

# Physicochemical study of CaCO<sub>3</sub> from egg shells

*Estudo físico-químico do carbonato de cálcio obtido a partir da casca de ovo*

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## Abstract

Calcium carbonate, a pharmaceutical excipient, is widely used as diluent in solid dosage forms. It is also used as a base for medicinal and dental preparations, a buffering and dissolution aid for dispersible tablets, a food additive and a calcium supplement. Egg shells are a rich source of mineral salts, mainly calcium carbonate, which corresponds to about 94% of the shell. Layer farms produce large amounts of shells, whose final disposal poses a challenge from the environmental standpoint. This work was designed to evaluate the physicochemical and thermal properties of calcium carbonate obtained from egg shells. The findings indicated that calcium carbonate from egg shells can be used as an alternative pharmaceutical excipient.

**Keywords:** thermal analysis; X-ray powder diffraction; egg shells; calcium carbonate.

## Resumo

O carbonato de cálcio é um excipiente farmacêutico amplamente utilizado como diluente em formas farmacêuticas sólidas. Também é utilizado para auxiliar na dissolução de comprimidos dispersíveis, como base para preparações dentais e medicinais, e como aditivos em suplementos alimentares. A casca de ovo é rica em sais minerais, principalmente o carbonato de cálcio que corresponde a 94% da casca. As indústrias de ovos produzem grande quantidade de casca e seu destino final é um desafio em termos ambientais. Este trabalho teve como objetivo avaliar as propriedades físico-químicas do carbonato de cálcio obtido a partir da casca de ovo. Os resultados demonstraram que o carbonato de cálcio obtido pode ser uma alternativa como excipiente farmacêutico.

**Palavras-chave:** análise térmica; difração de Raios-x; casca de ovo; carbonato de cálcio.

## 1 Introduction

Since ancient times fertile eggs, unfertilized eggs and chicken embryo eggs have been used by humanity as food and also in the treatment of diseases. We must take into account that eggs were not created for human being feed, but generating a new life, therefore, that is the reason why they are so complete and nutritive food<sup>4</sup>.

The egg shell has the mainly function to protect the chicken embryo acting as physical barrier for inhibiting microorganisms invasion and it also selects gaseous changes<sup>1,9</sup>.

According to Thapon and Bourgeois, 1994 shell is approximately 11% of the total weight of the egg and it presents contents of: calcium carbonate (94%), calcium phosphate (1%), magnesium carbonate (1%) and organic substances (4%). So, egg shell is a rich source of mineral salts, mainly calcium carbonate. Unfortunately, egg shell is an eggproduct industry residue.

Calcium carbonate, a pharmaceutical excipient, is mainly used as diluent in solid dosage forms. It is also used as a base for medicinal and dental preparations, buffering and dissolution aid in dispersible tablets, as well as food additive and calcium supplement<sup>3,6,14</sup>.

Nowadays, there is a great interest in finding new pure calcium carbonate sources<sup>6</sup>. Calcium carbonate obtained from bones flour, does not contain the same bioavailability of calcium obtained from synthetic sources. Calcium carbonate from oyster shells contains lead vestige among the others potential toxic elements such as aluminum, cadmium and mercury<sup>15</sup>. In the other hand, egg shell has an advantage for not containing toxic elements<sup>11</sup>.

Eggproducts industries produce great amount of shells and their final destiny is an environmental impact challenge. This work was designed to prepare and evaluate calcium carbonate from egg shell because it has a potencial application in the development of a new option of pharmaceutical excipient. The lack of information on these subjects suggests that there is a promising area to be explored.

In this context, the main objective of this study was to investigate the physical-chemical and thermal behaviour of calcium carbonate obtained from egg shell comparing to industrial calcium carbonate.

## 2 Experimental

### 2.1 Production of calcium carbonate from egg shell

The chicken egg shell, raw material (*Gallus gallus domesticus*, L.), Hy-line white eggs were obtained from Sohovos AB Brasil – Sorocaba – SP – Brazil eggproduct industry. The calcium carbonate was produced after it had gone through stages of: wash, dry, grind and purification. The details on the treatment of the egg shells are suppressed because the Soho-

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vos eggproduct industry is in process of intellectual property submission request.

## 2.2 Thermogravimetric analysis

The TG/DTG experiments were measured on Shimadzu thermobalance TGA-50. Approximately 6 mg of samples, using a platinum pan, were carried out from 25 to 900 °C in dynamic nitrogen atmosphere with the flow rate of 50 mL.min<sup>-1</sup> and heating rate of 10 °C.min<sup>-1</sup>.

Non-isothermal kinetic study was performed by application of Ozawa's method<sup>13</sup>. The kinetic study of both calcium carbonate, obtained from egg shell and industrial, were evaluated by thermogravimetric curves. The samples were heated at different heating rates (2.5, 5, 10, 15 and 20 °C.min<sup>-1</sup>) to target temperature 900 °C under dynamic nitrogen atmosphere of 50 mL.min<sup>-1</sup>. The equipment was preliminarily calibrated with standard reference of calcium oxalate.

## 2.3 X-ray powder diffraction (XRPD)

The XRPD patterns were recorded on an X-ray diffractometer (Siemens model D5000). The samples were irradiated with monochromatized CuK $\alpha$  radiation (1.54056 Å) and analyzed between 10-80° (2 theta). The voltage, current and pass time used were 40 kw, 40 mA and 1 s, respectively.

## 2.4 Morphology of particle

Microscopic observation of both calcium carbonates was performed under a microscope (Zeiss Axiostar Plus, Japan). The samples were mounted on a glass slide, viewed under normal light and pictures taken with a Zeiss MC80DX camera.

## 3 Results and discussion

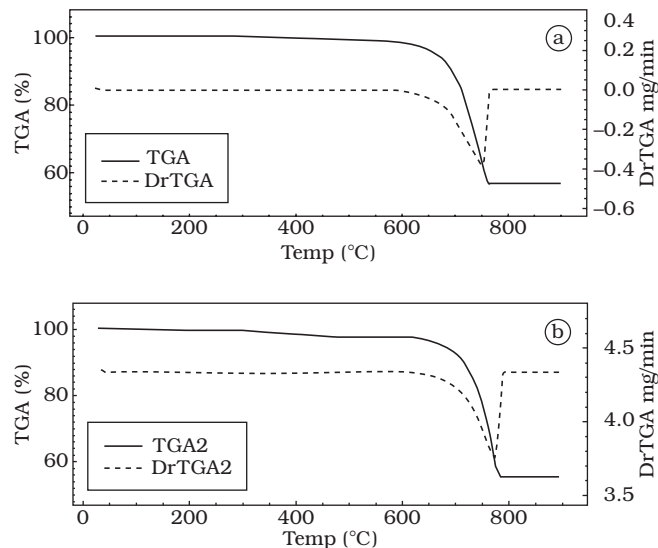
The thermal analysis method was used, as well as X-ray powder diffraction and microscopy. These combining techniques provide quick and proper interpretations, offering the thermal stability, molecular organization, particle size and the possibility of analytical quantification of substances<sup>7,8,12</sup>. The properties of calcium carbonate obtained of the egg shell was compared with the industrial calcium carbonate, purchased from LABSYNTH, batch number 71148 USP-FCC.

The thermogravimetric curve TG/DTG obtained for industrial calcium carbonate (Figure 1a) showed a thermal stability up to 600 °C with a small mass loss ( $\Delta m = 1.8\%$ ) corresponding to volatile material. The decomposition process occurs in a single step in a defined way, between temperature range from 601 to 770 °C, with a  $\Delta m = 41.7\%$  due to carbon dioxide release, given rise to calcium oxide:  $\text{CaCO}_3(\text{s}) \xrightarrow{\text{heat}} \text{CO}_2(\text{g}) + \text{CaO}(\text{s})$ . The calcium carbonate usually decomposes at temperatures over 600 °C without fusion process<sup>10</sup>.

The TG/DTG curve obtained for egg shell calcium carbonate is seen in Figure 1b. The curve showed thermal stability up to 630 °C with a mass loss of  $\Delta m = 2.6\%$  referring to volatile material. The thermal decomposition process occurs

at the temperature range from 636 to 795 °C with mass loss  $\Delta m = 42.5\%$ , which corresponds to carbon dioxide release, in a single step, in a defined way.

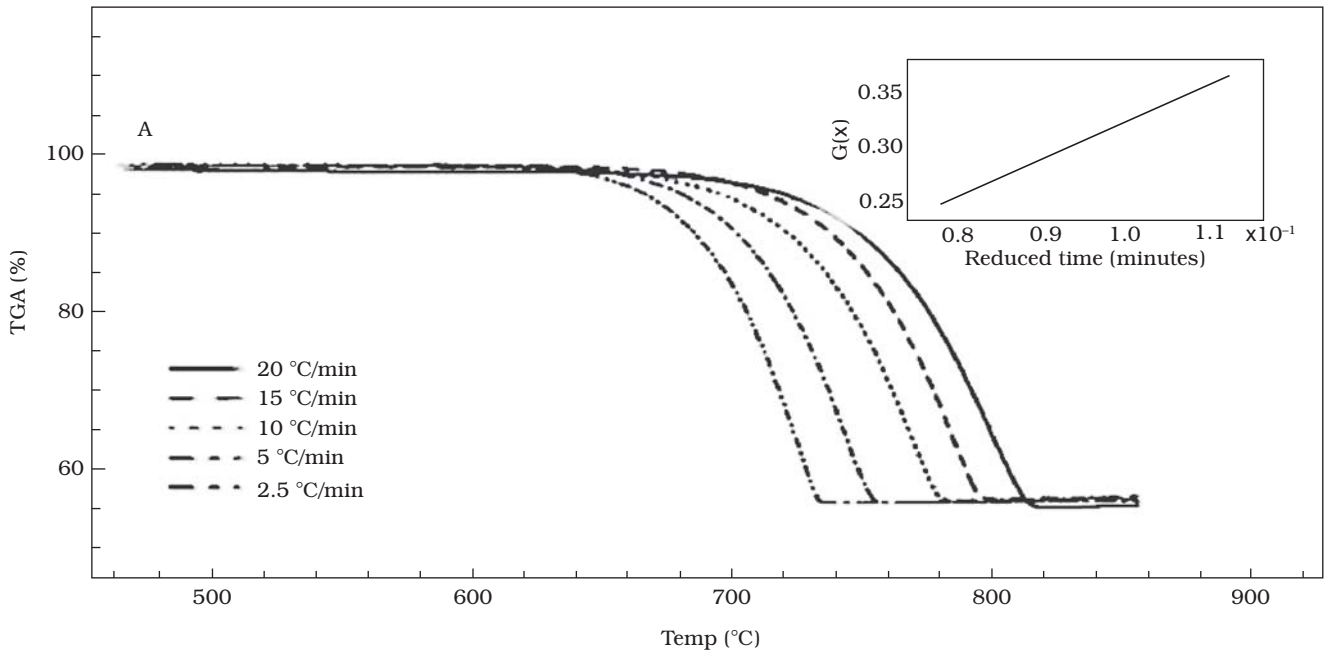
Through the thermogravimetric analysis it is possible to evidence that industrial calcium carbonate decomposes at temperature about 30 °C less than the calcium carbonate obtained from egg shell, with DTG<sub>peak</sub> of 749.9 and 771.5 °C for industrial and egg shell product, respectively.



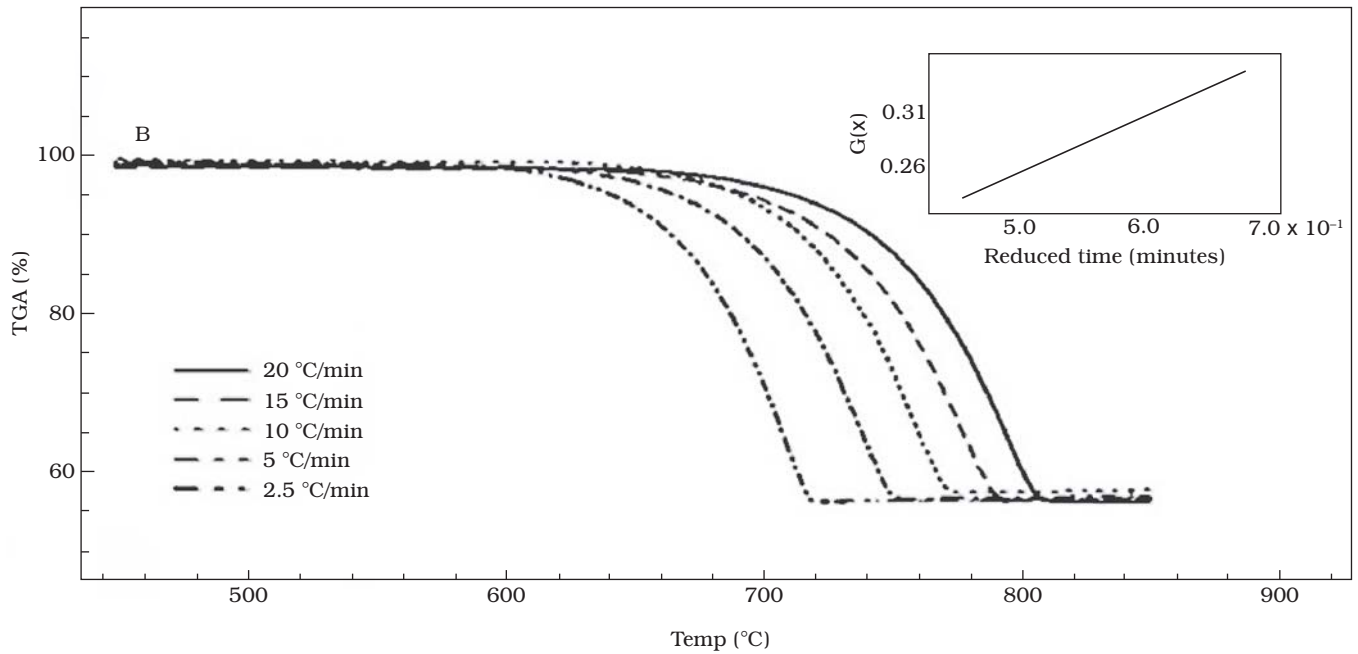
**Figure 1.** The TG/DTG curves measured on Shimadzu thermobalance TGA-50. Approximately 6 mg of samples, using a platinum pan, were carried out from 25 to 900 °C in dynamic nitrogen atmosphere with the flow rate of 50 mL.min<sup>-1</sup> and heating rate of 10 °C.min<sup>-1</sup>, a) Industrial calcium carbonate, and b) Egg shell calcium carbonate.

The kinetic data were calculated from plotting the mass loss vs. temperature of TG curves obtained to different heating rates for both calcium carbonates. Figures 2 and 3, demonstrate the superposition of TG curves obtained to industrial and egg shell calcium carbonate, respectively. The inserted figure demonstrates the linear tendency of reaction mechanism.

The activation energy ( $E_a$ ) and Arrhenius frequency factor ( $Z$ ) were calculated by Ozawa's method for each five TG curves. The activation energy was obtained from a plot of logarithms of heating rates ( $A$ ) as a function of the inverse of temperature ( $1/T$ ) for a constant  $G(x)$ , in which  $G(x)$  is the integrated form of the conversion dependence function,  $f(x)$ . The  $E_a$  values were  $47.83 \text{ kcal.mol}^{-1} \pm 0.6\%$  and  $49.25 \text{ kcal.mol}^{-1} \pm 0.2\%$  for industrial and egg shell calcium carbonate, respectively. It was evidenced that the activation energy required for the decomposition process of egg shell product is higher than industrial, which pronounces its largest thermal stability. The Arrhenius frequency confirms the stability of egg shell calcium carbonate; the obtained results were  $3.469 \times 10^9$  for industrial calcium carbonate and  $5.011 \times 10^9$  for egg shell calcium carbonate. For both products the reaction of degradation was governed by a zero order kinetic.



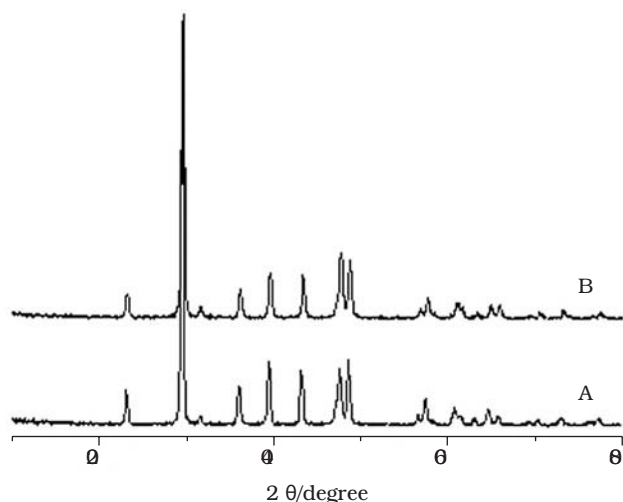
**Figure 2.** TG curves of industrial calcium carbonate obtained at different heating rates under dynamic nitrogen atmosphere.



**Figure 3.** TG curves of egg shell calcium carbonate obtained at different heating rates under dynamic nitrogen atmosphere.

In order to characterize the crystallinity patterns of industrial and egg shell calcium carbonate, XRPD analysis was performed for both samples. The diffractograms in Figure 4 indicate that diffraction patterns of industrial and egg shell

calcium carbonate have similar peaks. The patterns can be put upon being the differences only found in the intensity of the peaks. The sharp peaks of both samples are characteristic of the high crystallinity of samples.



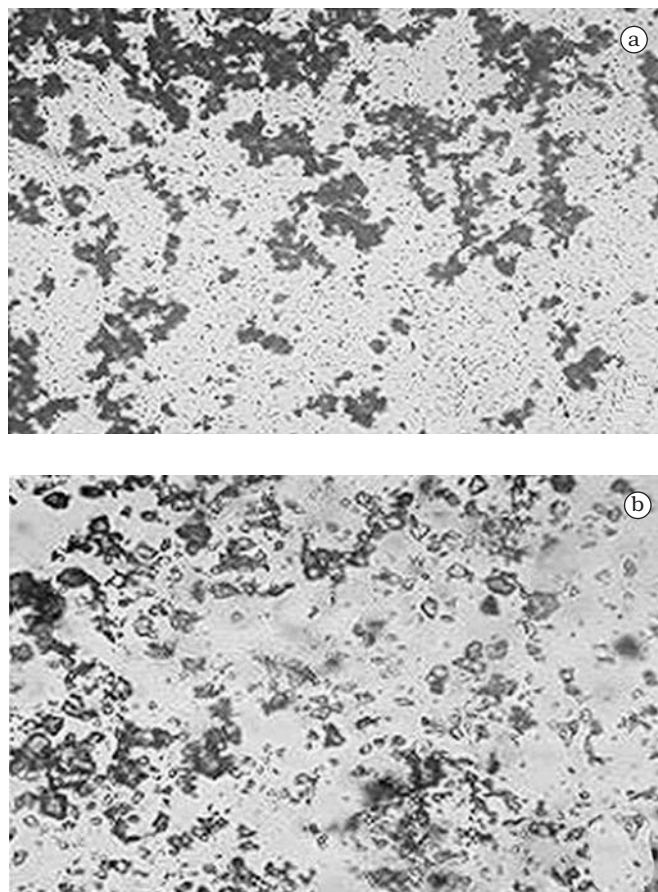
**Figure 4.** X-ray Powder Diffraction Patterns of industrial calcium carbonate (a) and egg shell calcium carbonate (b).

Table 1 shows the reflections,  $d$ -distances and relative intensities ( $I/I_0$ ) of the observed peaks in the patterns. The variation of samples reflections is small being larger in the relative intensity. Studies have been considering that the similarity of patterns is established if the scattering angles of the strongest reflections obtained from an sample agree to about  $\pm 0.2$  degrees with that of the reference material; and if the relative intensities of these reflections do not vary more than 20%<sup>2,5</sup>. The  $d$ -distance that considers the distance among the crystal plans is similar between carbonates, however, the values of the egg shell calcium carbonate is slightly smaller.

**Table 1.** X-ray powder diffraction data for industrial and egg shell calcium carbonate.

Industrial calcium carbonate			Egg shell calcium carbonate		
2 $\theta$ (degree)	$d$ (Å)	$I/I_0$ (%)	2 $\theta$ (degree)	$d$ (Å)	$I/I_0$ (%)
23.08	3.930	13	23.23	3.906	9
29.46	3.132	100	29.53	3.126	100
35.93	2.625	14	36.13	2.613	11
39.47	2.423	22	39.47	2.423	16
43.17	2.252	19	43.27	2.248	15
47.55	2.088	19	47.57	2.087	21
48.57	2.055	23	48.67	2.052	20
57.42	1.828	9	57.57	1.825	8

The morphology of particles was investigated by optical microscopy for both calcium carbonates. The photomicrographs of products are shown in Figure 5. The images of industrial product (Figure 5a) and egg shell product (Figure 5b) indicate that these powders are preferably crystalline, and the size of the egg shell product is larger than industrial calcium carbonate crystals. The difference found between the crystals size can be related with the thermal stability of egg shell product, once the structure and size of crystals are directly correlated with the stability.



**Figure 5.** Optical microscopy of industrial calcium carbonate (a) and egg shell calcium carbonate (b) at magnification of 400 x.

## 4 Conclusions

Through the thermogravimetric analysis it was evidenced that industrial calcium carbonate decomposes at a temperature of about 30 °C less than the calcium carbonate obtained from egg shell. The obtained kinetics parameters ( $E_a$ ) and ( $Z$ ) confirm that egg shell calcium carbonate is more stable comparing with the industrial. The XRPD analysis demonstrates that both products have similar crystallinity and the microscopy indicates that egg shell carbonate has largest particle size. The results showed that both products have similar physical chemical parameters, indicating that egg shell product should be an alternative of pharmaceutical excipient. Furthermore, studies have been accomplished about the influence of the egg shell calcium carbonate in the quality of pharmaceutical products like cosmetics.

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