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PROCESSES OCCURRING DURING THE SINTERING OF POROUS CERAMIC MATERIALS BY TG/DSC

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Ceramic blocks with high porosity and low heat conductivity are effective tools to improve the indoor comfort level and also to reduce energy consumption. The main objective of this study was focused on the development of the porous ceramic blocks processing with different pore forming agents by adapting a German technology to the Brazilian environmental conditions. In this process, the clay mixtures are homogenized before sampling as the sintering of porous ceramic materials was about 900–1100°C. TG/DTG, DSC and coupled MS experiments were carried. The formed products have low apparent density, high porosity and reasonable mechanical strength with a good heat and acoustic insulation properties.

Keywords: *ceramic blocks, clay, porous forming agents, thermal analysis*

Introduction

The application of ceramic blocks with high porosity in civil construction comes as an economical way to obtain a comfortable indoor environment and a low energy consumption. The application of these materials reduces the overall cost of construction, too. The adaptation of German technology in the production of high porosity ceramic blocks for the industrial and environmental conditions of Brazil and will be an incentive in civil construction. In addition, it will also represent a technological breakthrough in the process of manufacturing the Segment of Red Ceramic in Brazil. This will happen as soon as the demands of the referred products are placed under rigorous quality control in the production process.

These materials were tested as pore forming agents sawdust, paper-making and expanded polystyrene (EPS), then added to a red clay ceramic body used for the production of structural red bricks.

The use of pore forming agents in the lightweight clay blocks are designed to increase the thermal insulating property of wall systems resulting in the contribution to the reduction of heat energy consumption in the buildings.

Pore forming agents for clay products has therefore an unquestionably positive effect in which besides the heat energy saving which can be achieved the normal block properties, such as the agreeable room climate in particular produced by pore diffusion and heat capacity, are maintained. In addition, there are ecological advantages therefore supplement the amenities typically associated with blocks [1, 2].

The objective of this work was the study of the process of production of porous ceramic blocks with different pore forming agents using TG/DTG and DSC techniques to evaluate their thermal behavior.

Experimental

Porous ceramic block process

Kaolinite clay powder sample was collected from a deposit located in South-Eastern Brazil (Barra do Piraí). This deposit is representative and widely used by ceramic plants. Sawdust is an industrial waste from the factories and paper-making reject with 60 mass/mass% of water from Aracruz Celulose. Also the expanded polystyrene samples (EPS) were supplied by the Basf Company. These raw materials were dried and submitted to the following characterization techniques. Afterwards, the clay body mixtures containing different organic pore forming agents were homogenized, and through extrusion, it followed by drying and sintering between 900 and 1100°C. The porous ceramic blocks were processed with different morphologies and pore distributions, whose morphology and distribution of pores varied with the additive [1].

Three compositions were prepared: M1 (98% of kaolinite clay and 2% EPS), M2 (85% of kaolinite clay, 10% of sawdust and 5% paper-making reject) and M3 (76% of kaolinite clay, 18% of sawdust and 6% of paper-making reject). The samples were extruded in laboratory and dried for 24 h at 60°C and 10 h at 110°C followed by sintering at 900, 1000 and 1100°C. 45 samples were extruded and sintered in

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laboratory kiln at temperatures varying from 900 to 1100°C [3]. Five samples for each composition were then tested to obtain the firing technological properties related to the bulk density, apparent porosity and compression strength. The bulk density was measured dividing the dry mass by the external volume. The apparent porosity was determined according to standard procedure [4]. The compression strength was determined in an Instron 5582 Universal Testing Machine, according to standard procedure [5].

Thermal analysis

The thermal behavior of the samples was studied by means of thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) [6] methods using Netzsch STA 449C TG-DSC Jupter Aeolos coupled to mass spectrometer from room temperature to 1000°C. 10°C min^{-1} heating rate and nitrogen purging (flow rate: 70 mL min^{-1}) was applied. The sample masses were about 25 mg. A TG-DSC type S sensor, as well as platinum crucibles with pierced lids were used for the measurements.

Results and discussion

Physical properties of the samples of ceramic body mixtures after sintering between 900–1100°C are summarized in Table 1.

The test results of physical and mechanical properties of block samples show that the sawdust and paper-making reject combination provides the results which allow the potential application in the production of lightweight and economical new brick material.

Figure 1 shows the TG/DTG and DSC curves of sample M1. The TG curve shows four mass loss stages.

In the first stage water loss occurred resulting 0.65% decrease of the initial sample mass (Ti 67°C). In the second stage, the mass loss was 1.19% in the 200–325°C temperature range, which can be attributed to the dehydration of gibbsite. The third stage, where the mass loss was 1.43% (between 325.420°C) can be attributed to the decomposition of EPS. In the last stage the mass loss was ≈6.4% (Ti 420°C), which

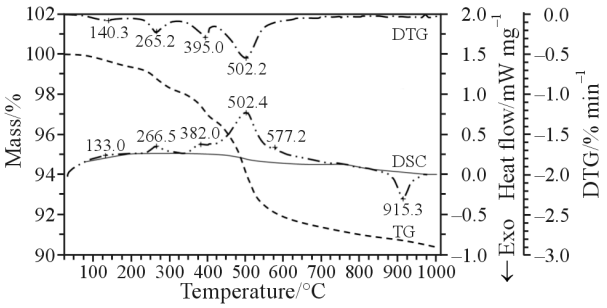

Fig. 1 TG/DTG and DSC curves of M1 sample

was due to the kaolinite dehydroxylation. Consequently, the DSC signal exhibited several overlapping endothermal and exothermal effects, which correlate well with the observed mass loss steps. The DSC peak at ≈577°C is the polymorph transformation of α- to β-quartz. At ≈915°C the metakaolinite transforms to a cubic phase described as spinel. Maxima in the mass loss rates occurred at 140, 265, 395, 502 and 924°C, respectively.

Figure 2 shows the mass spectrometry results of M1 sample. The ion current signals for m/e=18 and 44, which also correlate well with the observed mass loss steps indicate most probably the release of H_2O and CO_2 from M1 sample.

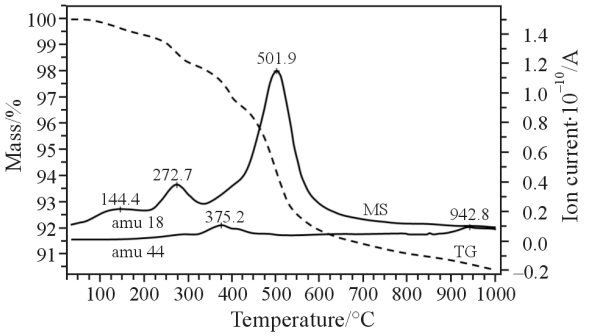

Fig. 2 TG and MS curves of M1 sample

Figure 3 shows the TG/DTG and DSC curves of M2 sample. TG curve exhibits four mass loss steps. The first one is the loss of 0.67% water (Ti 90°C). In the second stage the corresponding mass loss is 1.43% in the 200–300°C temperature range, which

Table 1 Physical properties of samples

Mixtures	Density/g cm^{-3}			AP/%			CS/MPa		
	900°C	1000°C	1100°C	900°C	1000°C	1100°C	900°C	1000°C	1100°C
M1	0.79	0.83	0.97	65.30	63.20	60.20	1.58	2.94	5.23
M2	1.04	1.09	1.24	60.73	58.88	52.20	3.69	6.09	11.27
M3	0.82	0.86	0.98	68.96	68.50	63.18	1.50	1.94	3.62

AP=apparent porosity, CS=compression strength

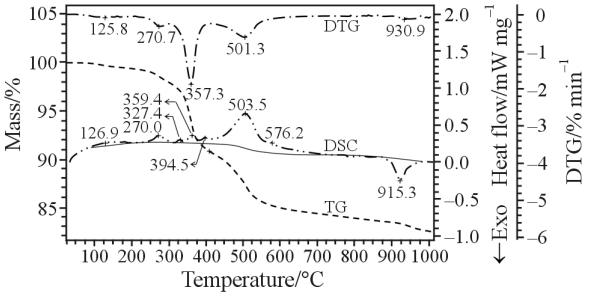

Fig. 3 TG/DTG and DSC of M2 sample

can be attributed to the dehydration of gibbsite. In the third stage the measured mass loss was 7.01% (300–405°C) which is representative to the decomposition of sawdust and paper-making. In the last, fourth stage the final mass is 7.31% (400–575°C), which suggest the dehydroxylation of kaolinite. Similarly to the previous one, the DSC curve shows several overlapping endo- and exothermal effects, which are in a good agreement with the mas loss steps. The DSC peak at 576°C indicating the polymorph transformation of α-quartz to β-modification, and at ≈920°C the metakaolinite transforms into a cubic phase described as spinel [7–10]. The DTG maxima corresponding to the maxima mass loss rates can be seen at 126, 270, 357, 501 and 930°C, respectively.

TG-MS curves of M2 samples are summarized in Fig. 4. The signals at *m*/*e*=18 and 44 are representative for the release of H_2O and CO_2 from the M2 sample.

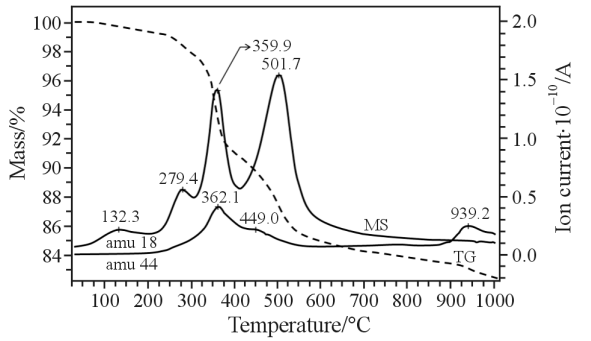

Fig. 4 TG and MS curves of M2 sample

Figure 5 shows the remaining specific mass per charge units with significantly smaller intensities, which are most probably due to the presence of organic molecules like COH_2, C_3H_3, C_3H_6 and C_3H_7.

The TG/DTG and DSC curves of M3 sample containing 76% of caulinitic clay, 18% of sawdust and 6% of paper-making are summarized in Fig. 6. The TG curve presents four stages: in the first stage water loss occurred 0.70% with (Ti 80°C); in the second stage the mass loss was 2.88% between 195–308°C, which can be attributed to the dehydration of gibbsite. In the third stage, the mass loss was

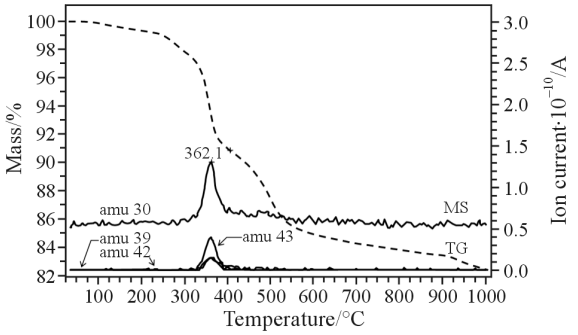

Fig. 5 TG and MS curves of M2 sample (ion current for *m*/*e*=30, 39, 42 and 43)

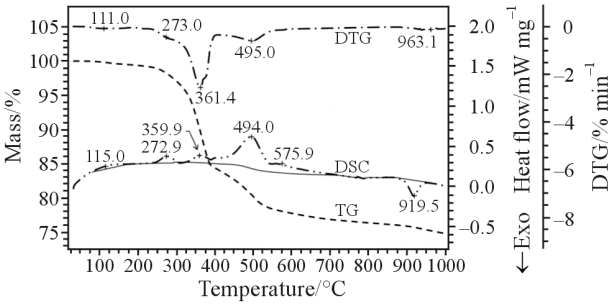

Fig. 6 TG//DTG and DSC of M3 sample

12.27% (temperature range: 308–400°C), which is due to the decomposition of sawdust and paper-making and in the fourth stage. The corresponding mass loss was 8.29% between 400–575°C, caused by the kaolinite dehydroxylation. In the DSC curve one can observe several endo- and exo-effects correlating well with the observed mass loss steps. The DSC peak at 576°C indicates the α-→β-quartz polymorph transition, and at ≈920°C the metakaolinite transforms into a cubic phase (spinel).

Figure 7 shows the mass spectrometry results for sample M3. The ion current signals for mass numbers 18 and 44, which also correlate well to the observed mass loss steps indicating most probably the release of H_2O and CO_2 from the M3 sample.

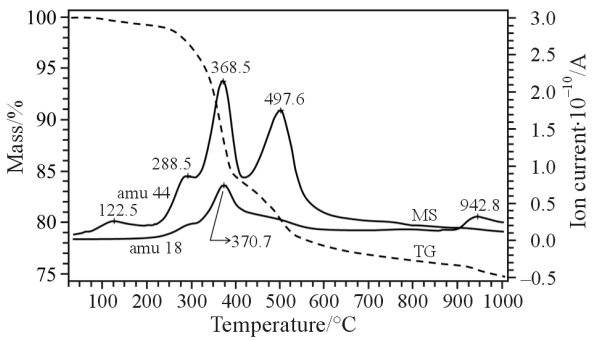

Fig. 7 TG and MS curves of M3 sample

Table 2 Summary of thermoanalytical results taken from the TG/DTG and DSC curves of the porous ceramic materials

Sample	Curve	Mass loss and mass loss rate maxima				
M1	TG/%	0.65	1.19	1.43	6.38	
	DTG/°C	140.3	265.2	395.0	502.2	–
	DSC/°C	133.0	266.5		≈350 to ≈775	915.3
	enthalpy/J g^{-1}	11.1	19.9		409.0	–88.4
M2	TG/%	0.67	1.43	7.01	7.31	0.02
	DTG/°C	125.8	270.7	357.3	501.3	930.9
	DSC/°C	126.9	270.0		≈320 to 740	919.5
	enthalpy/J g^{-1}	14.8	16.0		295	–67.3
M3	TG/%	0.70	2.88	12.27	8.29	1.14
	DTG/°C	111.0	273.0	361.4	495.0	963.1
	DSC/°C	115.0	272.9		≈320 to ≈715	919.5
	enthalpy/J g^{-1}	9.4	14.7		253.0	–36.9

The numerical data representative to the mass loss processes of the analyzed samples are summarized in Table 2.

Conclusions

The present study demonstrates that thermal analysis combined mass spectrometry investigations can be an effective tool to select the optimum conditions to obtain ceramic blocks with high porosity.

During the heating cycle of clay mixtures, the water loss and the decomposition processes could be separated. For the three samples, besides the indication of the mass loss steps DSC analysis showed the polymorph transition of α-→β-quartz at about ≈577 and at ≈915°C transformation of metakaolinite. The compression strength values of Ml, M2 and M3 samples are variable as a function of porosity increase and sintering mechanisms in the temperature range. For M1 sample the values were between 1.58 and 5.23 MPa. For M2 sample formation of smaller pores can be attributed to the burning of sawdust and paper-making and the values for the M3 sample the observed decrease is due to the increase of the amounts of the pore forming agents. Ceramic material obtained with high porosity can be classified according to its appropriate composition and reasonable mechanical strength, and besides improving the indoor comfort of a low cost house.

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