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THERMAL TRANSFORMATIONS OF TILE CLAY BEFORE AND AFTER KAOLIN ADDITION

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Abstract

The use of clays for ceramic filter processing may reduce its cost, leading to different applications, as water treatment. In this work, a low cost tile clay mixed with kaolin, for use in ceramic filters, were evaluated. Mineralogical and thermal changes occurring during sintering were characterized by differential thermal analysis, thermogravimetry, thermomechanical analysis and X-ray diffraction. An increase in the initial melting temperature of samples due to kaolin addition was observed. Mullite formation in kaolin was observed by DTA and in other samples by XRD. TMA analysis permitted the observation of pre-sintering step, around 850°C. This step is difficult to observe in other types of analysis.

Keywords: ceramic filters, clays, thermal analysis, X-ray diffraction

Introduction

Natural raw materials are mainly constituted by clays, silica and feldspar and have wide application in ceramic industry [1], as the right combination of these materials leads to ceramic bodies with properties appropriated to specific productive processes. As an example, kaolin [2, 3] is used to give a better workability to ceramic slurries; feldspars, as albite and orthoclase, are used as fluxes in whitewares and silicate glasses, reducing the sintering temperature of ceramic pieces; and silica is an inert material, used in whiteware ceramics, refractories and vitreous compositions [4]. The system composed of kaolinite, quartz and feldspar is characterized by the formation of primary and secondary mullite after thermal treatment, increasing the mechanical resistance of ceramic pieces [5].

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In the present work, different compositions, containing kaolinite, quartz and feldspars, were studied to obtain low cost ceramic filters, prepared by using the polymeric sponge impregnation method [6]. These filters are normally used for gas, diesel and fused metals filtration, made of high cost materials with a high sintering temperature [7]. The substitution of these materials by low cost ones may extend the use of these filters.

One step of ceramic processing is sintering at high temperatures. During sintering, polymorphic changes, endothermic and exothermic reactions are observed, and the knowledge of these transformations makes the control of the materials' properties easier. To evaluate these transformations, thermal analysis, as differential thermal analysis (DTA), thermogravimetry (TG) and thermomechanical analysis (TMA) [8], associated to X-ray diffraction (XRD) [9], permit the association between thermal and mineralogical changes [10].

The objective of this work is to verify thermal, thermomechanical and mineralogical changes of a tile clay, with known composition, before and after kaolin addition, in the amounts of 10 and 20% *w*/*w*.

Experimental

A tile clay from Santa Rita (Paraíba, Brazil) was used. This clay was characterized by chemical analysis. The tile clay (MP) and the kaolin (AC) were wet milled for 30 min, with ethanol, in a planetary ball mill (Servitech CT-242).

Samples only with tile clay and with 10 (10AC) and 20% *w*/*w* (20AC) of kaolin were analyzed as powder, by simple homogenization of raw materials, and as pellets. Pellets were prepared from aqueous suspensions with 70% *w*/*w* of solids and 2.0% *w*/*w* of sodium polyacrylate (PAA-Na), similarly to filter processing [11]. Slurries were scattered on a plain surface, to mold sheets. These sheets were dried at room temperature and at 110ºC for 24 h. From these sheets, pellets were molded.

Pellets composed only of tile clay were sintered at 1100°C, while those containing kaolin, were sintered at 1150 and 1200ºC. All samples were sintered for 2 h with a heating rate of 1ºC min^{-1} – these thermal treatment is usual in ceramic filters' sintering. For mineralogical characterization, samples before and after sintering were analyzed by X-ray diffraction, with CuK_{α} radiation (Siemens A-500).

Three different techniques of thermal analysis were used: DTA, TG and TMA. DTA essays (Shimadzu DTA-50) were done for kaolin and also for tile clay with and without kaolin addition. The analysis conditions are presented in Table 1. All analyses were done with a sample mass of 20.00±2.00 mg, in air atmosphere, at a heating rate of 10ºC min^{-1} up to 1200 ºC.

For TMA analysis (Shimadzu TMA-50), non sintered tile clay pellets with and without kaolin addition were used. Essay conditions were: heating rate of 10ºC min^{-1} up to 950ºC, with nitrogen flux of 50 mL min^{-1} and constant charge of 0.1 g. Thermogravimetric analysis (Shimadzu, TGA-50) of the tile clay pellets was also done, with a sample mass of 20.00±0.01 mg, with a heating rate of 10ºC min^{-1} up to 900ºC, using a N_2 flux of 20 mL min^{-1}.

Table 1 Analysis conditions for DTA

Material	Heating rate/°C min^{-1}	Final temperature/°C	Reference	Sample
Kaolin	10 50	1200	alumina	powder
Tile clay	10	1200	alumina sintered pellet* alumina sintered pellet	powder powder pellet pellet
10AC	10	1200	alumina sintered pellet* alumina sintered pellet	powder powder pellet pellet
20AC	10	1200	alumina sintered pellet* alumina sintered pellet	powder powder pellet pellet

*Prepared from sample 20AC sintered at 1200°C, due to its higher temperature of liquid phase formation

Results and discussion

X-ray diffractograms of the tile clay (Fig. 1a) indicate the presence of quartz, feldspars (albite and microcline), and haematite; in spite of presenting plasticity, clay presence is not observed in the tile clay, using XRD. XRD of kaolin (Fig. 1a) indicates the presence of kaolinite, besides small amounts of muscovite and quartz. Chemical analysis results of the tile clay are presented in Table 2.

Table 2 Chemical analysis result of the tile clay

Chemical analysis	Mass/%
L.o.I	6.31
Others	2.12
SiO_2	61.4
Fe_2O_3	4.09
Al_2O_3	20.9
CaO	traces
MgO	traces
Na_2O	1.8
K_2O	2.45

DTA curves of kaolin, with different heating rates, are presented in Fig. 1b. A large exothermic peak was observed between 100 and 500ºC, due to organic material decomposition. This transition is followed by an endothermic transition around 570ºC,

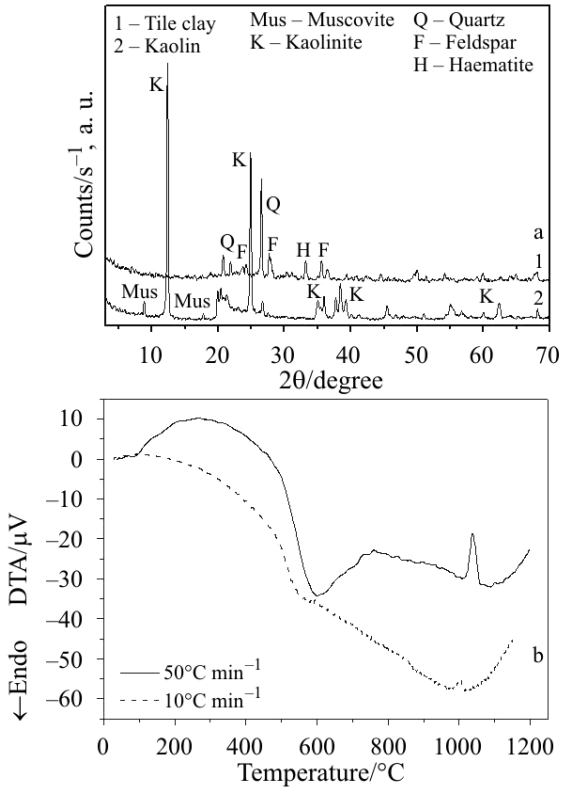

Fig. 1 a – X-ray diffractogram of tile clay and kaolin, b – DTA curves of kaolin, in heating rates of 10 and 50°C min^{-1}

due to the elimination of hydroxyl groups bound to Al, leading to metakaolinite formation (Fig. 2). According to literature, these transitions occur around 550ºC – the increase in heating rate moves the peak to a higher temperature [8, 12, 13]. This may be due to the temperature difference between sample and furnace, as ceramics are thermal insulators; another reason may be the change in metakaolin entropy, as a faster dehydroxylation rate favours a more disordered metakaolin phase [13]. On the other hand, the analysis done with a heating rate of 10ºC min^{-1} does not present a well defined peak [14, 15]. A high heating rate leads to mistakes in events quantification, but is useful in the detection of mineral transitions and melting's with small heat exchange. So, this is an interesting methodology in the study of clays.

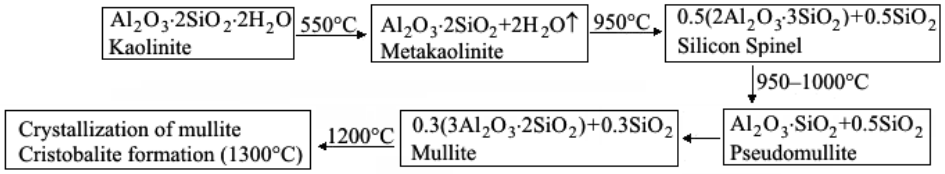

Fig. 2 Sequence of solid state reactions due to kaolinite transformations during thermal treatment [12]

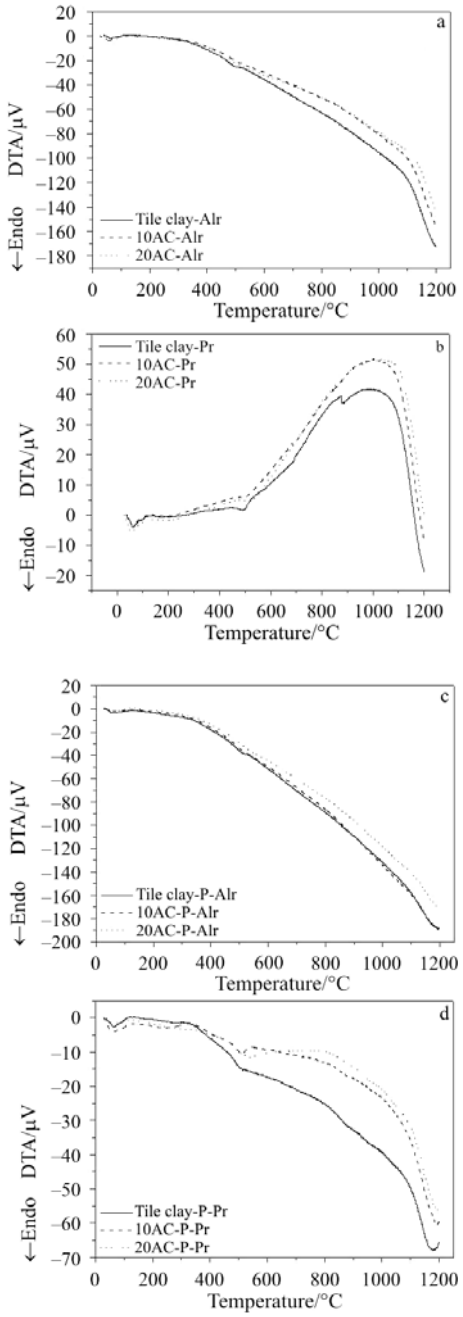

Fig. 3 DTA curves for samples: tile clay, 10AC and 20AC. a – Powdered sample, using alumina as reference, b – powdered sample, using a sintered pellet as reference, c – pellet shape, using alumina as reference, d – pellet sample, using a sintered pellet as reference

According to Fig. 2, a fast reorganization of oxides in the metakaolinite structure may be observed between 950 and 1000ºC, leading to the formation of a phase similar to α-alumina spinel, with composition close to $2Al_2O_3 \cdot 3SiO_2$. This transition is observed in Fig. 1b, as an exothermic peak at 1000ºC for a heating rate of 10ºC min^{-1} and at 1034ºC for a heating rate of 50ºC min^{-1}. A dislocation in peak temperature is observed as stated before. In this case, this may also be due to the amount of phase formed, which varies according to the heating rate [13]. Around 1200ºC, the beginning of another exothermic peak is observed, probably due to mullite crystallization.

DTA curves are presented in Fig. 3. The legends 10AC and 20AC indicate samples with 10 and 20% *w*/*w* of kaolin, respectively; the letter P indicates samples analyzed as pellets and the last term indicates the reference used: alumina (Alr) or sintered pellet (Pr).

In Fig. 3, it may be observed that material shape and reference greatly influence the results [14]. The analysis condition that leads to a better visualization of the characteristic transitions of these materials is the pellet sample, using a sintered pellet as reference (Fig. 3d).

The difference among curves with different reference materials, may be due to the difference in density and specific heat between sample and reference. When a sintered pellet is used, the difference is lower and curves have a better baseline. In relation to analysis using powdered samples or pellets, the difference may be due to kinetic factors – the beginning of a reaction is slower in pellets than in powders, so heat is absorbed or evolved in a higher amount during a smaller time, making the peaks better defined.

According to Fig. 3d, an endothermic peak is observed around 65ºC, due to water elimination. An endothermic transition around 500ºC is observed, probably due to metakaolin formation. Superimposed peaks are observed between 800 and 1000ºC, being difficult to separate the different transitions. Literature results indicate that these transitions may be related to metakaolin decomposition and also to quartz transformations [4].

The beginning of an endothermic transition may also be observed around 1100ºC, for all samples, as indicated in Fig. 3d. This transition may be related to feldspar melting – according to literature, potassium and sodium feldspars melt at 1150 and 1050ºC, respectively [4]. It was also observed that the higher the kaolin amount, the higher the feldspar melting temperature, as supported by the endothermic peak. For tile clay, this peak is observed around 1100ºC, with an increase to ~1120ºC for sample 10AC and to ~1132ºC for sample 20AC. This increase in feldspar melting temperature is confirmed by samples aspect after analysis – samples 20AC and 10AC do not fix in the alumina pan, while the tile clay one does.

X-ray diffractograms of the samples after sintering are presented in Fig. 4. Analysis of tile clay samples were not done after sintering at 1150ºC, due to the high amount of glassy phase, which leads to a high deformation of the ceramic samples, not being adequate for filter processing.

X-ray diffraction indicates mullite presence at 1150ºC, for kaolin samples. According to DTA analysis, mullite formation is only observed at 1200ºC. This differ-

ence may be due to the smaller heating rate used during sintering (1ºC min^{-1}), comparing to thermal analysis (10ºC min^{-1}) and also to the isothermal step at the end temperature, during sintering process (2 h). The presence of impurities may also change this temperature to smaller ones.

The X-ray diffractograms of samples sintered at 1150ºC (Fig. 4) also indicate feldspar presence. This phase is probably formed during cooling, as its melting temperature is 1050ºC. Haematite is also observed, due to the iron present in clays [16].

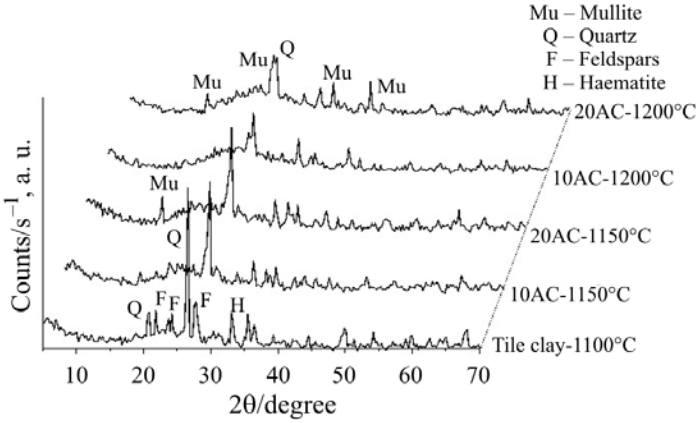

Fig. 4 X-ray diffractograms of samples after sintering. Tile clay sintered at 1100°C and samples 10AC and 20AC, sintered at 1150 and 1200ºC

After thermal treatment at 1200ºC, a glassy phase is formed – this is supported by the decrease of the height of the peaks and also by a band formation between 15 and 30º. This glassy phase is formed due to feldspar melting and quartz dissolution [5], as supported by the decrease observed in quartz peak height, comparing to mullite peak. Peaks corresponding to haematite are also observed.

XRD results confirm DTA analysis, for kaolin (Fig. 1b) – the exothermic peak that begins at 1200ºC is really due to mullite formation. As observed before, this formation is due to kaolinite transitions during thermal treatment. This way, mullite peak height is higher in sample 20AC than in sample 10AC (Fig. 4), due to the higher amount of kaolinite.

TMA and TG curves are presented in Fig. 5. Tile clay pellets present a shrinkage starting at 30ºC (Fig. 5a), while samples 10AC and 20AC present an expansion at 80 and 65ºC, respectively. With temperature increase, an expansion is observed due to the thermal expansion characteristic of the material. This expansion has a maximum of 0.55% for tile clay at 860ºC. For samples 10AC and 20AC, an abrupt expansion is observed followed by a shrinkage at 550ºC, probably due to dehydroxylation, as indicated by TG and DTA curves (Figs 5b and 1b). Samples with kaolin addition present a smaller total expansion of the pellets than samples with only tile clay – sample 10AC has an expansion of about 0.25%, while sample 20AC has an expansion around 0.40%.

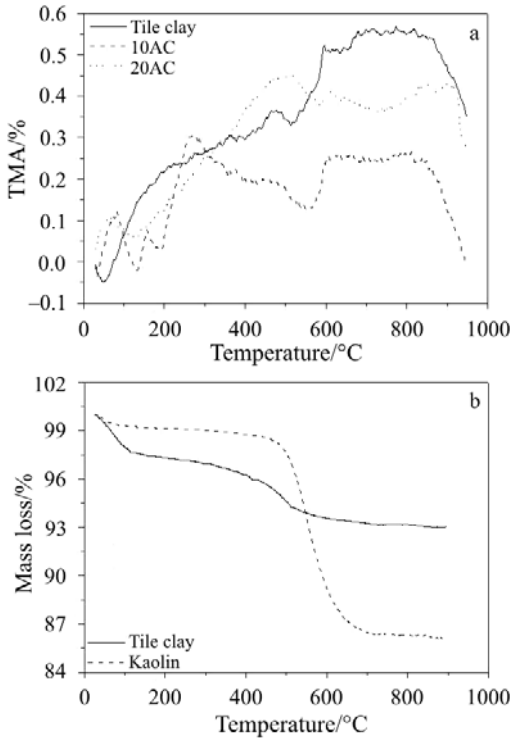

Fig. 5 a – TMA curves of samples tile clay, 10AC and 20AC, b – TG curves of tile clay and kaolin samples

This is probably due to the best particle packing of sample 10AC, as the respective suspension presents the best rheological properties, as observed in previous work [11].

The last step observed is the sample shrinkage above 800ºC. Thermogravimetric curves showed that tile clay and kaolin do not present mass loss above 700ºC (Fig. 5b), indicating that decomposition reaction may not occur. So, the shrinkage process is probably due to pre-sintering, corresponding to particles' accommodation. It is important to emphasize that pre-sintering is difficult to detect, being sometimes observed in dilatometry [17]. The beginning of pre-sintering varied according to the sample analyzed – for tile clay, this temperature is around 866ºC, for 10AC at 840ºC and for 20AC at 914ºC.

Conclusions

DTA curves of kaolin, using a heating rate of 50ºC min^{-1}, presented well defined peaks, due to metakaolinite and mullite formation. Kaolin addition to tile clay led to an increase of melting temperature, from 1100ºC in tile clay, to 1120ºC when 10% *w*/*w* of kaolin is used and 1132ºC, when 20% *w*/*w* is used.

The best DTA curves were obtained for samples in pellets, using a sintered pellet as reference. Feldspars' melting was observed, besides mullite formation. On the other hand, this phase was observed by X-ray diffraction after sintering at 1150ºC.

TMA curves indicated a shrinkage process due to particles approach, indicating a pre-sintering process. This process is influenced by particles' packing – sample 10AC, which was molded using the suspension with the best rheological properties, presented the smaller temperature of shrinkage beginning.

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