The influence of heat on elastic properties of illitic clay Radobica

Miroslav JANKULA,* Tomáš HÚLAN,* Igor ŠTUBŇA,* Ján ONDRUŠKA,* Rudolf PODOBA,** Peter ŠIŇ,** Peter BAČÍK**** and Anton TRNÍK*****†

*Department of Physics, Constantine the Philosopher University in Nitra, A Hlinku 1, 94974 Nitra, Slovakia
**Department of Structural Ceramics, Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 040 01 Košice, Slovakia
***Department of Physics, Faculty of Civil Engineering, Slovak University of Technology, Radlinského 11, 81368 Bratislava, Slovakia
****Department of Mineralogy and Petrology, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia
*****Department of Materials Engineering and Chemistry, Czech Technical University in Prague, Thakurova 7, 16629 Prague, Czech Republic

Brick clay from a locality Radobica, Central Slovakia, which was exploited for brick manufacturing in the past, was investigated for its possible reuse in the brick industry. The crystalline phases of the green sample were 48% of quartz, 37% of illite, 13%, of Na-feldspar and 2% of calcite. The measurements of Young’s modulus of clay samples were performed during heating up to 1100°C and also at room temperature on samples preheated at temperatures from 100 to 1100°C. It was found during firing that 1) the physically bound water is released in 3 steps (up to 300°C) and reaches ~2.5 wt %. The thermal expansion is decelerated by setting the crystal closer at low temperatures. Young’s modulus increases in its values (~36%) which is a result of the closer structure that is created via release of the physically bound water. 2) The mass loss during dehydroxylation (450–750°C) is ~3 wt %. The superposition of dehydroxylation and α → β transformation of quartz creates a step ~3% of the relative thermal expansion. Young’s modulus slightly decreases in its values, the dehydroxylation does not influence this trend. 3) Above 900°C, the intensive contraction due to sintering is observed and a steep increase (250%) of Young’s modulus takes place in this temperature interval. The irreversible changes of the Young’s modulus measured at room temperature after firings at the temperatures from the interval 100–1100°C give a different picture. Dehydroxylation affects Young’s modulus very significantly decreasing its values from 7.8 GPa (at 400°C) to 4.3 GPa (at 700°C). After dehydroxylation, the sintering increases Young’s modulus. Since the porosity remains relatively high (~30%) and a part of the glassy phase in the sample fired at 1100°C is relatively low (25%), the Young’s modulus is low even after firing at 1100°C (9.3 GPa).

©2015 The Ceramic Society of Japan. All rights reserved.

Key-words : Illitic clay, Elastic properties, Mechanical strength, Thermal analyses

[Received January 29, 2015; Accepted May 26, 2015]

1. Introduction

Clays, which contain kaolinite and/or illite, are essential ingredients for building ceramic manufacture for its plasticity, workability and green strength.1) The most common natural additional minerals included in clays are quartz, carbonates, feldspar, iron oxides and sulfides. In addition, clays usually contain some organic material. The structural features of the ceramics are developed during the shaping/molding the green ceramic product and its drying, and finally the structure and properties of the ceramic product are consolidated during the firing, in which physical and chemical processes occur among the different minerals.2,3,4) Required mechanical properties of the building ceramics are associated mainly with mechanical strength and Young’s modulus which are the most important. These two parameters are largely dependent on structural characteristics that develop during firing.3,4,5)

Young’s modulus and mechanical strength are important not only for building applications but also for a regime of the firing process where determine the maximum rate of heating. In spite of the importance of Young’s modulus for firing the building ceramic products, it was studied during heating and cooling very rarely. As far as we know, Young’s modulus of the green ceramic sample was measured during heating only for porcelain mixture,6) for heat-proof stove ceramics7) and for almost pure illite.8) Some common features can be observed in a development of Young’s modulus: 1) a loss of the remains of the physically bound water from pores increases the Young’s modulus of the green ceramic mass in a significant measure. For example, Young’s modulus of the green porcelain mixture increases ~30%5–8) 2) no significant changes of Young’s modulus were observed in the dehydroxylation region;3,9) 3) α → β transformation of quartz at 573°C, which is characterized with intensive expansion and sharp decrease of Young’s modulus of quartz grains in the ceramic mixture,3) does not influence elastic properties of the green ceramic sample during its heating;3,9,10) 4) sintering, which starts at ~700°C, increases the Young’s modulus.5,11)

In addition to direct observing the influence of heat on the mechanical properties during heating, a commonly used way how to find these relationships is the measurement of the mechanical properties after firing.1,4,11) To determine the suitability of some clay for ceramic productions, different tests are performed at room temperature on samples fired at temperatures higher than

 DOI http://dx.doi.org/10.2109/jcersj2.123.874

©2015 The Ceramic Society of Japan
700°C. The mechanical strength, porosity, irreversible shrinkage and absorbability are probably most often measured mechanical quantities. Development of the phases during firing is experimentally studied through thermal analyses, mainly: differential thermal analysis (DTA), thermogravimetry (TGA), thermolatometry (TDA) and X-ray diffraction (XRD). The material of the present investigation is the clay from locality Radobica, Central Slovakia. The clay was exploited for brick manufacturing in the past. Its re-exploiting can be attractive in a new ceramic mixture with a fly-ash, which is a perspective waste raw material for a green ceramic body. The goal of this paper is a study of the elastic properties of this clay during thermal treatment and also as a function of the firing temperature.

2. Experimental

2.1 Samples

The clay used to prepare the samples was excavated from a depth more than 1.2 m (at smaller depths the samples contained a large amount of organic mass and sample properties intensively varied). The clay was ground and mixed with distilled water to obtain a plastic mass with the water content 25 mass%. Cylindrical samples were prepared with a laboratory extruder. After open air free drying, the samples contained ~2 mass% of the physically bound water.

2.2 Measurement methods

The phase analysis was performed by powder X-ray diffraction using a diffractometer BRUKER D8 Advance with a Cu anticathode (Δλ = 1.54060 A), accelerating voltage 40 kV, and beam current 40 mA. For a quantitative analysis the Rietveld method was used with a corundum internal elaton. A content of quartz was also checked with DSC and content of illite with TGA.

A picture of the fracture area was obtained with a scanning electron microscope (SEM) Auriga Compact FIB-SEM from the Carl Zeiss Company, using an accelerating voltage 5 kV. Prior to the SEM observation, the samples were treated by carbon vapor deposition.

DTA and TGA were performed by the analyzer Derivatograph 1000 on compact bodies with dimensions of Ø20 × 20 mm and mass ~3.5 g. A reference compact sample for DTA, which had approximately the same size and mass as the measured green clay sample, was made from pressed Al₂O₃ powder. The experiments were repeated three times for each sample type to ensure reproducibility of our results. As blank curves, we used data from a second measurement of the same material under identical conditions. Therefore, any reversible processes that take place in the material cannot be registered in these two thermal analyses.

The relative expansion in dependence on the temperature was experimentally studied through thermal analyses, mainly: differential thermal analysis (DTA), thermogravimetry (TGA), thermolatometry (TDA) and X-ray diffraction (XRD). The samples were cooled in the furnace down to room temperature. Temperature of 1100°C was chosen for both types of measurement of the mass changes and in the DTA/TGA, and as 1100°C for TDA and mfg-TMA. In type 2 we measured the samples at room temperature that were preheated with a heating rate of 5°C·min⁻¹. The maximum temperature was chosen as 1050°C for the measurement of the mass changes and in the DTA/TGA, and as 1100°C for TDA and mfg-TMA. In type 2 we measured the samples at room temperature that were preheated with a heating rate of 5°C·min⁻¹ on 100, 200, …, 1100°C without a soaking at the highest temperature. The samples were cooled in the furnace down to room temperature. Temperature of 1100°C was chosen for both types of measurements because it is the presumptive highest firing temperature used in the industrial production of clay bricks and tiles. For the all measurements the ambient gas was air.

3. Results and discussion

The results of the XRD analysis were carried out at room temperature for green clay Radobica, and clay fired at 1000°C (see Fig. 1). Quantitative XRD analysis and thermal analyses DSC and TGA revealed that the green clay contained 48% of quartz, 37% of illite, 13% of Na-feldspar and 2% of calcite. Taking into account that a color of the fired samples was dark red, ferrous oxides are also present in the clay.

After firing at 1000°C, the main crystalline phases are 51% of quartz, 14% of Na-feldspar, 3% of hematite and 32% of illite. The modulated force thermomechanical analysis (mfg-TMA), which is based on the resonant vibration of the sample in the fundamental flexural mode, was used for the measurement of the resonant frequency. Young’s modulus E may be calculated for a cylindrical sample with a uniform cross-section by a formula given in that can be rewritten for varying dimensions and mass

\[ E = 1.675 \frac{m_{fl0} 1 + \mu}{d_{fl} 1 + \epsilon^2}, \]

where \( f \) is the resonant frequency of the fundamental mode of vibration and other quantities are the same as for Eq. (1). Since the sample is not slender (its dimensions were Ø12 × 130 mm), a correction coefficient \( T = 1.0429 \), which was calculated from a formula given in, was included into Eq. (2).

The mechanical strength was measured by the three-point-bending method. The sample of the size Ø12 × 120 mm was subjected to a loading force, which increased with a rate of 2 N·s⁻¹. A set of 10 samples were broken at room temperature after its firing at the selected temperature from the interval (100, 1100°C).

Two types of measurements were performed in the present study. In type 1 we used the green clay samples that were studied from the room temperature up to a temperature 1050 or 1100°C under heating at a linear rate 5°C·min⁻¹. The maximum temperature was chosen as 1050°C for the measurement of the mass changes and in the DTA/TGA, and as 1100°C for TDA and mfg-TMA. In type 2 we measured the samples at room temperature that were preheated with a heating rate of 5°C·min⁻¹ on 100, 200, …, 1100°C without a soaking at the highest temperature. The samples were cooled in the furnace down to room temperature. Temperature of 1100°C was chosen for both types of measurements because it is the presumptive highest firing temperature used in the industrial production of clay bricks and tiles. For the all measurements the ambient gas was air.

![Fig. 1. XRD pattern of the green clay sample (black line) and clay sample fired at 1000°C (gray line) Q – quartz, I – illite, F – feldspar, C – calcite.](image-url)
amorphous phase. From these data and from densities of these minerals (2.65 g cm\(^{-3}\) for quartz, 2.70 g cm\(^{-3}\) for illite, 2.56 g cm\(^{-3}\) for feldspar, 5.26 g cm\(^{-3}\) for hematite and 2.61 g cm\(^{-3}\) for sodium glass) as well as from the bulk densities, which are 1.92 g cm\(^{-3}\) for the green sample and 1.86 g cm\(^{-3}\) for the fired sample, we can estimate their porosities. We obtain \(\approx 30\%\) for the green sample and \(\approx 32\%\) for the sample fired at 1000°C. These values are approximately the same as measured porosities (Fig. 10). This relatively high porosity is also visible in SEM picture of the fracture surface in Figs. 2(a) and 2(b).

### 3.1 Development of the elastic properties during heating

The composition and microstructure of clay change during heating. In general, results of the thermal analyses DTA, TGA and TDA reveal the processes which take place in the clay. Young’s modulus is a function of the sample dimensions and mass. The temperature changes in these quantities must be taken into account, if a correct value of \(E\) should be obtained. All these influences as well as actual value of the resonant frequency must be considered in Eq. (2). Therefore, the values of Young’s modulus are calculated from the results of TGA, TDA and mf-TMA.

The endothermic peak in the DTA curve (Fig. 3) in the temperature range from 25 to 220°C represents the release of the physically bound water from the pores and surfaces of the crystals in the clay. This process is reflected by a relatively large decrease in the sample mass by 2% (Fig. 4), and a small contraction registered in the TDA curve (Fig. 5). The small value of the contraction and significant mass loss lead to a decrease in the bulk density (Fig. 6). From the mechanical point of view, the release of the physically bound water makes the contacts between crystals stronger and Young’s modulus increases \(\approx 36\%\). A very similar elastic behavior at these low temperatures was also found in ceramic mixtures based on kaolinite and illite.\(^6\)

In the temperature range from 220 to 400°C a DTA exothermic peak is visible, which is related to a burning of organic impurities (Fig. 3). This process leads to a small decrease of the sample mass by 0.5% (Fig. 4). The mass loss and expansion of the sample (Fig. 5) causes a continuing decrease in the bulk density (Fig. 6). We can also expect a creation of the additional pores instead of the burned organic material. Since the Young’s modulus depends directly on the bulk density and porosity, it decreases in this temperature region (Fig. 7).

The third process is dehydroxylation of illite which begins at 400°C and finishes at 800°C. It runs in two steps which reach the maximum rate at the temperatures 550 and 630°C being in accordance with the results given in.\(^23\) The dehydroxylation of illite is accompanied by mass loss as well as expansion of the
A consequence of the expansion and mass loss of the sample is a decrease in the bulk density. The values of Young’s modulus pass through very flat minimum between 400 and 800°C.

The sample has a relatively high amount of quartz that proves as a sharp minimum in the DTA curve and step in the TDA curve around 573°C as a consequence of the \( \alpha \rightarrow \beta \) transformation of quartz. This transformation causes the additional decrease of the bulk density. In spite of that, the Young’s modulus does not reflect the \( \alpha \rightarrow \beta \) transformation of quartz through its decrease.

The last interval, which covers the temperature above 800°C, is connected with the high-temperature reactions in illite, sintering and vitrification. Above 800°C the mass change is very slow, i.e. the dehydroxylation is completed. There are two peaks in the DTA curve: one endothermic (at 920°C) and one exothermic peak (at 975°C), which are typical for illite, and are ascribed to a creation of the glassy phase and transformation of metaillite into spinel. The shrinkage of the sample caused by sintering and changes in the metaillite lattice is steep and reaches ~2%. This contraction results in the increase of the bulk density. These high-temperature processes increase Young’s modulus 3.2 times during heating from 800 to 1100°C.

3.2 Mechanical properties after firings at room temperature

We also measured mechanical properties of the studied clay in a dependence on the firing temperature from the interval (25, 1100°C). To explain the results of Young’s modulus and mechanical strength, a mass change and a dimension change as well as porosity and bulk density were also measured. The measurements were performed at room temperature.

The values of the relative mass loss are depicted in Fig. 8. The mass loss is registered at the low temperatures (up to 200°C), which is caused by a release of the physically bound water (the initial moisture of the samples was ~1.5 mass %). The similar results we obtained during heating (Fig. 4). The next contribution to the mass loss is a burning of the organic matter. An increased rate of the mass loss, observed above 500°C, is connected with dehydroxylation of illite. The irreversible volume change, which is depicted in Fig. 9, is negligible up to 500°C. Above this temperature, the sample expands due to dehydroxylation. Then we observe a contraction above 800°C when the high-temperature reactions in illite, creation of the glassy phase and sintering begin.

A density and porosity after partial firings are shown in
spar, 216 GPa for hematite and the sample components (i.e. 94 GPa for quartz, 95 GPa for feld-

Young temperature (in Eq. (2)).

The values of Young’s modulus of the green sample, the volume and mass in a little degree. The main responsibility for changing the Young’s modulus have internal processes in the sample such as creation of new phases and sintering which influence the Young’s modulus only in a small degree. The main responsibility for changing the Young’s modulus have internal processes in the sample such as creation of new phases and sintering which influence the resonant frequency in Eq. (2).

The values of Young’s modulus are low for every firing temperature (Fig. 12) and are much lower than Young’s moduli of the sample components (i.e. 94 GPa for quartz, 95 GPa for feldspar, 216 GPa for hematite and ~65 GPa for glass). The Young’s modulus of the green sample, \( E = 7 \) GPa, is comparable with the Young’s modulus of other green ceramics, see for example.\(^{[26]}\) The remove of the physically bound water after low-temperature firings increases Young’s modulus. But dehydroxylation of illite decreases Young’s modulus significantly. This is probably caused with an additional porosity which increases during dehydroxylation. Young’s modulus raises its values above 800°C, which is connected with a sintering, but these values stay low. It can be explained with

1) the high porosity that varies between 28 and 33.5%,

2) the relatively low firing temperature and short time of the firing. Both of them were not sufficient for multilization and more intensive vitrification. A low degree of sintering and vitrification as well as the enduring of the pores is visible in Fig. 2(b).

3) the relatively low content of plastic constituent in the green sample. It does not allow create more glassy phase and mullite.

The next mechanical parameter, which we measured, was mechanical strength in dependence on the firing temperature (Fig. 13). The release of the physically bound water after low-temperature firings increases mechanical strength from 2.7 to 3.2 MPa. This trend is similar to a development of Young’s modulus. On the other hand, the dehydroxylation of illite has no effect on mechanical strength. Its values are almost constant in the temperature interval from 200 to 700°C as was also confirmed for traditional ceramics.\(^{[26]}\) Above 700°C, the mechanical strength rapidly increases due to sintering and reaches 9 MPa at 1100°C. In spite of the theoretical proportionality between mechanical strength and Young’s modulus, courses of these quantities seen in Figs. 12 and 13 are different. The mechanical flexural strength depends on sample surface defects and defect size while Young’s modulus depends on conditions inside the sample. That is why Young’s modulus reflected the dehydroxylation more sensitively than mechanical strength. The values of the mechanical strength as well as Young’s modulus of the investigated fired clay are smaller that those obtained for traditional ceramics in.\(^{[26]}\)

3.3 Elastic properties of the fired ceramics during heating

Finally, we studied relative expansion, bulk density and Young’s modulus of the sample fired at 1100°C during heating up to 1100°C. On the dilatometric curve (Fig. 14), we indicate quartz by a step of the thermal expansion around 573°C. The curve is bent down above 900°C that is caused by the press of the dilatometer’s rod on the softened sample. This typical behavior of the push-rod dilatometer is an indirect confirmation of the presence of the glassy phase.

Because the mass of the fired sample is constant, the bulk density is only a function of the relative expansion. The bulk density slightly decreases from its initial value 1723 kg m\(^{-3}\) at room temperature up to 1683 kg m\(^{-3}\) at 1000°C. In this temperature interval we can indicate only \( \alpha \rightarrow \beta \) transformation of quartz at 573°C as a small decrease of the bulk density.

Young’s modulus of the fired clay sample during heating up to 1100°C is depicted in Fig. 15. There is well visible \( \alpha \rightarrow \beta \)
transformation of quartz at 573°C when Young’s modulus rapidly increases from 9.4 to 20.3 GPa. This S-curve is characteristic for every ceramics with some content of quartz. This increase is caused by closing the circumference cracks around the quartz grains.11,27

4. Conclusions

Brick clay from a locality Radobica, Slovakia was investigated during heating up to 1100°C and also at room temperature after preheated at temperatures from 100 to 1100°C. The green clay contained 48% of quartz, 37% of illite, 13% of Na-feldspar and 2% of calcite. It was found:

- The mass loss increases almost linearly with the firing temperature and reaches 6% at 1100°C.
- The irreversible volume change after firings is negligible up to 500°C. Then we observe an increase in its values up to 800°C when the sintering begins. Above 800°C the intensive contraction due to sintering was observed.
- The relationship between Young’s modulus and firing temperature is complex. After the small increase of Young’s modulus after low-temperature firings, dehydroxylation lowers this mechanical parameter as long as the sintering takes place at and above 800°C. Then Young’s modulus again increases.
- The values of Young’s modulus and mechanical strength are low due to high porosity.
- The relatively low amount of illite, low firing temperature and short time of the firing were not sufficient for Mullitization and more intensive vitrification.

Acknowledgements This research was supported by the grant VEGA 1/0162/15, VEGA 1/0869/13, project “PROMATECH” ITMS No: 2622020186, and by the Czech Science Foundation, Project No. P105/12/G059.

References

1) V. Das Kshama, B. V. Mohan, M. Lalithambika and C. G. R. Nair, Ceram. Int., 18, 359–364 (1992).
2) J. Hlaváč, “Technology of silicates”, SNTL, Praha (1981) [in Czech].
3) B. Čiículos, I. Novák and I. Horváth, “Mineralogy and crystal-chemistry of clays”, SAV, Bratislava (1981) [in Slovak].
4) N. N. Kruglitsky, B. M. Datsenko and B. I. Moroz, Ceram. Int., 18, 78–80 (1984).
5) C. M. F. Vieira, P. R. N. da Silva, F. T. da Silva, J. L. Capitaneo and S. N. Monteiro, Revista Matéria, 10, 526–536 (2005).
6) I. Štúbba, A. Trník, F. Chmelík and L. Vozár, “Advances in Ceramics characterization, raw materials, processing, properties, degradation and healing”, InTech, Rijeka Croatia (2011) pp. 229–244.
7) A. Trník, I. Štúbba, G. Varga, P. Bačík and R. Podoba, J. Ceram. Soc. Japan, 119, 645–649 (2011).
8) T. Húlan, A. Trník, I. Štúbba, P. Bačík, T. Kaljuvee and L. Vozár, Mater. Sci.-Medzg., in press. (2015).
9) S. Kumbach and F. R. Schilling, Eur. J. Mineral., 26, 211–220 (2014).
10) I. Štúbba, A. Trník, R. Podoba, R. Sokoláš and P. Bačík, J. Ceram. Soc. Japan, 120, 351–354 (2012).
11) I. Štúbba, A. Trník and L. Vozár, Ceram. Int., 33, 1287–1291 (2007).
12) C. Mahodaran, P. Sutharsan, S. Dhanapadian, R. Venkatachalapathy and R. M. Asanulla, Appl. Clay Sci., 54, 20–25 (2011).
13) A. Haq, Y. Iqbal and M. RiazKahn, J. Pak. Mater. Soc., 3, 77–90 (2009).
14) S. Ferrari and A. F. Gualtieri, Appl. Clay Sci., 32, 73–81 (2006).
15) A. Aras, Appl. Clay Sci., 24, 257–269 (2004).
16) P. M. Velasco, M. P. M. Ortiz, M. A. M. Giró and L. M. Velasco, Constr. Build. Mater., 63, 97–107 (2014).
17) R. Podoba, L. Podobník and A. Trník, Építőanyag, 64, 28–29 (2012).
18) I. Štúbba, A. Vázanová, G. Varga and D. Hruňy, Proc. Conf. “Research and teaching of physics on the context of university education”, SPU Nitra (2007) pp. 69–74.
19) T. Húlan, A. Trník and I. Štúbba, Bulletin of the Moscow State Regional University, 2014, 21–29 (2014).
20) ASTM C 848:88: Standard test method for dynamic Young’s modulus, shear modulus and Poisson’s ratio for ceramic whiteware by sonic resonance, (published in 1999, Standard Documents, Philadelphia USA).
21) E. Schreiber, O. Anderson and N. Soga, “Elastic constants and their measurement”, McGraw-Hill Book Co., New York (1973).
22) I. Štúbba, P. Šín, A. Trník and L. Vozár, Meas. Sci. Rev., 14, 35–40 (2014).
23) A. F. Gualtieri and S. Ferrari, Phys. Chem. Miner., 33, 490–501 (2006).
24) CSN 72 1083: Thermal analyses of ceramic raw materials. (published in 1973, Czechoslovak State Standard) [in Czech].
25) D. L. Carroll, T. F. Kemp, T. J. Bastow and M. E. Smith, Solid State Nucl. Mag., 28, 31–43 (2005).
26) I. Štúbba, A. Trník, P. Šín, R. Sokoláš and I. Medvedť, Mater. Technol., 45, 375–378 (2011).
27) A. Trník, I. Štúbba, G. Varga, M. Keppert and P. Bačík, Mater. Sci.-Medzg., 19, 461–464 (2013).