Thermogravimetry and thermodilatometry as auxiliary analyses for dynamical thermomechanical analysis of clays

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Abstract
The natural illitic clay was mixed with powder calcite (22 wt.% in the dry mixture), distilled water, and 3% solution of polyvinyl alcohol to obtain a plastic mass for samples. To determine the correct temperature dependence of Young's modulus, thermogravimetry (TG), thermodilatometry (TDA), and impulse excitation technique (IET) have to be performed in the same temperature regime. The effect of the size of TDA sample on Young's modulus was negligible. Contrary to the TDA sample, the form of the TG sample had a significant effect. When results from a small TG powder sample are substituted into the formula for Young's modulus, relative error up to 10% can result in the temperature region in which changes of some mineral components occur. In this study, we showed the importance of using compact samples with the same cross-section for TG, TDA, and IET in order to obtain correct values of Young's modulus during thermal treatment of the illitic clay.
Keywords: thermal analysis, sample size, thermogravimetry, thermodilatometry, Young's modulus
Kulcsszavak: termikus analízis, mintaméret, termogravimetria, termodilatometria, Young-modulus

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1. Introduction

It is important to understand how mechanical properties of traditional ceramics behave not only during firing of the product, but also when the product is in fire or when it is used in a work environment at elevated temperatures. Firing of clays with a high content of kaolinite and/or illite transforms a raw (unfired) body into ceramic products. The raw body exhibits changes during heating that result from dehydration, dehydroxylation, high-temperature reactions, sintering, and transitions of quartz [1, 2], which affecting the properties of the final fired body. To study these changes, methods of thermal analyses are used. The most commonly used ones are differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG), and thermodilatometry (TDA). When ceramic materials are intended to be used in high-temperature environment, e.g. at firing, it is also important to know the mechanical properties of ceramic material, as well as changes caused by the heat. The suitable method for this purpose is the dynamical thermomechanical analysis (D-TMA) [3, 4].

In DTA, the sample of interest and the reference sample undergo identical thermal cycles, and the temperature difference between the samples is recorded and plotted against time or against temperature. Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference sample. Thus, a DTA curve provides data on dehydration, dehydroxylation, and high-temperature reactions. The ideal reference material is a substance with no thermal events over the temperature range of interest. In DTA, alumina (Al_2O_3) powder is used as the reference material for the analysis of inorganic compounds.

In TG, the mass of a sample is monitored also against time or temperature. This technique is used to characterize clay materials that experience mass loss related to dehydration, dehydroxylation and decomposition. D-TMA is based (in most cases) on measuring the resonant frequency of the vibrating sample during its heating/cooling or heating at constant temperature.

DTA and TG are often performed simultaneously in the DTA/TG analyzer, in which small powder samples (tens of mg in modern analyzers) are used. For some cases, it is preferable to measure compact samples of sizes and masses comparable to samples used in TDA or D-TMA. It is known that the sample size plays a significant role in thermal analyses. For example, DTA and DTG peaks occur at higher temperatures for larger samples. In large samples comparable to some industrial bodies, dehydration and dehydroxylation take place simultaneously – dehydroxylation begins on the surface at ~420 °C and dehydration finishes in the middle even at such slow heating rate as 3 °C/min [5].

Samples for DTA/TG, D-TMA, and TDA had the same cross-section [4, 6, 7]. The sample for DTA/TG had a shape of cylinder of dimensions Ø10×20 mm^2 or prism 10×10×20 mm^3

both with an opening Ø3×10 mm² for a thermocouple. The reference sample was made from a pressed alumina powder and had the same shape and dimensions as the measured sample. A similar sample for DTA was shortly described in [8], where is stated that this sample gives sharper DTA peaks than a powder sample in a crucible.

Young's modulus can be measured only indirectly. To determine its value, some physical quantities have to be measured and substituted into a relevant formula. The sonic resonance method (SRM) or impulse excitation technique (IET) [4, 9–11], which are non-destructive and sufficiently sensitive, can be successfully used for D-TMA if an appropriate temperature regime is applied. A flexural vibration of the measured cylindrical or prismatic sample is mostly used because of the simplicity and reliability of its excitation and measurement at elevated temperatures. For the flexural vibration, Young's modulus E may be calculated using formula [10–12]

$$E = \left(K\frac{l^2 f_0}{d}\right)^2 \frac{m}{V}T \tag{1}$$

where f_0 is the resonant frequency of the fundamental mode, m is the mass of the sample and V is its volume, l is the length, and d is the dimension of the sample in the vibration plane (i.e. diameter or thickness). The values of the constant K are:
K = 1.12336 for a circular cross-section and the fundamental resonant frequency,
K = 0.97286 for a square cross-section and the fundamental resonant frequency.

The correction coefficient $T = 1$ if $l/d \geq 20$. If not, T must be calculated from the formulae given in [10, 11] or can be found in tables in [12]. To obtain T, Poisson's ratio of the measured material must be known. The value 0.2 can be considered for ceramics [4, 9]. In practice, the ratio of l/d varies between 10 and 15. Using the values of T from [12], the sufficiently accurate relationship between T and l/d for the actual temperature t can be written as

$$T(t) = 0.9859 + 0.609\frac{d(t)}{l(t)} \text{ for a circular cross section} \tag{2a}$$

$$T(t) = 0.9704 + 0.950\frac{d(t)}{l(t)} \text{ for a square cross section} \tag{2b}$$

During heating of ceramic material, the mass, length and cross-section alter their values depending on the temperature. Young's modulus is also a function of the resonance frequency f_0. Therefore, three thermal analyses (TG, TDA, and D-TMA) must be performed to obtain the correct values of Young's modulus. Calculation of Young's modulus can be simplified if TG and TDA are omitted. This necessarily leads to an error, which can reach 7.5% [6]. It follows that TG and TDA are auxiliary analyses that help obtain more exact values of Young's modulus.

The length and diameter/thickness of the sample can be written as $l(t) = l_0 + \Delta l(t)$ and $d(t) = d_0 + \Delta d(t)$, where l_0 and d_0 are their values at the room temperature and $\Delta l(t)$, $\Delta d(t)$ are contributions from the thermal expansion measured by dilatometer. Since ceramic material is considered isotropic, $\Delta l(t)/l_0 = \Delta d(t)/d_0 = \varepsilon$. The term $d(t)/l(t)$ in *Eq. (2a)* and *(2b)* can be expressed as

$$\frac{d(t)}{l(t)} = \frac{d_0\left(1+\frac{\Delta d(t)}{d_0}\right)}{l_0\left(1+\frac{\Delta l(t)}{l_0}\right)} = \frac{d_0(1+\varepsilon)}{l_0(1+\varepsilon)} = \frac{d_0}{l_0} \tag{3}$$

Similarly, $m(t) = m_0 + \Delta m(t)$ is the mass of the sample at the temperature t, where $\Delta m(t)$ is the mass loss measured with a TG analyzer. Then *Eq. (1)* using *Eq. (2a)*, *Eq. (2b)* and *Eq. (3)* can be written as

$$E(t) = 1.6067\frac{m_0\left(1+\frac{\Delta m(t)}{m_0}\right)l_0^3 f(t)^2}{d_0^4\left(1+\frac{\Delta l(t)}{l_0}\right)}\left(0.9859 + 0.609\frac{d_0}{l_0}\right) \tag{4a}$$

for a circular cross-section and

$$E(t) = 0.9465\frac{m_0\left(1+\frac{\Delta m(t)}{m_0}\right)l_0^3 f(t)^2}{d_0^4\left(1+\frac{\Delta l(t)}{l_0}\right)}\left(0.9704 + 0.950\frac{d_0}{l_0}\right) \tag{4b}$$

for a rectangular cross-section. Usually, if the investigated ceramic samples are fired at a temperature above 800 °C, its mass is constant, i.e. $\Delta m(t) = 0$ and *Eq. (4a)* and *(4b)* can be simplified.

The aim of the article is to assess the differences between the results of Young's modulus when powder samples or compact samples are used in thermal analyses TG and TDA. Also, the importance of using uniform samples across the analyses in order to generate results suitable for determination of their elastic constants during their thermal treatment is shown.

2. Experimental

Natural clay from Füzérradvány (north-eastern Hungary) was ground and sieved to get a powder, which was then mixed with powder calcite ($CaCO_3$) in the mass ratio $m_{clay}/m_{calcite}$ = 78/22. This mixture was mixed with the distilled water and 3% solution of polyvinyl alcohol to obtain a plastic mass from which prismatic samples were pressed. Their dimensions after drying were 9×9×120 mm³. Thermal analyses were performed as follows:

- TG for small powder samples (40 mg) in alumina crucible on the TG/SDTA Mettler-Toledo analyzer.
- TG for compact samples 8×8×15 mm³ on the DTA/TG analyzer Derivatograph 1000 [13]. The sample had a hole Ø3×6 mm² for alumina double capillary rod with thermocouple. The reference sample of the same shape and dimensions made from pressed alumina powder was used for DTA.
- TDA for samples 8×8×20 mm³ and 4×4×20 mm³ on the dilatometer Netzsch DIL 402 C.
- D-TMA for sample 8×8×110 mm³ on the IET apparatus [14].
- The heating rate for all analyses was 5 °C/min.
- The temperature interval for all analyses was from room temperature up to 1100 °C.

The analyzer Derivatograph performs simultaneously TG and DTA. Although DTA does not give any quantity for Eq. (3a) or Eq, (3b), DTA helps to get a better picture of the processes in the studied sample.

The result of $\Delta l(t)/l_0$ from TDA, $\Delta m(t)/m_0$ from TG, and resonant frequency from D-TMA were substituted into Eq. (4b) to determine the thermal behavior of Young's modulus.

3. Results and discussion

Results of TG are pictured in *Fig. 1*. The main processes are mirrored here – removal of the physically bound water (up to 200 °C), dehydroxylation of illite/smectite (420 °C – 650 °C) and decomposition of calcite above 600 °C, which has a steep decline and is sharply ended. The curves differ as commonly known for TG when samples of different mass are used: the development and termination of processes are shifted to higher temperatures for larger samples.

An example illustrating how the different mass losses influence Young's modulus at 750 °C is as follows (see *Eq. (5)*). When only the relative mass losses of the compact sample (6%) and powder sample (14%) are substituted in *Eq. (4b)*, the ratio of Young's moduli is

$$\frac{E_{TG\ of\ powder\ sample}}{E_{TG\ of\ compact\ sample}} = \frac{1-0.14}{1-0.06} = 0.915\,. \qquad (5)$$

This result implies, that the use of TG results obtained using small powder samples can lead to a relative error of ~10%.

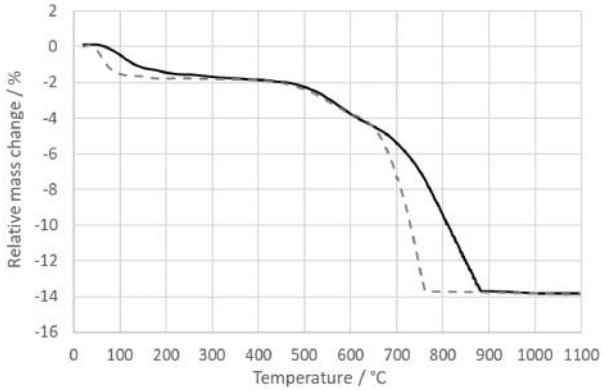

Fig. 1 *The curves of relative mass change for a 40 mg powder sample (dashed line) and a 3 g compact sample (solid line)*
1. ábra *A relatív tömegváltozás görbéi egy 40 mg-os porminta (szaggatott vonal) és egy 3 g-os tömör minta (folytonos vonal) esetén*

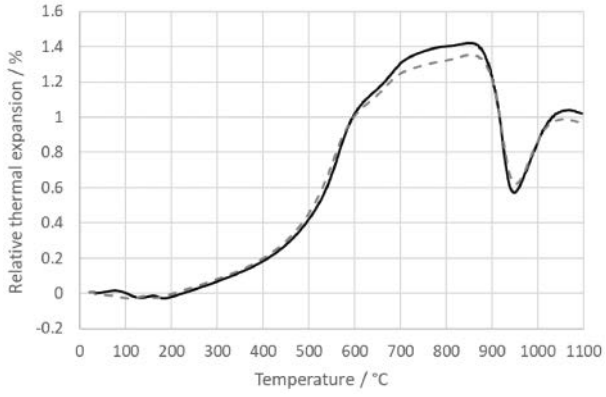

Fig. 2 *The curves of relative thermal expansion for a thin sample (dashed line) and a thick sample (solid line)*
2. ábra *A relatív hőtágulás görbéi egy vékony minta (szaggatott vonal) és egy vastag minta (folytonos vonal) esetén*

Results of TDA are shown in *Fig. 2*, in which TDA curves for the thin sample (cross-section 4×4 mm²) and the thick sample (cross-section 8×8 mm²) are compared. Common dilatometers can measure samples with a cross-section of 8×8 mm², which in our case is the cross-section of the sample for D-TMA. If a thinner sample (4×4 mm²) is used, TDA results can differ to a small extent, but not more than 0.1%, and no shift between the curves is observed (*Fig. 2*). The ratio of Young's moduli is

$$\frac{E_{TDA\ of\ thin\ sample}}{E_{TDA\ of\ thick\ sample}} = \frac{1+0.014}{1+0.013} = 1.001\,. \qquad (6)$$

This result implies that TDA of the samples with different cross-sections does not give remarkable difference between Young's moduli.

Fig. 3 shows temperature development of Young's modulus calculated from Eq. (4b), using TG results for the powder sample and the compact sample. The maximum difference between them is ~0.3 GPa in the region of the calcite decomposition, which represents 10%. The shown thermal development of Young's modulus is typical for firing the clays [4].

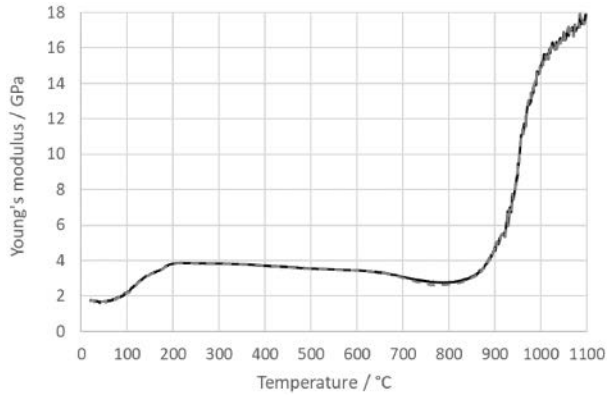

Fig. 3 *The curves of Young's modulus when TG of the small powder sample was used (dashed line) and when TG of the compact sample was used (solid line) The difference between Young's moduli computed using the powder sample versus the compact sample in TG is driven by the processes that change the structure of some components of clay during heating.*
3. ábra *A Young-modulus görbéi, a kis porminta TG-adatai alapján (szaggatott vonal), illetve a tömör minta TG-adatai alapján (folytonos vonal) A Young-modulus értékeinek különbségét, amely a por és a tömör minta TG-adatai alapján számított értékek között jelentkezik, azok a folyamatok okozzák, amelyek a hevítés során megváltoztatják az agyag egyes komponenseinek szerkezetét.*

4. Conclusions

Natural illitic clay from Füzérradvány (Hungary) was mixed with powder calcite (22 wt.%), distilled water, and 3% solution of polyvinyl alcohol to obtain a plastic mass, from which prismatic samples were pressed. To determine the temperature dependence of Young's modulus, TG, TDA, and D-TMA have to be performed using three analyzers. The aim of this article was to show the influence of using different sample sizes and forms in TDA and TG on Young's modulus. The influence of the size of a TDA sample, which must be made from a compact material, was negligible. Contrary to the TDA sample, the form (solid or power) of the TG sample had a significant effect. If the small powder sample was used for TG, and its results were substituted into formula for Young's modulus, the relative error up to 10% can arise in the temperature region, where the change of some component is realized, e.g. decomposition of calcite in the described example.

In this study we also showed the importance of using compact samples with the same cross-section for TG, TDA, and IET in order to obtain correct values of Young's modulus during thermal treatment of the illitic clay.

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