Use of fly ash in ceramic tiles: elastic properties during firing

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Two green ceramic materials were studied during heating from room temperature to 1100°C. One material (CG) contained clay (60 mass %) and grog (40 mass %), while the other (CGF) contained clay (60 mass %), grog (20 mass %), and fly ash (20 mass %). The investigated green ceramics are a mixture of minerals (kaolinite, illite, muscovite, calcite, and quartz). The main improvement of the mechanical properties between 20 and 300°C is due to the liberation of physically bound water. In the temperature region from 300 to 900°C very small changes of the sample volume are observed, and Young’s modulus slightly increases. From 900 to 1100°C, the sintering and creation of new phases causes a large shrinkage of the sample volume, and Young’s modulus dramatically increases its value. The total shrinkage of the sample volume during heating is ~6% for CG and ~24% for CGF. The relative change of Young’s modulus is ~220% for CG and ~190% for CGF.

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1. Introduction

In the past decades there has been continuing effort to use various kinds of waste in the ceramic industry, thus helping to minimize their adverse impact on the environment. For example, organic waste has been successfully used in the manufacturing of porous bricks with a low thermal conductivity, or calcite waste has been used as a flux, decreasing the irreversible contraction during firing of the bricks and tiles.

Another waste intensively studied for reuse applications in civil engineering is fly ash from thermal power stations. It is an alternative source of minerals that are usually present in the composition of building ceramics. In fact, there are similarities between fly ash and traditional minerals, such as their composition and fine particles, because fly ash is a mixture of SiO₂, Al₂O₃, Na₂O, Fe₂O₃, CaO, TiO₂, and some other minerals. Moreover, it has been concluded that fly ash added to a raw mixture leads to an improvement of mechanical properties of the fired ceramics. In particular, the mechanical strength of the ceramic tiles with fly ash as a raw material fulfills the necessary requirements for handling under industrial conditions.

When reusing fly ash in the ceramic industry, the main challenge is to find its optimal amount in a ceramic mixture from the viewpoint of the final properties of ceramic products as well as the production process. The latter is based on firing of the ceramic mixture, which is energetically demanding. To save time and energy, it is desirable to carry out the firing as short time as possible, without causing any damage to the fired body. Therefore, it is crucial to use a safe upper limit of the heating or cooling rate of the ceramic bodies. Its estimation is a complex task that requires the knowledge of the mechanical strength $\sigma$, Young’s modulus $E$, Poisson’s ratio $\nu$, thermal diffusivity $\alpha$, and coefficient of linear thermal expansion $\alpha$ as functions of the actual temperature during firing. A slight simplification is that the mechanical strength can be approximately calculated from Young’s modulus, as the two are mutually proportional.

It must be taken into account, however, that firing may strongly affect the properties of the manufactured building ceramics, such as the mechanical strength, density, firing shrinkage, water absorption, and porosity. The reason is that the raw mixture from which they are prepared usually contains a high amount of kaolinitic and/or illitic clay and these materials exhibit changes in their physical properties due to dehydration at lower temperatures, phase changes during dehydroxylation, high-temperature reactions, and sintering. In addition, quartz, feldspar, and calcite are very common components of ceramic clays, and these minerals also change their composition and structure during firing.

The objective of this paper is an experimental investigation of mechanical behavior during firing of two ceramic materials that are employed for the production of ceramic tiles. In one material fly ash was added, while the other one contains no fly ash. To study the processes running in these ceramic materials during firing, we shall conveniently use a series of thermal analyses—the thermogravimetry (TGA), differential thermal analysis (DTA), thermodiattometry (TDA), and modulated-force thermomechanical analysis (mTMA)—combined with the X-ray diffractometry (XRD).

2. Experimental

2.1 Samples

Two types of samples, denoted as CG and CGF, were prepared for the investigation of elastic properties. Both samples contained clay and grog, and sample CGF contained fly ash in addition (see Table 1). The clay, denoted as B1, was supplied by the

Table 1. Composition of samples (mass %)

| Sample | Clay (%) | Grog (%) | Fly ash (%) |
|--------|----------|----------|-------------|
| CG     | 60       | 40       | 0           |
| CGF    | 60       | 20       | 20          |

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LB-Minerals Ltd., Czech Republic. It consists of kaolinite (65 mass %), illite (25 mass %), muscovite (3 mass %), free quartz (5 mass %), and 2 mass % of undefined filler.\(^{21}\) The gog was made from clay B1 fired at 1000°C with a soaking time 90 min at the highest temperature. The fly ash came from the electric power plant in Hodonin, Czech Republic. The chemical compositions of clay B1 and fly ash are given in Table 2.

The gog and fly ash were ground and sieved and then mixed with clay B1 and water to obtain a plastic mass with a water content \(\sim 25\) mass %. Subsequently, cylindrical samples with diameters 11.5 mm were prepared with a laboratory extruder. Finally, the samples were freely dried in the open air after which they contained \(\sim 2\) mass % of physically bound water.

### 2.2 Resonant mf-TMA

The resonant mf-TMA is based on the resonant vibration of a sample in the fundamental flexural mode. We used it for the measurement of Young’s modulus \(E\) during heating at a rate 5°C·min\(^{-1}\) from room temperature to 1100°C on samples with the initial dimensions \(\phi 11 \times 140\) mm. The resonant frequency \(f(t)\) at a temperature \(t\) was used to calculate the modulus, using the formula\(^{22,23}\)

\[
E(t) = 1.65623 \frac{m_0 l_0^3}{d_0} + \frac{1 + \alpha(t)}{1 + \varepsilon(t)} \cdot f^2(t),
\]

where \(l_0\), \(d_0\), and \(m_0\) are the sample length, diameter, and mass at room temperature, respectively. The relative thermal strain \(\varepsilon(t) = \Delta l(t)/l_0\) and the relative mass loss \(\alpha(t) = \Delta m(t)/m_0\) of the sample were measured by dilatometer and TG analyzer, respectively. In Eq. (1) an equal relative expansion of the sample in both directions, axial and radial, is assumed and a correction due to a short sample length \((l_0 < 20d_0)\) is taken into account. We used an mf-TMA apparatus described in detail previously.\(^{23}\)

### 2.3 TDA, TGA, and DTA

According to Eq. (1), the determination of Young’s modulus requires the measurement of the actual dimensions and mass of the sample during heating. This task was carried out by the TDA and TGA analyses. Given the relative strain \(\varepsilon(t)\) as measured by dilatometer and the sample length and diameter \(l_0\) and \(d_0\) at room temperature, we determined the length \(l(t)\) and thickness \(d(t)\) of the sample at the temperature \(t\). Similarly, we determined the mass \(m(t)\) at the temperature \(t\) from the relative mass loss \(\alpha(t)\) measured by a TGA/DTA analyzer Derivatograph 1000 (Hungary). The density \(\rho\) at the temperature \(t\) is then given as

\[
\rho(t) = \rho_0 \frac{1 + \sigma(t)}{1 + 3\varepsilon(t)}.
\]

The initial density was measured to be \(\rho_0 = 1540 \text{ kg} \cdot \text{m}^{-3}\) for CG and \(\rho_0 = 1410 \text{ kg} \cdot \text{m}^{-3}\) for CGF.

To reduce the temperature shift between the TGA, TDA, and mf-TMA curves, the samples for these analyses were prepared with the same cross-section. The sample length was 40 mm for the TDA and 20 mm for the TGA and DTA.

A heating rate 5°C·min\(^{-1}\) was the same for the TDA, TGA, DTA, and mf-TMA. Green samples were heated in the air up to 1100°C, which is assumed to be the highest firing temperature used in the clay building ceramics industry.\(^{19}\) A reference compact sample for the DTA with an approximately the same size and weight as the measured green ceramic sample was made from pressed Al\(_2\)O\(_3\) powder.

### 2.4 XRD analysis

The XRD analysis was performed by a diffractometer Philips PW 1170 with a Cu anticathode (\(\lambda_{Cu} = 0.15406\) nm), accelerating voltage 40 kV, beam current 25 mA, and scanning rate 1°20’·min\(^{-1}\).

### 3. Results and discussion

The results of the XRD analysis were carried out at room temperature for green clay B1, clay B1 fired at 1000°C, and fly ash (see Fig. 1) as well as for samples CG and CGF fired at 1000 and 1100°C (see Fig. 2). We identified the following phases in the samples: quartz, kaolinite, and illite/muscovite in clay B1, and quartz, calcite, anhydrite, and CaO in fly ash. During heating at temperatures above 1000°C, mullite, calcian feldspar anorthite, and a mineral of melilite group (presumably gehlenite) were created in both CG and CGF samples.\(^{26,27}\) Comparing the XRD patterns for 1000 and 1100°C, it is clear that the amount of mullite increased with temperature.

The results of the TGA for the mass losses of samples CG and CGF are given in Fig. 3. They show that several drops in the sample mass of CG can be identified. One occurs at \(\sim 150°C\) and is due to the liberation of physically bound water from the pores and surfaces of the crystals in the samples. This process is reflected by a relatively large decrease in the mass by \(\sim 2\) and \(\sim 2.5\) % for sample CG and CGF, respectively. The other one occurs in the 250–400°C range and is due to the burning of organic additives in clay B1. This was confirmed by the evolved gas analysis (EGA) which recorded CO\(_2\) during heating from 300 to 500°C.\(^{21}\) Another decrease is sudden (by \(\sim 6\)%) and takes place between 500 and 650°C and corresponds to the dehydroxylation of kaolinite. The dehydroxylation is accompanied by shrinkage of the samples as well as a mass loss.\(^{26,27}\) These three drops are present also for sample CGF. However, this sample undergoes yet another sudden drop in the mass within the range \(\sim 650–800°C\). It corresponds to the decomposition of calcite (contained in fly ash) given as CaCO\(_3\) → CaO + CO\(_2\) and is accompanied by a mass loss of 44% of calcite.\(^{59}\) Since all these four processes are related to the consumption/release of heat, they are represented as maxima/minima peaks in the DTA curve (see Fig. 4). Besides these four peaks, there is a maximum peak that corresponds to the collapse of the dehydroxylated phyllosilicate structures at \(\sim 960°C\). This process does not affect the sample masses and, therefore, it is not present in the TGA curves from Fig. 3.

The results of the TDA in the temperature interval between room temperature and 1100°C are given in Fig. 5. They show the thermocapillometric behavior of samples CG and CGF in detail before a dramatic contraction above the temperature 900°C occurs. Below this temperature, the relative expansion is very
small and varies between $-0.06\%$ and $+0.05\%$ for sample CGF and between $0\%$ and $+0.15\%$ for sample CG. Although sample CG and CGF were prepared and stored under the same condition, sample CGF contained notably larger amount of physically bound water (see Fig. 3), which caused its contraction up to $200^\circ\text{C}$. On the other hand, the liberation of physically bound water in this range slowed down the expansion of sample CG to some extent. Between $200^\circ\text{C}$ and $850^\circ\text{C}$ the behavior of the relative expansion of both samples CG and CGF is practically identical. In particular, we observe contraction during dehydroxylation ($500^\circ\text{C}$ to $570^\circ\text{C}$) and expansion near the $\alpha \rightarrow \beta$ transformation of quartz ($570^\circ\text{C}$). The fast contraction above $900^\circ\text{C}$ is a superposition of several effects that are accompanied by the contraction. These are, intensive sintering and the collapse of the metakaolinite lattice; in addition, for the CGF sample the decomposition of calcite also takes place here. The results of the TGA curves from Fig. 3 and the TDA curves from Fig. 5 were used to calculate the density of samples CG and CGF as a function of the temperature by Eq. (2). The so obtained density curves are shown in Fig. 6. For both CG and CGF samples they decrease in the temperature region from 20 to $900^\circ\text{C}$. Obviously, this is caused by significant mass losses vs. small volume changes in both samples. Note that the most sudden density drop occurs for both samples in the dehydroxylation region (around $550^\circ\text{C}$). At temperatures above $900^\circ\text{C}$, the sample masses are almost constant, but their volumes rapidly contract, which leads to substantial increases in the sample densities.

Young’s modulus, like other elastic properties, is a function of the sample dimensions and density. The temperature changes in the latter quantities must be taken into account, if a correct value of $E$ is to be obtained. All these influences are considered in Eq. (1). The curves of the $\text{mf-TMA}$ results calculated from this equation are shown in Fig. 7. In the range $20–250^\circ\text{C}$ Young’s
modulus increases by $\sim 45\%$ for sample CG and by $\sim 21\%$ for sample CGF. This is typical of the mf-TMA of green ceramics with an equilibrium amount of physically bound water.\textsuperscript{18} The liberation of this water from pores and crystal sides makes the contacts between crystals stronger.

In the subsequent range, between $\sim 250$ and $\sim 500^\circ \text{C}$, Young’s modulus remains approximately constant. The next development is determined by the dehydroxylation of kaolinite and illite. This process begins at the temperature $\sim 420^\circ \text{C}$ and finishes at $\sim 700^\circ \text{C}$,\textsuperscript{20} as is also clear from Fig. 4. The dehydroxylation is associated with a mass loss and the creation of a defect microstructure in the dehydroxylated minerals. This is well known for kaolinite.\textsuperscript{29} Therefore, one would expect that there should be a decrease in Young’s modulus during these processes and after their termination. However, our results of the mf-TMA from Fig. 7 do not show any decrease in the modulus at the temperatures above $\sim 500^\circ \text{C}$ for both samples CG and CGF in spite of the fact that $\sim 50\%$ of the samples material underwent the dehydroxylation in this temperature range. A possible explanation may be an improvement of the contacts between crystals of dehydroxylated minerals as well as between these crystals and other components (quartz, grog, feldspar, and calcite). The mechanism of such a contact improvement has not been established so far; solid-state sintering might be such a mechanism, as was suggested in firing of bricks made from very fine kaolinitic clay particles at the firing temperature $\sim 600^\circ \text{C}$.\textsuperscript{30} Another explanation may be due to the fact that the dehydroxylation is a source of electrically charged defects.\textsuperscript{29} Many of them are assumed to be located on the crystal faces and, consequently, the attractive van der Waals electrostatic forces fortify samples.

After the dehydroxylation (above $700^\circ \text{C}$) the thermal behavior of Young’s modulus is still similar for both samples CG and CGF, exhibiting an increase with temperature. However, in the interval from $850$ to $1100^\circ \text{C}$ we registered a steep increase in the modulus. Such behavior may be attributed to solid-phase sintering. In addition, the collapse of the metakaolinite lattice and a subsequent formation of spinel at $\sim 950^\circ \text{C}$ (the exothermic peak in Fig. 2) and mullite at the highest temperatures also lead to an improvement of Young’s modulus.\textsuperscript{31} Another possible source of this improvement may occur in the CGF sample. Indeed, around anorthite crystals, being larger than their father crystals, a radial stress is created, which heals microcracks. Such a phenomenon was observed during heating in porcelain in the region of the $\alpha \rightarrow \beta$ transformation of quartz.\textsuperscript{32,33}

The total shrinkage of the sample volume during the whole heating ($20$–$1100^\circ \text{C}$) was measured to be $\sim 6\%$ for sample CG and $\sim 24\%$ for sample CGF. The corresponding relative change of Young’s modulus is $\sim 220\%$ for CG and $\sim 190\%$ for CGF.

The mechanical strength is also a crucial mechanical parameter of every ceramic material. It is not only of practical importance for the final fired ceramics, but it is also important during firing. We did not measure the mechanical strength of the studied
samples during firing. Rather, we used that the mechanical strength and Young’s modulus are mutually correlated: the relationship between them is approximately linear with a value of the regression coefficient close to 1.\textsuperscript{71} This allowed us to obtain a reliable picture of the development of the mechanical strength during firing from the profile of the temperature dependence of Young’s modulus. Namely, the mechanical strength has the same type of behavior during firing as the modulus.

Our above measurements show that, from the viewpoint of mechanical properties, the heating stage of the sintering and creation of new phases causes a shrinkage of the sample volume and Young’s modulus as well as the mechanical strength are significantly improved.

4. Conclusions

Two green ceramic materials denoted as CG (without an addition of fly ash) and CGF (with an addition of fly ash) containing clay (60 mass %), grog (40 or 20 mass %), and fly ash (0 or 20 mass %) were investigated during heating from room temperature to 1100°C. The obtained results lead to the following conclusions.

- The investigated green ceramics are a complex mixture of minerals (kaolinite, illite, muscovite, calcite, and quartz). Typical processes which run in this mixture are the liberation of physically bound water (20–300°C), dehydroxylation of kaolinite and illite (400–600°C), \( \alpha \to \beta \) transformation of quartz, decomposition of calcite (700–850°C), transformation of phyllosilicates into spinel phase and mullite (above 950°C), creation of gehlenite and anorthite (above 950°C), and sintering (above 700°C).
- The main improvement in Young’s modulus \( E \) at lower temperatures corresponds to the liberation of physically bound water. \( E \) increases here by \( \sim 45\% \) for CG and \( \sim 21\% \) for CGF.
- In the temperature region from 300 to 900°C very small changes in the sample volume are observed, and \( E \) slightly increases above 500°C for CG and above 700°C for CGF.
- From \( \sim 900 \) to 1100°C, where the sintering and creation of new phases causes a shrinkage of the sample volume, \( E \) dramatically increases.
- The total shrinkage of the sample volume during heating (20–1100°C) is \( \sim 6\% \) for CG and \( \sim 24\% \) for CGF. The relative change of Young’s modulus is \( \sim 220\% \) for CG and \( \sim 190\% \) for CGF.

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