). Table 1 describes the producing conditions thoroughly. All combinations of those parameters were selected, which led to the production of 80 different samples.

Compression analysis

Compression tests were conducted using an Instron 4482 testing apparatus. Three different specimens for each sample were fitted to the instrument. The uniaxial compression tests were performed at room temperature (25°C). Constant deformation rate of 0.5 mm/min was used for all examined materials and data acquisition was performed in a rate of 3 points/sec. Force and deformation were recorded electronically and the resulting stress

Table 1. Materials and producing conditions

| | CONDITIONS | | | | |
|--------------------------------------|------------|-----|-----|-----|-----|
| | 90 | 100 | 200 | 315 | — |
| Bauxite grain size (μm) | 90 | 100 | 200 | 315 | — |
| Resin content (%) | 0 | 3 | 6 | 10 | — |
| Molding pressure (MPa) | 60 | 100 | 200 | 300 | 400 |

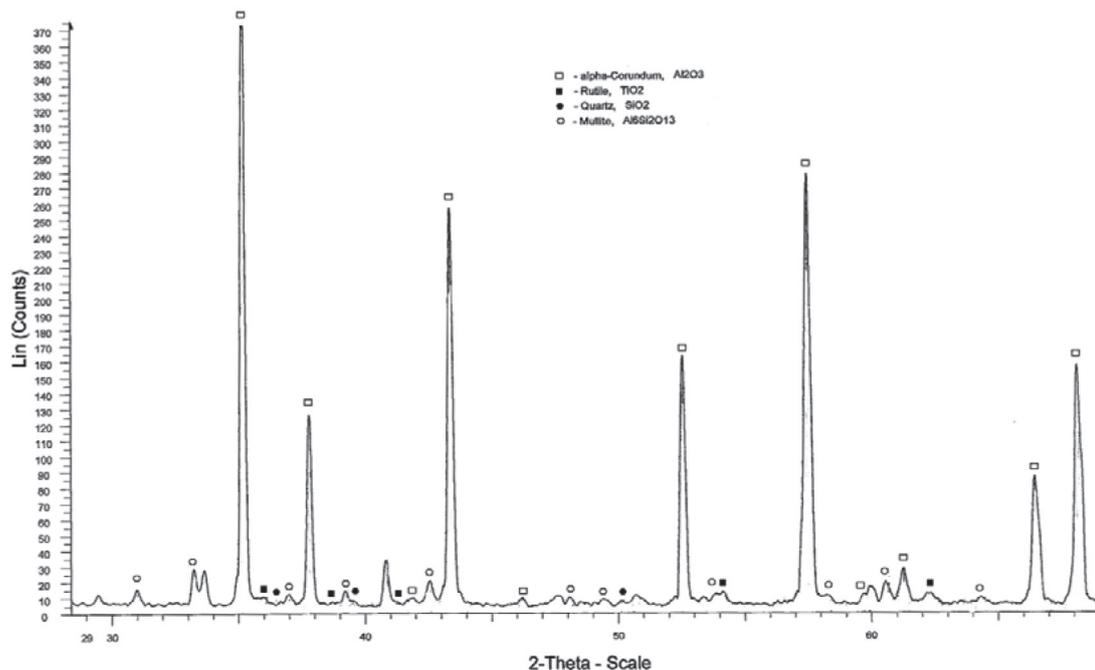


Figure 1. XRD analysis of shaft kiln bauxite

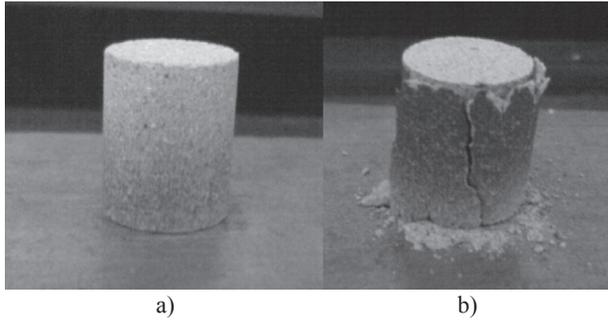


Figure 2. Cylindrical specimens (a) before and (b) after compression test.

– strain compression curves were constructed. The compression test was continued until there was a break point of the specimens. Figure 2 illustrates the specimen before and after the compression test.

MATHEMATICAL MODELING

Several mathematical models were examined in order to predict the value of stress, strain, elasticity, and viscoelastic parameters against molding pressure for the compression tests [18, 19].

The selected mathematical models that were the most appropriate and simple, according to the compression data, are summarised on Table 2. The stress strain equation (equation 1) that describes the viscoelastic behaviour involves four parameters: the maximum stress (σ_{max}), the corresponding strain (ϵ_{max}), the elasticity parameter (E), and the viscoelastic parameter (p) [19]. Maximum stress and strain represent the break point of the specimen during compression test. The elasticity parameter represents the linear part of the stress-strain curve and shows the elastic nature of the material. The viscoelastic exponent represents the exponential part of the curve.

$$\sigma = E\epsilon + (\sigma_{max} - E\epsilon_{max})(\epsilon / \epsilon_{max})^p \quad (1)$$

where σ_{max} is the maximum stress, ϵ_{max} is the maximum strain, E is the elasticity parameter, p is the viscoelastic exponent and σ, ϵ are the predicted values.

Molding pressure affected all the above parameters. In particular, maximum stress and corresponding strain were found to increase, in all different resin contents and raw bauxite's grain size as molding pressure increased. In addition, the viscoelastic exponent seemed to decrease while increasing the molding pressure. On the contrary, the elasticity parameter seemed to differ for each material. This experimental behavior is well defined by the following equations.

$$\sigma_{max} = \sigma_i + \sigma_i(P/\bar{P})^k + \sigma_0(P/\bar{P}) \quad (2)$$

Table 2. Mathematical models selected for the compression data.

Stress-Strain Equation

$$\sigma = E * \epsilon + (\sigma_{max} - E * \epsilon_{max}) * (\epsilon / \epsilon_{max})^p$$

Parameters

| | | |
|------------------|------------------------|-------|
| σ_{max} | maximum stress | (MPa) |
| ϵ_{max} | maximum strain | (-) |
| E | elasticity parameter | (MPa) |
| p | viscoelastic parameter | (-) |

Parameters Equations

$$\sigma_{max} = \sigma_i + \sigma_i * (P/\bar{P})^k + \sigma_0 * (P/\bar{P})$$

$$\epsilon_{max} = \epsilon_0 * (P/\bar{P})^m$$

$$E = E_i + E_i * (P/\bar{P})^n + E_0 * (P/\bar{P})$$

$$p = p_0 * (P/\bar{P})^t$$

where

| | | |
|------------|------------------|-------|
| P | molding pressure | (MPa) |
| ϵ | strain | (-) |
| σ | stress | (MPa) |

$$\epsilon_{max} = \epsilon_0(P/\bar{P})^m \quad (3)$$

where $\sigma_i, \sigma_0, k, \epsilon_0, m,$ are constants and P is the molding pressure.

The values of E and p were correlated to the molding pressure through the following relations.

$$E = E_i + E_i(P/\bar{P})^n + E_0(P/\bar{P}) \quad (4)$$

$$p = p_0(P/\bar{P})^t \quad (5)$$

where $E_0, E_i, p_0, n, t,$ are constants and P is the molding pressure.

RESULTS AND DISCUSSION

The typical stress - strain curves that were obtained from compression tests and the estimated curves from mathematical model described above, considering for bauxite grain size of 315 μm , are presented in Figure 3. Accordingly, the corresponding curves referring to 90, 100, 200 grain sizes were plotted. The samples present a controlled fracture, typical of a tough material and as alumina is the primary phase and mullite the secondary phase it seems that mullite forms a stiff and interlocked skeleton between α -alumina grains, giving a reinforced effect [15]. The calculated stress-strain curve results from Equation (1). This equation contains two parameters,

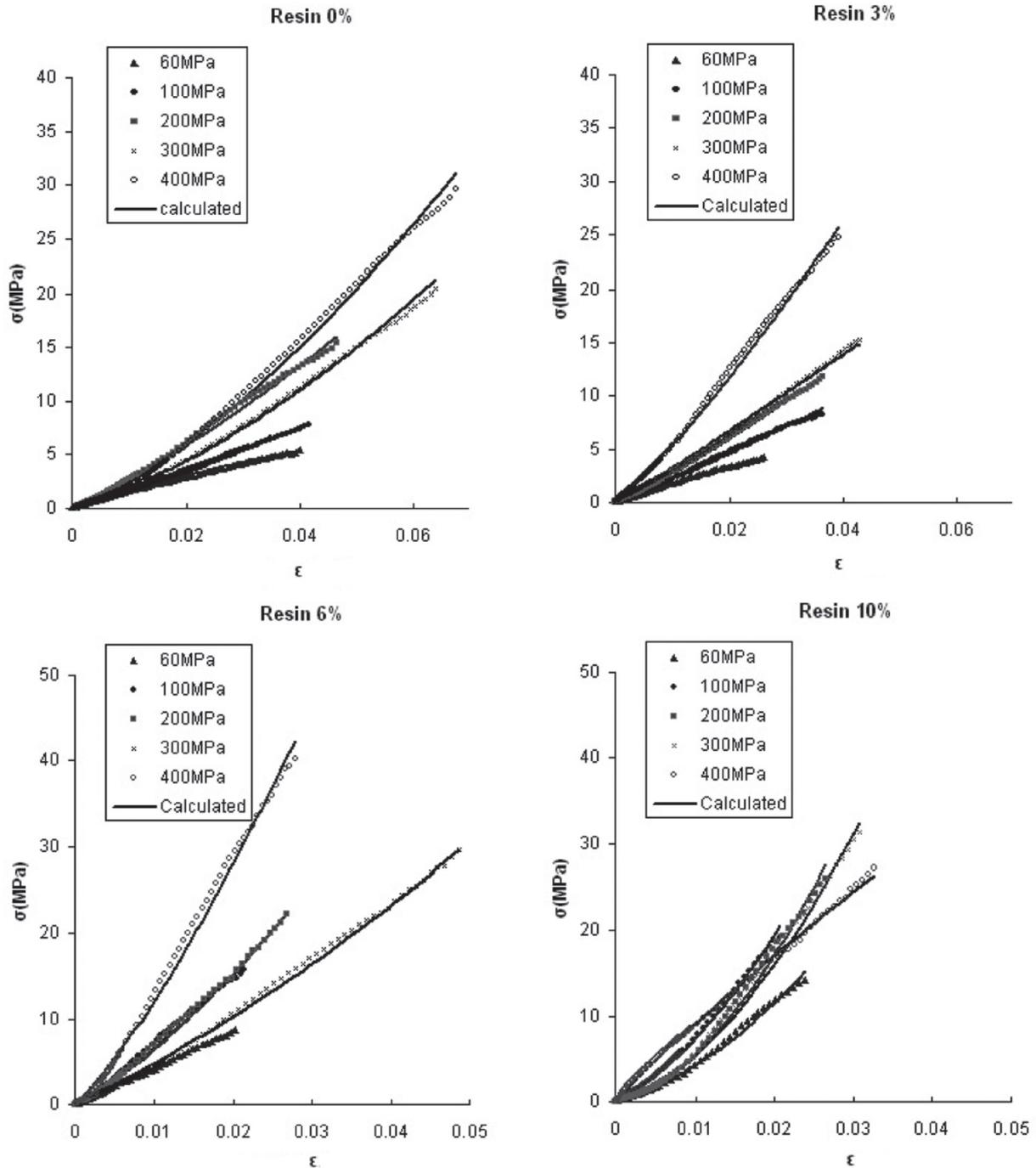


Figure 3. Stress-strain compression curves for bauxite grain size 315 μm and for varying resin contents

maximum stress (σ_{max}) and maximum strain (ε_{max}), referring to the break point of the material, the elastic parameter (E), which corresponds to the slope of the first linear part of the curve and the viscoelastic parameter (p).

The values of the above parameters (σ_{max} , ε_{max} , E and p), resulted from the stress-strain equation, were calculated using Equations (2-5), for various molding pressures for each sample. The results of parameter estimation of the mathematical model are summarized in Tables 3-10. The correlation of maximum stress and maximum strain with molding pressure is presented in

Figures 4 and 5, respectively.

Maximum stress seemed to increase when increasing the molding pressure for all samples (Figure 4). All different resin contents seemed to influence similarly maximum stress apart from resin 10%, as shown from the curves in Figure 3. It is noticed that higher resin content in the samples leads to higher maximum stress. This statement is also in accordance with Bonsall's work [20] where it was reported that higher resin content leads to more dense product, and therefore they will withstand higher loads. As far as grain size is concerned, the value

Table 3. Results of parameter estimation for maximum stress and maximum strain for bauxite grain size < 90 μm

| Parameter | Resin 0% | Resin 3% | Resin 6% | Resin 10% |
|-----------------|----------|----------|----------|-----------|
| σ_i | 0.06 | 5.12 | 3.13 | 10.59 |
| σ_0 | 10.27 | 10.09 | 34.86 | 10.33 |
| k | 7.04 | 2.31 | 6.40 | 0.21 |
| \bar{P} | 200.00 | 237.10 | 270.93 | 200.82 |
| ε_0 | 0.02 | 0.02 | 0.03 | 0.03 |
| m | 0.51 | 0.47 | 0.62 | 0.34 |
| \bar{P} | 200.00 | 200.00 | 200.00 | 200.00 |

Table 4. Results of parameter estimation for maximum stress and maximum strain for bauxite grain size < 100 μm.

| Parameter | Resin 0% | Resin 3% | Resin 6% | Resin 10% |
|-----------------|----------|----------|----------|-----------|
| σ_i | 4.29 | 3.78 | 6.65 | 4.20 |
| σ_0 | 10.88 | 9.92 | 9.98 | 24.99 |
| k | 1.81 | 1.68 | 0.81 | -0.77 |
| \bar{P} | 200.41 | 200.65 | 175.96 | 200.89 |
| ε_0 | 0.02 | 0.03 | 0.02 | 0.03 |
| m | 0.37 | 0.31 | 0.40 | 0.37 |
| \bar{P} | 198.00 | 210.00 | 200.00 | 200.00 |

Table 5. Results of parameter estimation for maximum stress and maximum strain for bauxite grain size < 200 μm.

| Parameter | Resin 0% | Resin 3% | Resin 6% | Resin 10% |
|-----------------|----------|----------|----------|-----------|
| σ_i | 3.19 | 5.99 | 6.45 | 7.41 |
| σ_0 | 4.94 | 10.06 | 9.00 | 12.72 |
| k | 2.17 | 1.65 | 1.87 | 0.59 |
| \bar{P} | 198.99 | 256.49 | 202.98 | 185.45 |
| ε_0 | 0.03 | 0.03 | 0.02 | 0.03 |
| m | 0.20 | 0.29 | 0.53 | 0.44 |
| \bar{P} | 198.99 | 199.99 | 199.98 | 200.00 |

Table 6. Results of parameter estimation for maximum stress and maximum strain for bauxite grain size < 315 μm.

| Parameter | Resin 0% | Resin 3% | Resin 6% | Resin 10% |
|-----------------|----------|----------|----------|-----------|
| σ_i | 3.17 | 2.91 | 5.90 | 10.38 |
| σ_0 | 7.09 | 4.35 | 9.76 | 3.67 |
| k | 1.86 | 2.21 | 1.38 | 0.57 |
| \bar{P} | 201.22 | 200.00 | 206.63 | 199.59 |
| ε_0 | 0.03 | 0.04 | 0.03 | 0.03 |
| m | 0.31 | 0.23 | 0.20 | 0.32 |
| \bar{P} | 199.33 | 198.26 | 199.99 | 199.21 |

Table 7. Results of parameter estimation for elasticity and viscoelastic parameters for bauxite grain size <90 μm .

| Parameter | Resin 0% | Resin 3% | Resin 6% | Resin 10% |
|-----------|----------|----------|----------|-----------|
| E_i | 210.83 | 64.55 | 96.16 | 426.12 |
| E_0 | 13.58 | 288.99 | 38.74 | 342.27 |
| n | -0.43 | -1.23 | -1.28 | 1.13 |
| \bar{P} | 202.79 | 200.00 | 200.20 | 200.18 |
| p_0 | 3.11 | 1.74 | 2.29 | 2.91 |
| t | -0.21 | -0.15 | -0.15 | -0.13 |
| \bar{P} | 192.67 | 200.11 | 180.02 | 200.16 |

Table 8. Results of parameter estimation for elasticity and viscoelastic parameters for bauxite grain size <100 μm .

| Parameter | Resin 0% | Resin 3% | Resin 6% | Resin 10% |
|-----------|----------|----------|----------|-----------|
| E_i | 52.98 | 147.46 | 127.68 | 212.16 |
| E_0 | 261.66 | 450.00 | 127.63 | 102.24 |
| n | -1.31 | -0.98 | -0.92 | -0.74 |
| \bar{P} | 200.05 | 200.00 | 200.20 | 200.18 |
| p_0 | 1.70 | 1.69 | 1.83 | 1.86 |
| t | -0.23 | -0.41 | -0.13 | -0.23 |
| \bar{P} | 200.00 | 199.81 | 180.02 | 200.17 |

Table 9. Results of parameter estimation for elasticity and viscoelastic parameters for bauxite grain size <200 μm .

| Parameter | Resin 0% | Resin 3% | Resin 6% | Resin 10% |
|-----------|----------|----------|----------|-----------|
| E_i | 70.23 | 461.30 | 73.41 | 117.49 |
| E_0 | 35.38 | -672.03 | 197.23 | 63.60 |
| n | -0.59 | 1.51 | -1.25 | -1.08 |
| \bar{P} | 300.00 | 200.00 | 200.20 | 200.18 |
| p_0 | 1.80 | 1.92 | 1.85 | 2.03 |
| t | -0.21 | -0.24 | -0.08 | -0.13 |
| \bar{P} | 200.00 | 200.00 | 180.02 | 200.17 |

Table 10. Results of parameter estimation for elasticity and viscoelastic parameters for bauxite grain size < 315 μm .

| Parameter | Resin 0% | Resin 3% | Resin 6% | Resin 10% |
|-----------|----------|----------|----------|-----------|
| E_i | 28.51 | 29.57 | 82.56 | 25.01 |
| E_0 | 68.62 | 195.31 | 217.95 | 221.79 |
| n | -1.23 | -1.02 | -0.93 | -1.72 |
| \bar{P} | 200.00 | 200.00 | 200.20 | 200.18 |
| p_0 | 1.82 | 1.63 | 1.42 | 1.80 |
| t | -0.10 | -0.18 | -0.06 | -0.09 |
| \bar{P} | 200.00 | 200.10 | 180.02 | 200.16 |

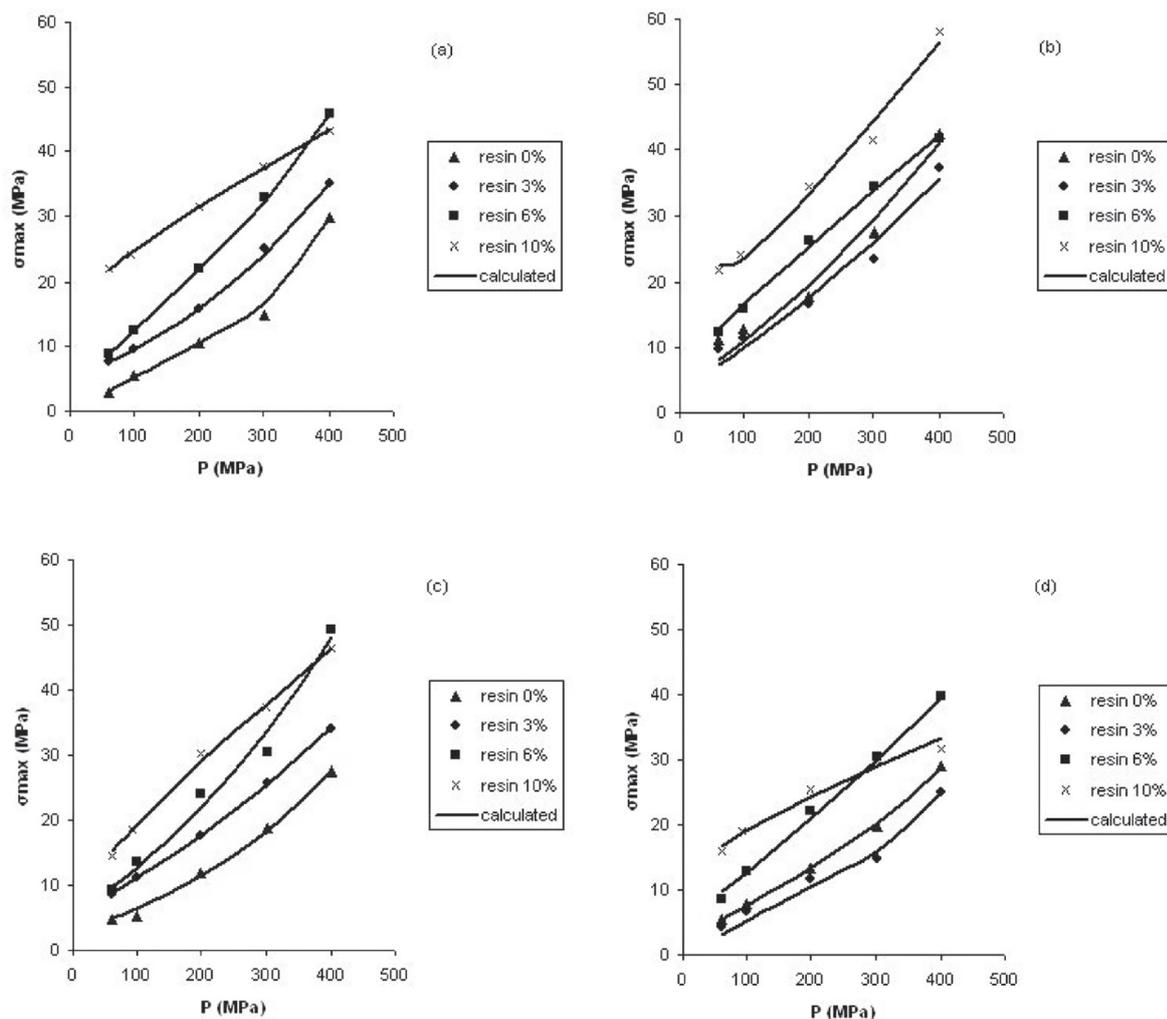


Figure 4. Maximum stress versus molding pressure for bauxite grain size a. 90 μm , b. 100 μm , c. 200 μm and d. 315 μm .

of 100 μm was found to be the one leading to specimens with maximum compressive strength. On the other hand, the lower compressive strength was found for bauxite's grain size equal to 315 μm , as expected [21].

Maximum strain which was observed for the various resin contents is shown in Figure 5. The increment in molding pressure showed an increment in maximum strain. On the other hand, maximum strain seems to decrease when larger granules exist in the raw materials. As far as the influence of the resin content is concerned it affects maximum strain in two distinct modes, according to the grain size. When grain size is lower than 100 μm the sample presents an increment in maximum strain while increasing the resin content. On the contrary bauxite granules equal to 200 or 315 μm lead to samples with lower strain.

In the proposed model for maximum stress and strain, the other two parameters, the elasticity parameter (E) and the viscoelastic exponent (p) depend on the molding pressure as shown in Figures 6 and 7.

Elasticity parameter seems to indicate a particular behavior, as shown in Figure 6. It appears that there is a critical value of molding pressure between 100 and 200 MPa, where elasticity parameter exhibits a minimum value and then increases. Modulus of elasticity is connected to porosity of the material, as claimed elsewhere [14, 22]. Specifically, less dense materials obtained by lower molding pressures or resin contents should present lower value of the elasticity parameter. In this study, it is shown that this claim stands only when porosity is lower than 20% and in this case with porosities larger than 20% (25-35%) less dense material might show slightly higher elasticity parameter. For molding pressure higher than 200 MPa the above statement is confirmed. In addition, larger grain size leads to higher elasticity parameter, as shown in Figure 6 and proved by Chaim et al.[22]. Finally, Figure 7 indicates the significant change of viscoelastic parameter p according to molding pressure. In particular, p seems to diminish while both molding pressure and raw materials' grain size increases.

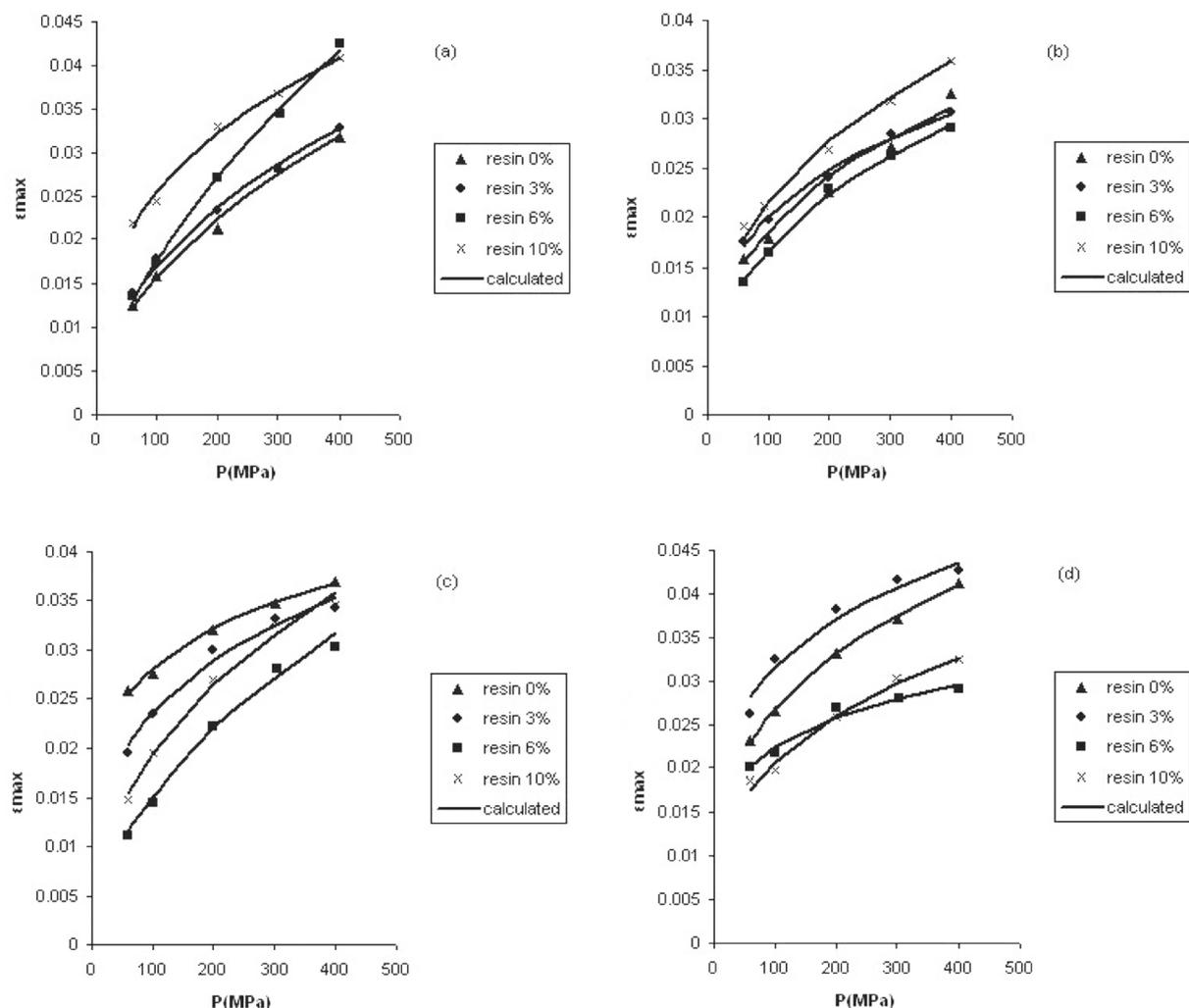


Figure 5. Maximum strain versus molding pressure for bauxite grain size a. 90 μm , b. 100 μm , c. 200 μm and d. 315 μm .

CONCLUSIONS

In this study mechanical properties of bauxite refractories with phenol-formaldehyde resin as binder were investigated. The failure of the samples was initiated by the formation and growth of microcracks. The stress - strain data obtained from the compression test were modeled using parameters with physical meaning. Maximum stress (σ_{max}), maximum strain (ϵ_{max}), elasticity parameter (E), and viscoelastic parameter (p) were correlated to molding pressure. After data processing it was noticed that when increasing molding pressure maximum stress, maximum strain and elasticity

parameter increased, while the viscoelastic parameter decreased. Resin content increases compressive strength, while bauxite's grain size leads to samples with lower stress and strain resistance.

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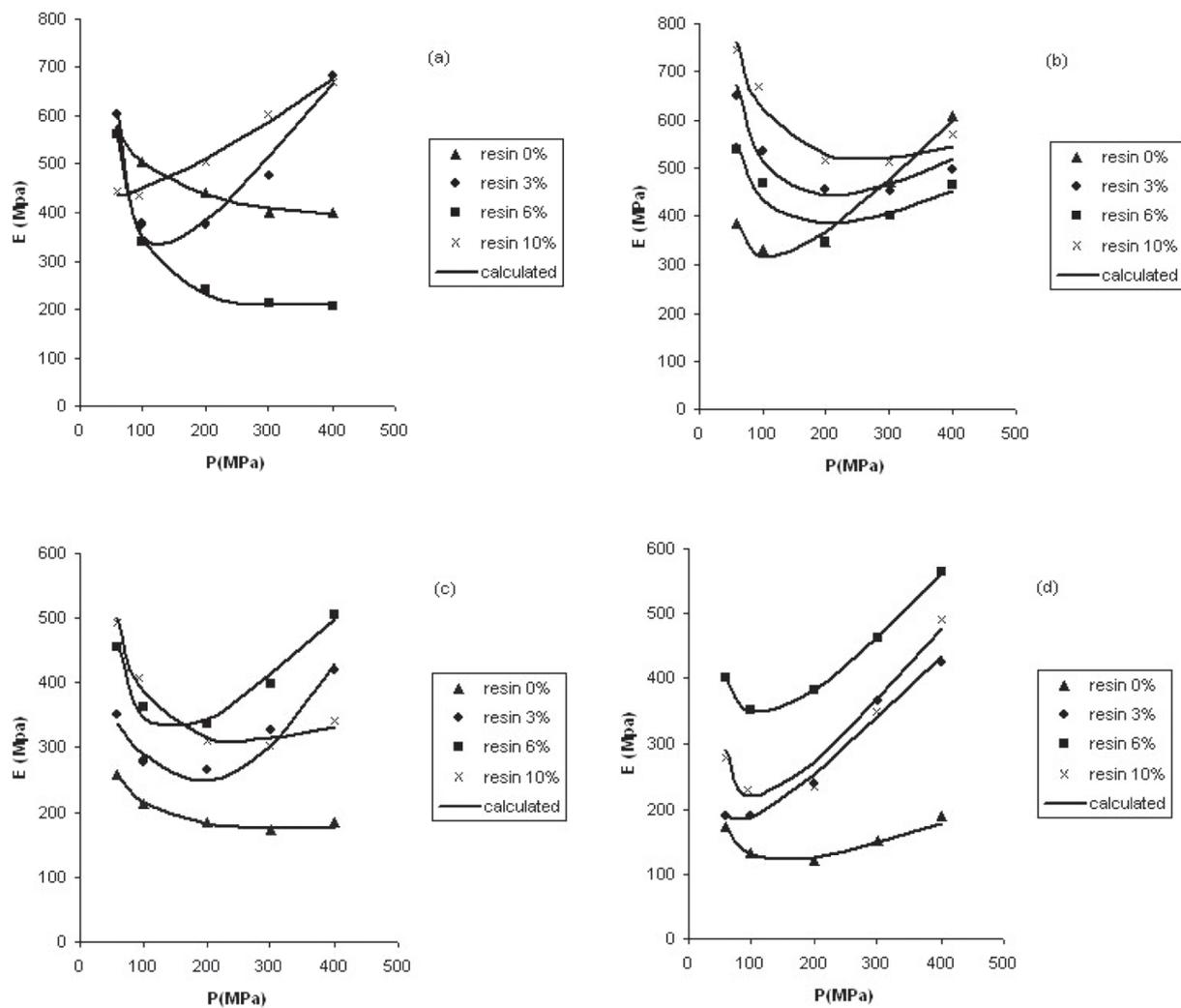


Figure 6. Elasticity parameter versus molding pressure for bauxite grain size a. 90 μm , b. 100 μm , c. 200 μm and d. 315 μm .

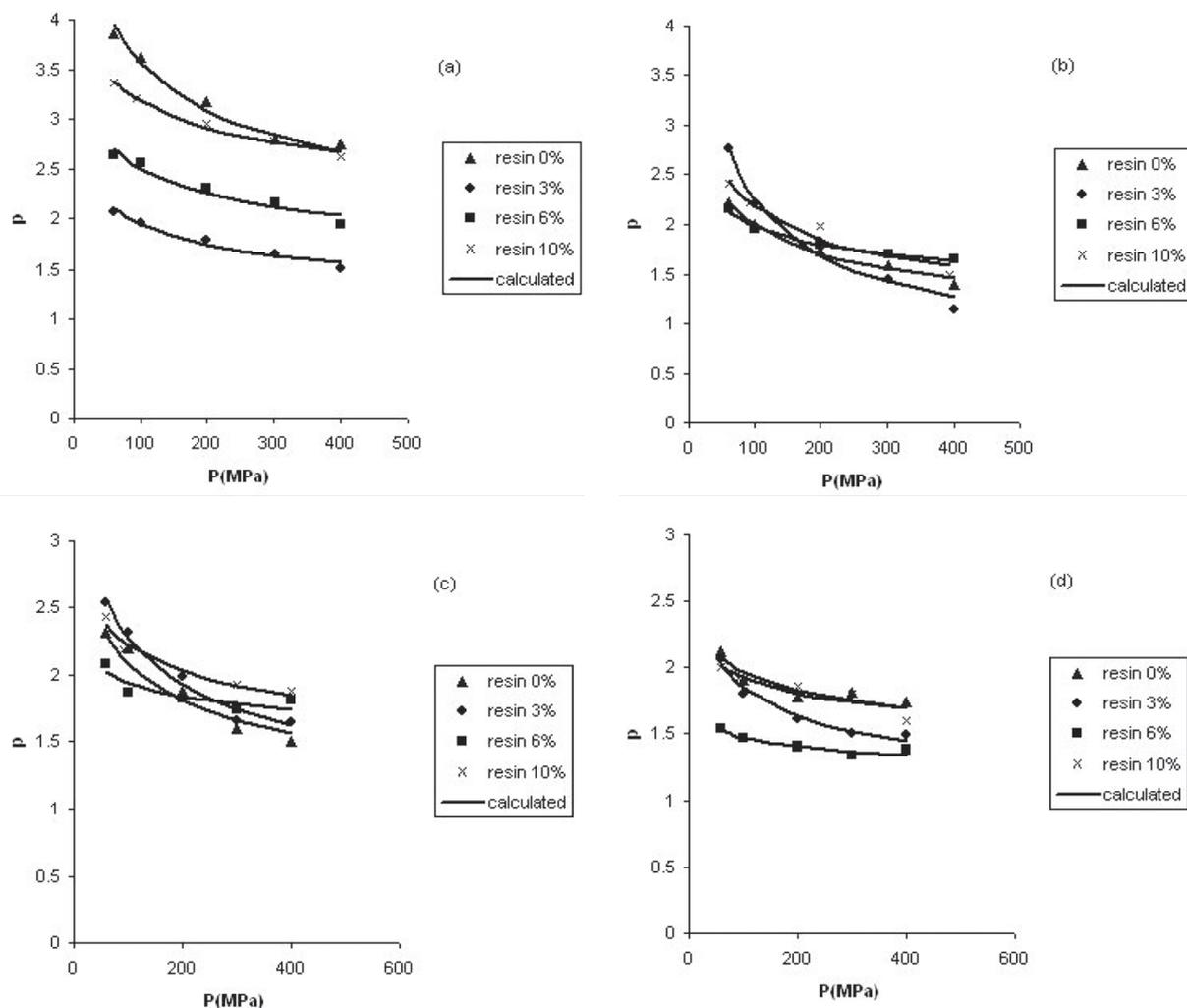


Figure 7. Viscoelastic parameter versus molding pressure for bauxite grain size a. 90 μm , b. 100 μm , c. 200 μm and d. 315 μm .

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