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TG AND DSC STUDIES ON PLASTER RESIDUES AS RECYCLED MATERIAL

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The aim of the present work is to study plaster residues produced in industries in Goiás State (Brazil). The study analyzes the trituration and dehydrating processes of the plaster and compares its chemical, mechanical and physical characteristics to the natural plaster samples aiming its possible recycling.

Plaster samples were submitted to X-ray diffraction, infrared spectroscopy, thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses.

By the comparison of the results obtained for both samples it was observed that they have similar chemical characteristics. No reason was found against the use of recycled plaster.

Keywords: *DSC, plaster, recycling, TG*

Introduction

Plaster (which is the general nomination of the $CaSO_4$ chemical composite) is a widely used material in civil construction, but like all other construction materials it generates excessive amount of rubbish. CONAMA 307 (05-jul-2002) (Environmental National Agency) classifies this rubbish as a 'Class C' residue for which there are still no economically viable technologies or applications that allow its recycling.

Generally, calcium sulphate hemihydrate ($CaSO_4\cdot1/2H_2O$) is classified as a hydraulic binder and is assigned as plaster. There are also other types of calcium sulphate, as $CaSO_4\cdot2H_2O$ (crude gypsum) and anhydrite without water ($CaSO_4$).

Therefore, plaster material is no longer a waste but a by-product of phosphoric acid preparation which could replace natural gypsum for most of the applications of the latter, such as in the manufacture of plaster and cement industry. Recycling of phosphate rock in the phosphogypsum form was studied [2].

The present work aims to study the plaster residues produced in industries in Goiás State (Brazil) via triturating and dehydrating processes and then the comparison of their chemical, physical and mechanical characteristics to the natural plaster samples aiming the possible reuse of plaster residues.

Experimental

Plaster as a construction material

Gypsum is a sedimentary rock composed essentially by crude gypsum. The quality of gypsum is evaluated through the amount of crude gypsum. The more crude gypsum is in the rock, the better its quality. The rocks found in Brazil are pure enough to contribute to the production of high whiteness plaster.

Brazil has around 1.250 billion tons of crude gypsum reserves. It has the biggest reserve of the planet. United States and Canada has respectively 700 billion and 450 billion tons of this mineral in their reserves [3].

After the extraction the rock is calcined and then submitted to triturating and burning [4]. Calcination is a thermal process in which the gypsum is dehydrated at temperatures from 140 to 160°C. The temperature range gives the desired gypsum hemihydrate ($CaSO_4\cdot1/2H_2O$). The crude gypsum looses 3/4 of its water and transforms to hemihydrate. The hemihydrate state can exist in α- and β-forms according to the wet (under saturated steam pressure) or dry (under atmospheric pressure) calcination process, respectively.

α- and β-hemihydrates have the same crystalline structure, although their morphology (size and surface of the crystal) are different due to the preparation method. As it is shown in Table 1, the calcination temperature influences the final appearance of the plaster.

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Table 1 Terminology and characteristics of crystalline phases of the calcium sulphate plaster [5]

Name of crystalline phase	Usual designations	Crystalline structure	Chemical formula and abbreviations	Temperature of industrial production/°C
Gypsum	calcium sulphate dihydrate	monoclinic	$CaSO_4{\cdot}2H_2O$, DH	<40
Bassanite	calcium sulphate hemihydrate, common plaster, hemihydrate, β-hemihyrate, β-plaster	rhombohedral	$CaSO_4{\cdot}1/2H_2O$, HH – β	120–140 in dry atmosphere
Bassanite	odontological plaster, α-hemihydrate, α-plaster, autoclaved plaster	rhombohedral	$CaSO_4{\cdot}1/2H_2O$, HH – α	80–180 in humid atmosphere under pressure
Anhydrite III	soluble anhydrite	hexagonal	$CaSO_4$, ANIII – α	290 – dry way, 110 – humid way
Anhydrite II	anhydrite, natural anhydrite, synthetic anhydrite, calcinated anhydrite	rhombic	$CaSO_4$, ANII – s – (slowly soluble) ANII – u – (unsoluble), ANII – E – Estrichgips	300–900
Anhydrite I	high temperature anhydrite	cubic	$CaSO_4$, ANI – α $CaSO_4$	non-commercial

Table 2 Possible hydration reactions of construction plaster phases, leading to a progressive hardening of the fresh paste [5]

Phase	Hydration reactions
β-Hemihydrate	$CaSO_4 \cdot 1/2H_2O+3/2H_2O \rightarrow CaSO_4 \cdot 2H_2O+111.9\pm0.50\ J\ g^{-1}$
β-Anhydrite III	$CaSO_4III+2H_2O \rightarrow CaSO_4 \cdot 1/2H_2O \rightarrow CaSO_4 \cdot 2H_2O+175.3\pm0.5\ J\ g^{-1}$
β-Anhydrite II	$CaSO_4II+2H_2O \rightarrow CaSO_4 \cdot 2H_2O+98.0\pm0.50\ J\ g^{-1}$

After calcination the substance was ground and selected by granulometric separation to fractions and then classified according to its setting time, in agreement with the NBR 13207 code (Brazilian Association Technical Norms) [6].

In order to be able to use in civil construction, plaster is hydrated through a chemical reaction between anhydrous material and water, resulting in a dehydrate form, as it is shown in Table 2.

The plaster hydration mechanism can be understood by the dissolution–precipitation phenomenon (crystallization theory). This phenomenon involves the hydration of hemihydrate ($CaSO_4 \cdot 1/2H_2O$) and anhydrite ($CaSO_4$) followed by the precipitation of the dihydrate ($CaSO_4 \cdot 2H_2O$) [2]. Furthermore, construction plasters consists of essentially hemihydrates [6].

Hydration is an exothermal process when heat evolves. According to Jeulin *et al.* [7], when plaster is placed to water a net of needles is naturally formed, establishing the crystallization theory (dissolution–precipitation).

The morphology of plaster crystals depends on the conditions of hydration reactions. The variations of the hydration conditions modify the plug-in degree, texture and crystal distribution. According to [8], the dihydrate ($CaSO_4 \cdot 2H_2O$) is composed of two types of linking the weak and the strong ones. By heating the dehydrate product at 90°C for 10 h, the weak bounds (composed of 3/2 water molecules) are totally destroyed resulting hemihydrate. Heating at 350°C for 10 h, half of the water molecule is completely removed from the substance. Then the strong bounds form $CaSO_4$ anhydrite.

The crystalline structure of the compounds becomes different by the release of water molecules as the temperature increases. The dihydrate and hemihydrate product have a hexagonal symmetry but they exhibit a small variation in the X-ray diffraction peaks. On the other hand, the anhydrite product has an orthogonal form, which indicates a gradual reduction of the crystalline structure as the water molecule is released. Such a reduction of the crystalline structure results collapse in the microstructure of the substance [8].

TG/DTG techniques were also used to verify the physico-chemical transformations during the study of lime and gypsum mixtures [9]. The technique has potentially for analyses of thermoplastic elastomer (TEPs) [10] and polymer [11] recycled materials.

Methods

The plaster and the plaster residue were extracted from a single batch of material in order to reduce the viability of the sample.

Then, the plaster residue was submitted to greenhouse drying (dehydration process) at a constant temperature of 100°C until constant mass was reached. Later it was worn out in a ball mill (Los Angeles abrasion) for 16 min. This time it was considered technically and economically viable after the analysis of the joined results. The plaster residue sample will be referred as ‘recycled plaster’. All the described assays shown below were carried out for two samples, natural and recycled plaster (Figs 1 and 2).

Fig. 1 Natural plaster

Fig. 2 Recycled plaster

The samples were submitted to X-ray diffraction, IR spectroscopy, thermogravimety (TG), and differential scanning calorimetry (DSC) analyses.

IR experiments were carried out in the 4000–600 cm^{-1} wavenumber range in KBr disks.

TG analyses were performed by using Mettler Toledo TGA/SDTA 851^e system. Samples (about 6 mg) were placed to alumina crucibles. Samples were heated from 25 to 1000°C at a heating rate of 10°C min^{-1} under N_2 atmosphere (50 mL min^{-1}).

DSC analyses were conducted in a Mettler Toledo DSC 822^e equipment in the 25–600°C temperature range at a heating rate of 10°C min^{-1} under N_2 atmosphere (50 mL min^{-1}). The sample masses were about 5–6 mg. An empty aluminium crucible was used as reference.

Results and discussion

The IR spectra of the two samples did not present any difference as they were compared. The characteristic absorption bands for the β-hemihydrate in the two samples are indicated by arrow in Fig. 3.

IR spectra of the different pure sulphates were analyzed. However, the identification of the composites was difficult in their mixtures. To distinguish the α- and β-phases was possible by the double-band peaks at 600 cm^{-1} [12]. The recycled plaster sample presented a similar curve to that of the natural one.

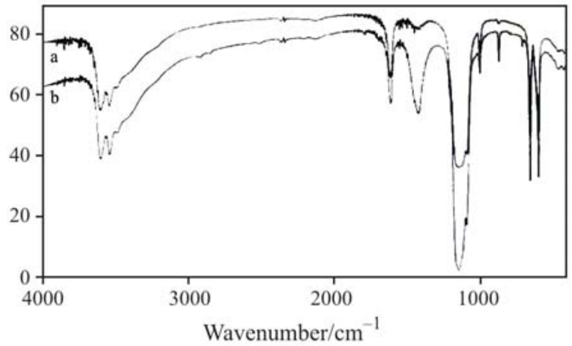

Fig. 3 FTIR spectra of a – natural plaster and b – recycled plaster

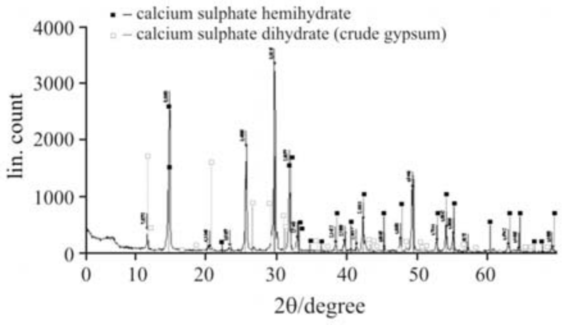

Fig. 4 X-ray diffractogram of natural plasters: calcium sulphate hemihydrate and calcium sulphate dihydrate (crude gypsum)

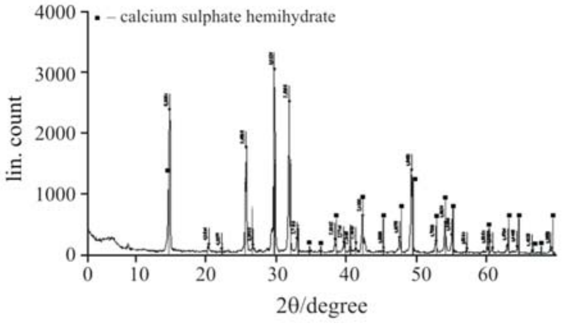

Fig. 5 X-ray diffractogram of the recycled plaster, calcium sulphate hemihydrate

The FTIR curve of the recycled plaster was quite similar to that of natural plaster has.

The X-ray diffraction analysis of the dust natural plaster sample allowed the identification of the calcium sulphate hemihydrate as the main constituent of the substance, and crude gypsum as its minor constituents. In the dust recycled plaster sample, the analysis allowed only the identification of the calcium sulphate hemihydrate. This result was expected after the dehydration (Figs 4 and 5).

The results of TG and DSC analyses also evidenced the same behavior both for the natural plaster and for the recycled plaster samples, which indicates that there were no modifications in the composition and/or structure of the plaster as it can be seen in Figs 6 and 7.

The steps between points A and B in the TG curve correspond to the endothermic reaction of formation of the soluble anhydrite at approximately 150°C.

DSC curves of the samples presented similar profiles with endothermic and exothermic affects (Fig. 7). According to Brown and Gallagher [13] an exothermic effect with a peak around 380°C indicates the crystalline anhydrite modification.

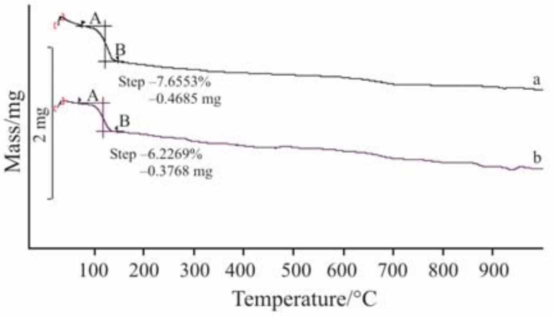

Fig. 6 TG curves of the dust samples; a – natural plaster and b – recycled plaster

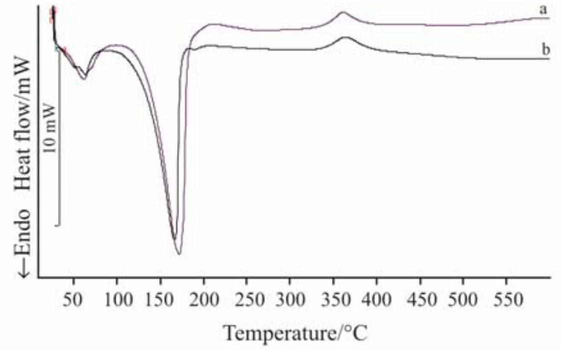

Fig. 7 DSC curves of the dust samples; a – natural plaster, b – recycled plaster

Fig. 8 Recycled plaster frame

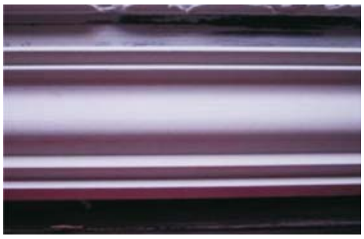

Fig. 9 Natural plaster frame

By the comparison of the DSC curves one can observe, the thermal behavior of the recycled plaster (sample II) practically the same that of the reference sample, natural plaster (sample I).

One possible use of the plaster and recycled plaster is the home decoration to cover walls, ceilings with them. Figures 8 and 9 are the comparative photos of a piece of decoration wall cover made of the two different kinds of plasters. Practically there are no visible differences between them underlining their unique application for the above purpose.

Conclusions

From this study one can reach the following conclusions:

- When results of the analyses confirm the similar behavior, consequently similar chemical characteristics for both samples. No difference was found which could hinder the use of the recycled plaster material.
- Thermoanalytical techniques were important tools in the study in the re-use of residue material, since chemical and physical changes were not detected when natural and recycled plaster samples were compared.
- It is possible to re-use the hydrated plaster residues without harming the required properties.
- It was possible to produce different subjects by using recycled plaster.

Since the primary use of plasters itself results a large amount of waste, searching for recycling and re-using possibilities having even more distinguished importance.

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