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Thermal analyses of commercial magnesium stearate pseudopolymorphs

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Abstract

Two commercial magnesium stearate powders in two well-characterised structural states are investigated using DSC and coupled TGA–DTA under dry nitrogen flow. They consist of either a mixture of crystalline hydrates or a poorly crystallised so-called anhydrate. Following the degassing of unbound water, 1 or 3 weight-loss peaks are observed below about 100 °C, each associated with one heat loss peak at the same temperature. The present results and a review of graphical data from literature show that the so-called anhydrate always contains a significant amount of water. At the beginning of the dehydration process, the heat loss is the same as the standard heat of vaporisation of water and then gradually departs from it by positive values. The idea according to which the mixture of dihydrate and trihydrate loses water to form the anhydrate cannot be quantitatively reconciled with the present and other gravimetric results.

Keywords: Magnesium stearate; Hydrate; Dehydration; TGA; DSC

1. Introduction

A number of experimental investigations have been carried out to measure and elucidate the variability of certain physical properties of magnesium stearate (abbreviated to MgSte in the following): its atomic structure, crystallinity, water content, thermal stability and granular properties supposedly influence one or several of its functional properties, in particular, its lubricating capacity. Though, as an industrial product, MgSte is not a high purity single-phase material and is available in different hydration and crystalline states. This is probably one reason for the apparent diversity of observations reported in the relevant literature, a synthetic review and analysis of which is, to the authors' knowledge, still lacking. This paper is aimed at filling that vacancy by comparing these with the accurate graphical and numerical results of thermal analyses of two representative commercial stearate powders in clearly identified initial states. Indeed, it follows a previous paper [1] that reported detailed results from X-ray powder diffraction analyses of the very same materials. In agreement with the literature, two structural states could be differentiated. It was shown that they could be reached reversibly at room temperature by changing the partial pressure of water vapour, and their modification with increasing temperature was described in detail up to the melting that appeared to take place gradually above 100 °C. A majority of the various MgSte powders described in the literature fits in that description.

The thermal stability of MgSte has been investigated in several publications by thermogravimetry (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Coupled TGA–DTA was used by Müller [2], DSC by Hattiangdi et al. [3], Brittain [4], and Elder [5]. Miller and York [6], Wada and Matsubara [7], Barra and Somma [8] and Sharpe et al. [9] used both TGA and DSC. In most cases, X-ray diffraction (XRD) was also used

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to characterise the structural and crystallisation state of the materials, as the search for a correlation between the structural, thermal and functional properties motivated most authors.

However, the results of these previous structural and thermal analyses are in partial qualitative agreement only and provide no evidence that such a correlation actually exists. At increasing temperature under dry gas flow, all investigated materials exhibit one or several successive exothermic weight losses up to ca. 100–110 °C and then one or several thermal events. Schematically, it can safely be stated that dehydration takes place in the first range and fusion (at least certain thermal effects associated with it) in the range 105–125 °C. There are several obvious reasons for the poor quantitative agreement observed between the various published results. They can be found as much in the different analytical conditions, as in the poor resolution and quality of some reported results as well as in the different synthesis, drying and preservation conditions and purity of the investigated materials. In several reports, the lower temperature part of the thermograms from room temperature (RT in the following) up to 45, 60 or even 80 °C is simply ignored. Except in one case [7] the DSC thermograms have not been integrated to yield enthalpy values (and this cannot reasonably be done afterwards, using the reported graphical data). The enthalpy values reported in [7] for 11 different materials range from 1.96 to 21.18 $\mathrm{J\,g^{-1}}$. Another recently published example of diversity, which is clearly attributable to the origin of the materials, can be found in [5]. The DSC thermograms of three commercial MgSte powders are reported in [5]. They show one, two or four endotherms at different temperatures below 130 °C and then a small one at 145 °C assigned by the author to a liquid crystalline phase transition. No exotherms can be seen up to 220 °C. Such exotherms can be noticed between 150 and 200 °C [4,7] in the thermograms of certain commercial products but not in those of the pure phases [9,10]. Unfortunately, the temperature range scanned in these last cases is limited to 140–150 °C, respectively. Nonetheless, exothermic events are consistent with the idea that inorganic impurities, namely magnesium salt(s) residues [7], may undergo chemical transformation in the heating process.

2. Materials and techniques

Two representative commercial powders from vegetable origin are investigated. They are hereinafter referred to as VF and VG from the names of their producer, FACI and GREVEN, respectively. A detailed description of the modifications of their structural characteristics following interaction with water vapour at RT and thermal treatment in a dry atmosphere has been previously published [1].

Any commercial MgSte material is expected to contain a certain amount of non-stearic chains, essentially palmitic. The palmitic and stearic acid weight fractions have been measured in VF and VG using HPLC, following the European pharmacopoeia recommendation. The results are shown in Table 1 and have been converted into values of the mole fraction X of palmitic chain in the mixed soap $\mathrm{Mg[Ste_{1-x}Palm_x]}$. A small fraction of other unidentified aliphatic chains that amounts to only 4 wt.% in both VF and VG is present. This is ignored in all subsequent computations: it would affect the numerical values (e.g. molar mass) by a fraction of a percent only. Both batches can be regarded as rather pure commercial products. Even though the materials are still referred to as MgSte in the following, the actual molar masses of the anhydrous molecules $\mathrm{Mg[Ste_{1-x}Palm_x]}$ are used in calculating the total water content as measured by the Karl-Fisher technique and of weight losses as measured by thermogravimetry. Except for one paper by Wada and Matsubara [7], the palmitic–stearic acid ratio is never reported in other publications. Where needed, in order to convert fractional weight losses found in the literature into numbers of moles of water, a typical “average” palmitic/stearic ratio of 30/70 in mass is assumed (the corresponding molar mass equals 575 g).

The VF ad VG batches are investigated in their “as-received” state and also after modification in the following conditions:

(a) degassing of VG under high vacuum at RT, here 25 ± 2 °C during several days as required for the pressure in the degassing chamber to return to its base value, indicating completion of the process. By this treatment, the mixture of crystallised hydrates is transformed into the poorly

Table 1
Determination of stearic and palmitic acid contents by HPLC

	VF	VG
Stearic acid (wt.%) [range]	84.0_3 [83.8–84.2]	81.0_0 [80.8–81.2]
Palmitic acid (wt.%) [range]	12.1_7 [12.1–12.3]	15.2_7 [15.1–15.4]
Total (wt.%)	$96.2_0 \pm 0.1$	$96.2_3 \pm 0.1$
x in $\mathrm{Mg[Ste}_x\mathrm{Palm}_{1-x}]$	0.862	0.841
M_0 ($\mathrm{g\,mol^{-1}}$)	583.5	582.3
1 mol H_2O per mol $\mathrm{MgSte{\cdot}1H_2O}$ (weight loss in wt.%)	2.995	3.001
1 mol H_2O per mol $\mathrm{MgSte{\cdot}2H_2O}$ (weight loss in wt.%)	2.901	2.914
1 mol H_2O per mol $\mathrm{MgSte{\cdot}3H_2O}$ (weight loss in wt.%)	2.826	2.831

The molar mass M_0 of the anhydrous soap is computed by setting the total stearic and palmitic weight fractions equal to unity. Values of the weight loss in wt.% corresponding to the loss of 1 mol of water per mole of mono-, di- and tri-hydrate are indicated.

crystallised anhydrate that cannot be structurally differentiated from that of as-received VF [1]. Partial results of the characterisation of one VG sample degassed under similar vacuum conditions at 50 °C are also mentioned in Section 3.

(b) Ageing of VF in an incubator at 25 ± 0.1 °C in an atmosphere with 85 ± 1% RH, during periods of time ranging from 1 to 4 months. According to literature [9], and references cited herein, such conditions would ensure the crystallisation of the trihydrate starting from the anhydrate phase. However, it has been observed that the same mixture of crystallised hydrate as in VG is thus obtained. The present report also shows that the phase composition of the material aged during the longest period (4 months) was not homogeneous throughout the treated powder bed.

The water content of the as-received and modified batches has been measured by standard Karl-Fisher (K-F in the following) and/or thermogravimetric methods. Weight losses were obtained by TGA as detailed next and by using the infrared balance method following the standardised analysis conditions prescribed by the European pharmacopoeia, i.e. heating at 100 °C until constant weight.

Coupled TGA–DTA, on the one hand, and DSC, on the other hand, have been carried out under high purity nitrogen flow (10 $cm^3 min^{-1}$) using the STD 2960 and DSC analysers of TA Instruments. In both series of experiments, the reference samples consisted of a comparable weight of glass beads, and a unique heating rate, $\beta = 2\,°C\,min^{-1}$ was used. Most TGA, DTA and DSC thermograms published in the literature were reportedly acquired at either 10°C min^{-1} (most frequently), 5 °C min^{-1} [7] or 2 °C min^{-1} [6,9,11]. In order to help evaluate the influence of that parameter, and compare results from different literature sources, we carried out calibration experiments at 2 and 10 °C min^{-1}. The maximum temperature of a DTA event observed at $\beta = 10\,°C\,min^{-1}$ was found 20 ± 3% higher than that of the same event observed at $\beta = 2\,°C\,min^{-1}$. In other words, events observed in the 50–100 °C temperature range at 2 °C min^{-1} would occur between 60 and 120 °C at 10 °C min^{-1}.

3. Results

All as-received and modified materials differ in their water content but the later value clearly depends on whether it is obtained using the K-F or TGA techniques. In the former case (the K-F analysis) it is found equal to 1.70 for the as-received VF and 2.43 for the as-received VG. The figures are in mole of water per mole of MgSte and this will be abbreviated to mpm in the following. In a modified VF batch aged 2 months in the standardised conditions mentioned above, the measured value is 2.26, which corresponds to an uptake of 0.56 mpm. As shown previously [1] this is sufficient to cause the diffraction band of the rotator phase to disappear at the expense of the fine diffraction lines of the crystallised hydrates.

Another important observation is that the water content measured by the K-F method systematically exceeds by about 0.5 mpm the result obtained by the standardised infrared balance method. In fact, heating up to 150 °C in air proves necessary to reach agreement with the K-F method. The difference with the water content values assessed by TGA is still somewhat larger, in excess of about 0.7 mpm. The data are plotted in Fig. 1 which also includes a point computed from numerical and graphic data taken from Wada and Matsubara (the weight loss of one of their materials only, namely Mg-st F, can be estimated with sufficient accuracy). A comparable difference is observed in that case also.

The results of the thermal analyses of four representative samples are shown in Figs. 2–5. Each figure consists of a set of three plots with the same temperature scales, and shows the results obtained by TGA (integral and differential curves), DTA, and DSC (obtained independently from the former two). The TGA–DTA experiments in Figs. 2 and 3 have been duplicated and the reproducibility is satisfactory.

The similarity of the DTGA and DTA traces below ca. 100–105 °C in every figure is evidence that the gravimetric and calorimetric data are strongly correlated in that temperature range. The similarity of the DTA and DSC traces is evidence that the calorimetric data obtained by different techniques in distinct experimental set-ups are accurately reproducible. Accordingly, the numerical results obtained by DSC can be directly compared or combined with the gravimetric data. To this end, the heat flow curves obtained in the DSC experiments have been integrated with respect to time and the result plotted versus temperature along with the raw data. This allows the evaluation of the cumulated evolved heat, expressed in $J\,g^{-1}$ and its comparison with the TGA curves as detailed later on. Because *all* TGA and DSC curves show a plateau over a narrow interval located somewhere between

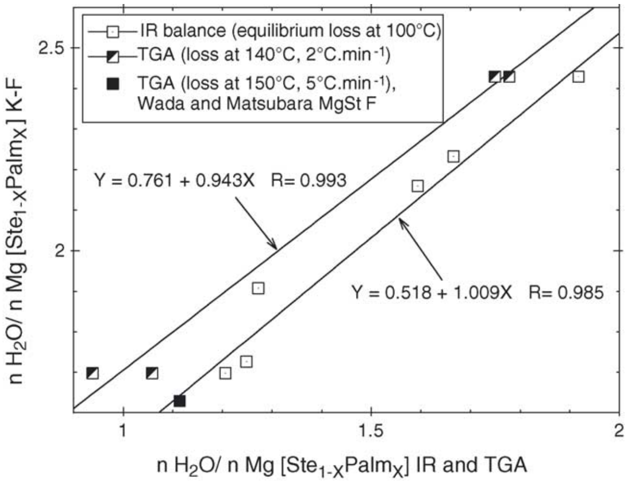

Fig. 1. Water content of various MgSte samples as measured using the K-F method and TGA and expressed in mole H_2O per mole MgSte (shortened as mpm in text).

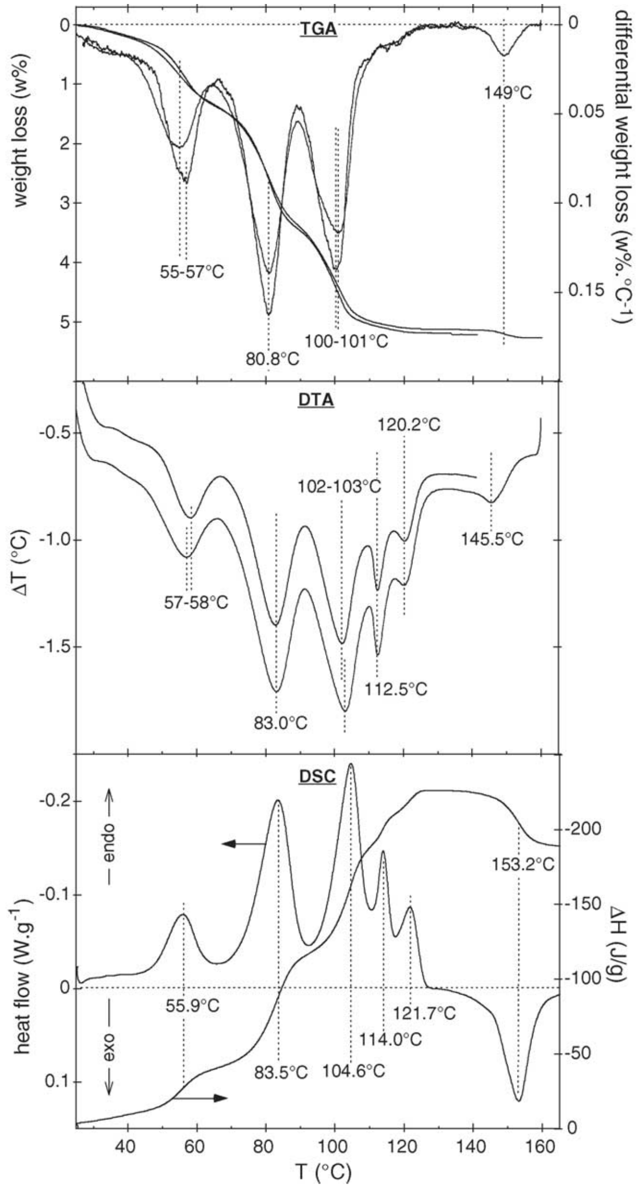

Fig. 2. Thermal analyses of batch VG as received.

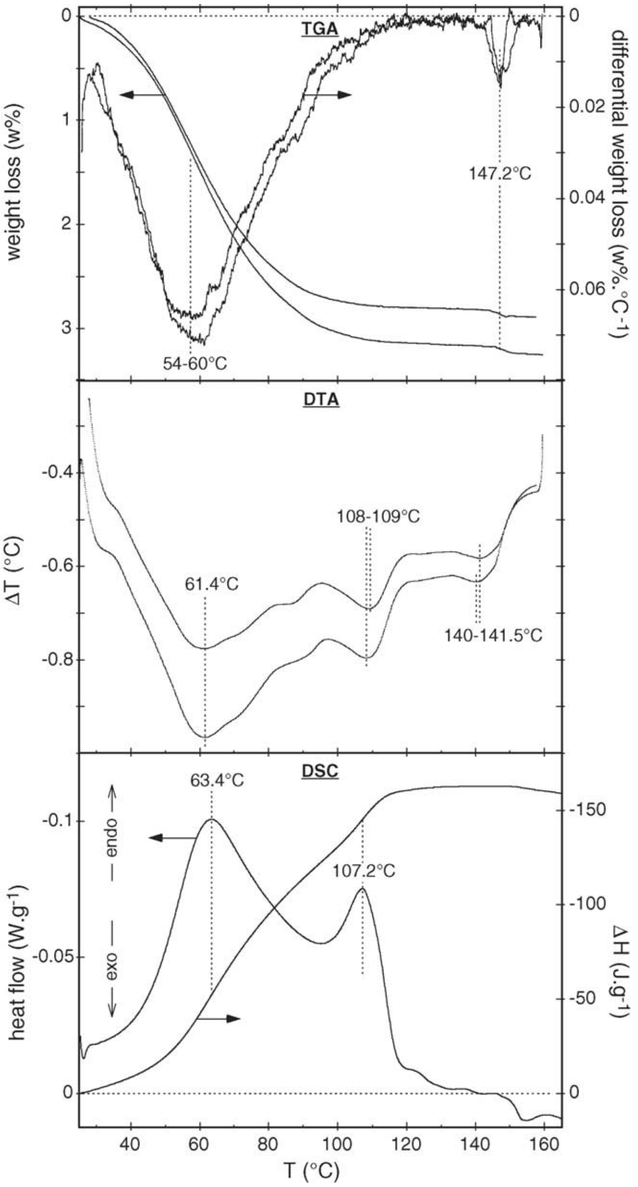

Fig. 3. Thermal analyses of batch VF as received.

120 and 140 °C (but not near RT), this is taken as the origin of the ordinate of the DSC curves. The corresponding (and always small) heat flow value is subtracted from the raw data prior to integration.

The numerical values for the partial weight losses determined at the peak temperatures of the DTGA curves and of the heat losses determined at the peak temperatures of the DSC curves are listed in Tables 2 and 3. The weight loss values are in mpm and were computed considering that the sample weight at 130–140 °C is that of the anhydrous material (as already assumed in computing the abscissa values of the data point in Fig. 1). The values of enthalpy changes associated with each thermal peak are expressed in kJ per mole of anhydrous MgSte.

A close examination of the figures shows that all materials start loosing weight and heat at RT as soon as dry nitrogen is set to flow through the cell. This is most likely due to the degassing of unbound surface moisture (referred to as adsorbed water in the following), and is complete in all cases around 40 °C.

The two "anhydrates", as-received VF and VG degassed at RT, show very similar gravimetric and thermal curves below the plateau, say below 130 °C in Figs. 3 and 4: a single broad weight loss peak and a first broad heat loss peak, centred between 51 and 63 °C. The TG peaks are not symmetrical and may possibly include a weak unresolved component around 80–90 °C. The second heat loss peak at 107–109 °C has no resolved gravimetric counterpart but the weight loss curves actually returns to the zero level above 120 °C only. The total weight loss at 130 °C represents some 0.94–1.05 mpm for the as-received VF, and 0.9 for the VG degassed at RT.

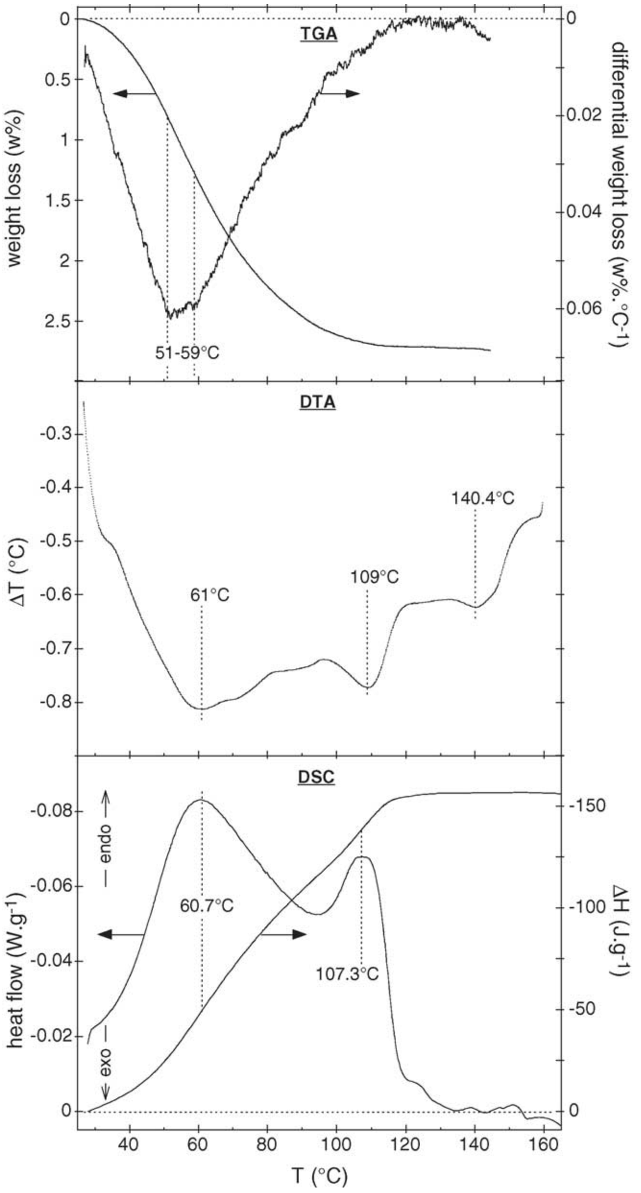

Fig. 4. Thermal analyses of batch VG, vacuum degassed at 25 °C.

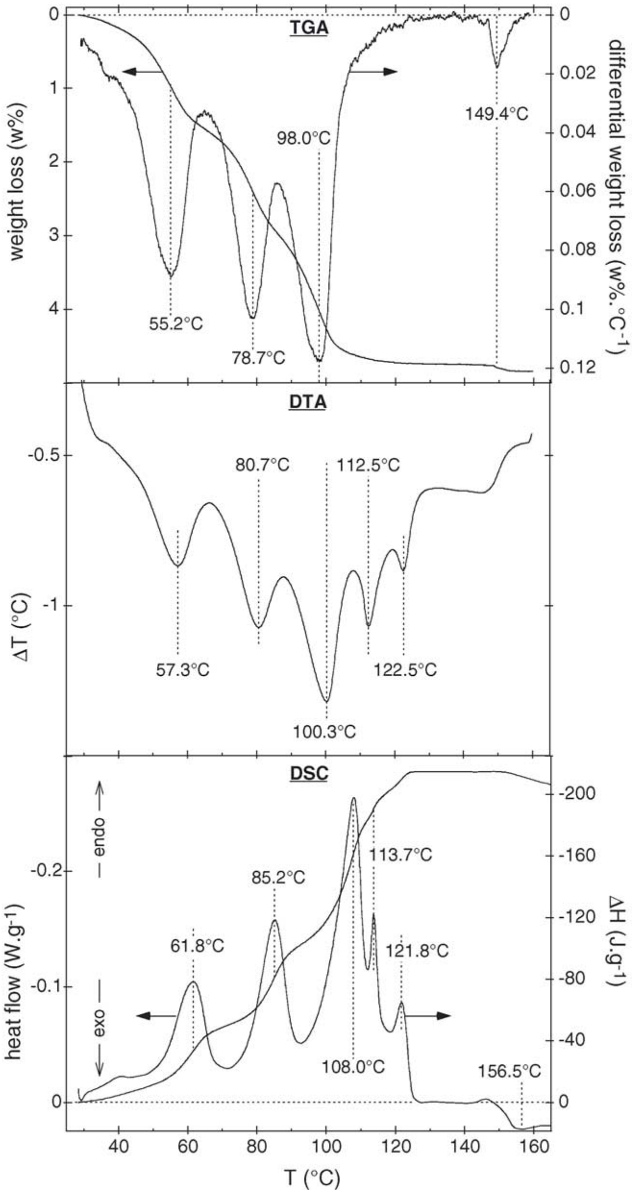

Fig. 5. Thermal analyses of batch VF, aged 4 months 85% RH.

As for the crystalline hydrates, in the lower temperature range from RT to 108 °C, several weight and heat losses are obviously related. As already mentioned, and not taking into consideration the degassing of surface water below ca. 40 °C, either 3 (in two cases) or 2 (in one case) very sharp peaks can be observed. The peak temperature taken from the six graphs of Figs. 2 and 5, fall into narrow ranges: 55.0–61.8 °C for peak #1, 78.7–85.2 for peak #2 and 98–108 °C for peak #3. Inspection of the TGA and integrated DSC traces allows the conclusion that both vary with temperature in a very similar way. The comparison can be made more quantitative by interpolating the heat flow curves over the temperature values for the corresponding TGA traces. Fig. 6a, the heat loss expressed in kJ mol^{-1} is plotted versus the weight loss expressed in mpm for the crystallised as-received VG and modified VF. It is clear that the amount of heat released is roughly proportional to the amount of water evolved and initially not much different from what would be obtained if liquid water were used in place of the MgSte samples. Indeed, the equation for the dotted straight line in the figure was computed assuming a constant heat loss per mole of evolved water, equal to 43.6 kJ mol^{-1}, the standard heat of vaporisation for liquid water. In other words, it represents the heat that would be released by the vaporisation at equilibrium of the same weight of liquid water as lost by the analysed samples. The same data reduction and representation was done for the anhydrates in Fig. 6b. In both figures there is a *gradual* drift of the experimental values from the straight line just mentioned and this is in accordance with the increasing values of the partial heat losses in Table 2.

Table 2
Results of thermal and gravimetric analyses of crystallised hydrated materials, as-received VG and modified VF

	VG, as-received (Fig. 2)		VF, modified (Fig. 5)	
	TGA (mpm)	DSC ($kJ\,mol^{-1}$)	TGA (mpm)	DSC ($kJ\,mol^{-1}$)
#0	0.057–0.068		0.046	
#1	0.397–0.414	−18.98	0.486	−26.40
#2	0.694–0.682	−46.91	0.475	−32.12
#3	0.600–0.613	−44.37	0.608	−49.93
#4		−13.02		−11.82
#5		−9.64		−7.17
#6	0.015 wt.%	+23.37	0.10 wt.%	

Peak identification in first column: #0 = loss of adsorbed water; #1–3 = partial dehydration steps, #4, 5 = thermal events without gravimetric counterpart, #6 = loss of unidentified species. Weight losses are in mole H_2O per mole MgSte except for weight loss #6 that is in weight percent. Partial heat losses are expressed in kJ per mole MgSte.

In the narrow temperature range 108–130 °C, the single broad peak characteristic of the anhydrates (around 107 °C) either splits into two fine components at 114 and 122 °C (peaks #4 and #5 in Table 2) or narrows and shifts to 117 °C (result not shown in a figure). These temperature values are close to those reported by Sharpe et al. [9] for the fusion of pure magnesium stearate and palmitate (115 °C). The underlying fundamental question is obviously to decide whether the pair of DSC peaks just mentioned signals the fusion of two distinct soap phases (with identical X-ray diffraction spectra) or the thermotropic mesomorphism of a single phase.

At last, a small but well-defined weight loss peak is detected at 146–150 °C. It seems to be coupled with an exotherm at 153 °C in the DSC curves for the as-received VG only (Fig. 2).

4. Discussion

4.1. Water content of commercial pseudo-polymorphs

A certain number of similar observations reported in the previous section and in the literature point to the same conclusions. First, most commercial magnesium stearate materials seem to be made of either a mixture *in variable proportions* of the crystallised hydrates or of the poorly crystallised so-called anhydrate. When the anhydrate VF is stored 2 months in humid air, the uptake of water measured by the K-F method amounts to 0.56 mpm. In comparison, the difference between the weight losses at 140 °C in Fig. 5 (VF modified) and in Fig. 3 (as-received VF) is in the range 0.57–0.68 mpm. For the commercial materials A and B of Rajala and Laine [10] exposed to dry and humid atmospheres, the difference can be estimated at 0.75 and 0.35 mpm, respectively. In [8] the difference amounts to 0.77 mpm between samples MgSt#111 and MgSt#112, and to 0.55 between samples MgSt#211 and MgSt#212. This is evidence that, at room temperature, changing the water content by only a fraction of a mpm is sufficient

Table 3
Results of thermal and gravimetric analyses of anhydrates, as-received VF and modified VG

	VF, as-received (Fig. 3)		VG, degassed at 25 °C (Fig. 4)	
	TGA (mpm)	DSC ($kJ\,mol^{-1}$)	TGA (mpm)	DSC ($kJ\,mol^{-1}$)
#0	–	–	–	–
#1	0.937–1.052	−73.54	0.905	−70.93
#2	–	–	–	–
#3	–	–	–	–
#4	–	−24.24	–	−19.5–25.9
#5				
#6	0.05–0.07 wt.%			

Peak identification in first column as in Table 2. Weight losses are in mole H_2O per mole MgSte; partial heat losses are given in kJ per mole MgSte. Weight loss #6 in weight percent.

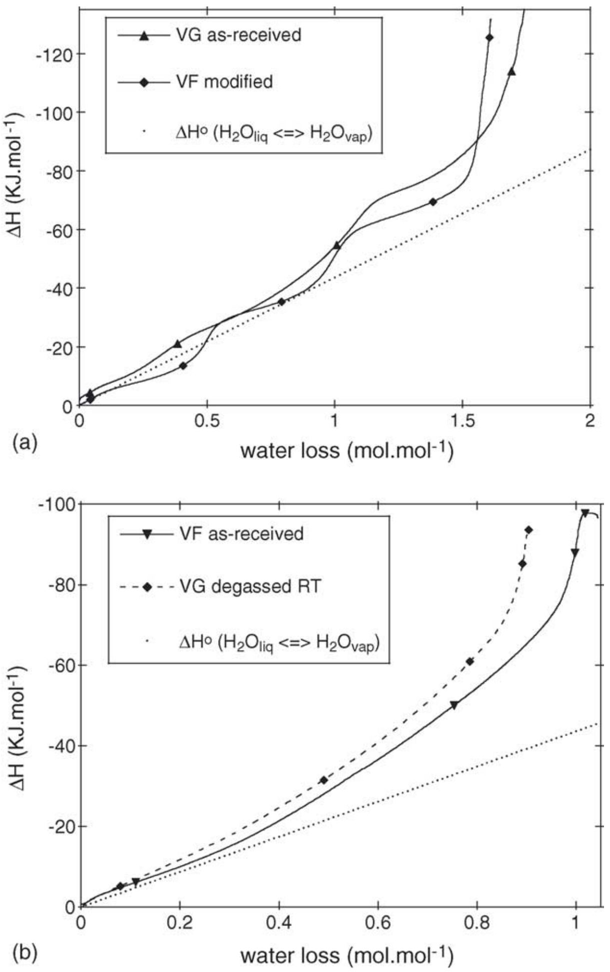

Fig. 6. (a) Heat loss vs. weight loss as obtained from distinct DSC and TGA experiments for crystallised materials as-received VG and modified VF. For details on the integration of the DSC curves see text. The slope of the dotted line is equal to the molar standard heat of vaporisation of liquid water; (b) heat loss vs. weight loss as obtained from distinct DSC and TGA experiments for the poorly crystallised so-called anhydrates: as-received VF and modified VG. For details on the integration of the DSC curves see text. The slope of the dotted line equals the molar standard heat of vaporisation of liquid water.

to bring about the change in structure from the rotator to the crystalline phases and vice versa, as described in [1]. As seen in the following, it proves difficult to reconcile this in quantitative terms with the (reversible) conversion of a mixture of stoechiometric trihydrate and dihydrate into anhydrous MgSte.

Another conclusion is that the water content of the so-called anhydrate is not zero. Instead, based on results of TGA analyses only, it amounts to about 1 mpm, ranging from 0.90 mpm for the VG fully degassed at RT, to 0.94–1.05 mpm for the as-received VF. In comparison, Müller [13,14] indicates ca. 1 mpm. From the point of least slope in the TG traces reported by Rajala and Laine [10], one can estimate the change at 0.99 mpm in material A, and 1.06 in material B. The loss of sample MgSt#12–14 in [8] can be roughly estimated at 0.85 mpm. This material exhibits the same X-ray diffractogram as our VG degassed at 50 °C in [1] the weight loss of which was found to be 0.903–0.906 mpm. Obviously, there is ample evidence that the actual composition (measured by TGA) of the so-called anhydrate exposed to ambient conditions is close to that of a monohydrate. Its formula will be noted MgSte-$(1-x)\mathrm{H_2}0$, where x is meant to take a small value compared to unity.

4.2. *Mechanism of dehydration of the crystallised hydrates*

According to Sharpe et al. [9] and to Rajala and Laine [10], the dehydration of pure magnesium stearate dihydrate takes place in a *single* gravimetric and thermal step.

The same holds for the trihydrate [9] but surprisingly *not* for the homologous pure Mg-palmitate trihydrate (characterised by four thermal events). The X-ray diffractograms of the dihyrates in [9,10] are also very different. Based on this, the previous conclusion should be regarded as questionable.

Our XRD results [1] strongly support the idea that the small palmitic fraction does *not* form separate palmitate phases, either anhydrate or hydrates, in the VF and VG materials. Otherwise, based on the numerical data taken from [9] two well-separated sets of harmonics would have been observed in the diffractograms of the *anhydrates*. On the other hand, when the mixture of crystallised hydrates (as-received VG) was heated (step by step) in a dry atmosphere, the layered crystal structure assigned to the trihydrate disappeared first followed by the layered crystal structure of the dihydrate. Finally, at 55 °C, the structure (rotator phase) was the same as that of the sample fully degassed at 50 °C and analysed after return to ambient conditions. In the TG and DSC analyses considered now, the same sequence of events is expected to take place. Though, such a picture is not in agreement with the numerical results for the TG analysis. Based on the foregoing and assuming the initial state is a mixture of di- and tri-hydrates only, the reaction should be written as:

$$n_\mathrm{T}\mathrm{MgSte}\cdot 3\mathrm{H_2O} \rightarrow n_\mathrm{T}\mathrm{MgSte}\cdot(1-x)\mathrm{H_2O} + n_\mathrm{T}(2+x)\mathrm{H_2O_{vap}} \tag{1}$$

$$n_\mathrm{D}\mathrm{MgSte}\cdot 2\mathrm{H_2O} \rightarrow n_\mathrm{D}\mathrm{MgSte}\cdot(1-x)\mathrm{H_2O} + n_\mathrm{D}(1+x)\mathrm{H_2O_{vap}} \tag{2}$$

$$\mathrm{MgSte}\cdot(1-x)\mathrm{H_2O} \rightarrow \mathrm{MgSte} + (1-x)\mathrm{H_2O_{vap}} \tag{3}$$

$$n_\mathrm{T}\mathrm{MgSte}\cdot 3\mathrm{H_2O} + n_\mathrm{D}\mathrm{MgSte}\,2\mathrm{H_2O} \rightarrow \mathrm{MgSte} + (3n_\mathrm{T}+2n_\mathrm{D})\mathrm{H_2O_{vap}} \tag{4}$$

Here n_T and n_D stand for the mole fractions of trihydrate and dihydrate, respectively, and $n_\mathrm{T}+n_\mathrm{D}=1$. As mentioned above, it is clear from in situ XRD that the structural state of VG degassed at 50 °C must be the same as the intermediate structural state reached by the system at similar temperatures in a TGA or DSC experiment. Accordingly, it is legitimate to assume that this structural state is reached after completion of the intermediate reactions (1) and (2) above, and thus to assign peaks #1 and #2 in the DTGA curves to these reactions and peak #3 to reaction (3). According to reaction (4), the total water loss of the mixture of hydrates should always be comprised within 2 (if $n_\mathrm{D}=1$) and 3 (if $n_\mathrm{T}=1$). This is never in accordance with the TGA results. The sum of the partial losses #1, #2 and #3 in Table 2 is found to be in the range 1.57–1.71. The same can be said for other similar hydrated materials from the literature. As an example, the modified batch MgSt#212 in [8] characterised by the very same X-ray diffractogram and DSC trace as our VG as-received exhibits a weight loss at 140 °C equal to 1.5 mpm of anhydrous soap. Obviously, such a discrepancy cannot be resolved by assuming that the trihydrate first decomposes to form the dihydrate in reaction (1). The weight loss would be unchanged. In contrast, the total water content measured by the K-F method in as-received VG is about 2.4 mpm. Thus one possible but partial explanation might be that the fraction of water corresponding to the difference between the K-F and TGA analyses is retained in the material during and after fusion. Though it remains that the amount of water involved in the structural change associated with reactions (1) and (2) is lower than unity (see Sections 1-4 above) and this cannot be reconciled with.

Numerical values for n_T, n_D and x satisfying the system of Eqs. (1)–(4) and the observed fractional weight loss values can be obtained at the expense of additional chemical assumptions.

Firstly, a certain amount of anhydrate may be assumed in the initial state. The mole fraction of anhydrate n_A would have to take values ranging from 0.33 to 0.58, which is incompatible with the XRD spectra of VG and VF in [1]. A refinement assuming that the water content of the anhydrate formed in situ by reactions (1) and (2) is lower than what is present initially in the anhydrate would require still higher values ($0.41 < n_A < 0.68$).

A second assumption might be that an inert phase or a fraction of the soap structure does *not* participate in the reaction with water vapour, The required concentration of that phase would be 19.6–19.9 wt.% in VG as-received, and 29.7 wt.% modified VF, respectively. Its molar mass can also be computed: values in the range 467–533 g mol^{-1} with a mean equal to 490.5 g mol^{-1} are obtained. This is different from the molar mass of magnesium stearate or palmitate and of the stearic and palmitic acids.

At last it may also be conceived that the hydrates are not stoichiometric. If so, however, the departures from stoichiometry (if it is assumed proportional in the two phases) would have to be quite large to account for the experimental water losses. As an example, in the case of VG, the di- and trihydrates would have to have the following compositions: $MgSte{\cdot}1.51H_2O$ and $MgSte{\cdot}2.27H_2O$, respectively, which is strikingly at variance with the results of Sharp et al. [9]. Notice that the combination of the last two assumptions above introduces too many adjustable variables to be tested numerically.

4.3. *Dehydration of the “anhydrate” and correlation between heat and weight losses*

Results reported here and in the literature which show the weight loss of the anhydrate phase in TG experiments are fundamentally surprising. Even the anhydrate prepared by Sharpe et al. [9] by quantitative decomposition of pure stoichiometric dihydrate exhibits a substantial weight loss (2 wt.%). This can only be explained by reaction of the anhydrous material with water vapour from the ambient atmosphere. Based on the heat loss values in Fig. 6a and b, and on the water content measured by the K-F technique, there is no doubt that the observed loss from the so-called anhydrates essentially is a loss of water. Both figures distinctly show that the initial weight loss is accompanied by the same heat-loss as the vaporisation of water. However an increasing departure from that value takes place with the progress of dehydration. As for the hydrated materials, Fig. 6a and the numerical values in Table 2 show a “weakly pronounced” stepwise increase in accordance with the idea that they are mixtures of distinct crystalline phases with different thermodynamic properties. More puzzling is the non-linear trend in Fig. 6b and the sharp final increase in both Fig. 6a and b. In both structures, the water molecules are “sandwiched” between the aliphatic molecular layers in a similar way, forming a quasi two-dimensional sub-lattice (the distance between the successive water–magnesium containing layers is such that they cannot interact significantly). Only the details of their hydrogen bonding with the oxygen atoms of the polar heads and their co-ordination with the Mg atoms [12] can vary with the water content. A relation between the observed variation of the heat of dehydration and the local “defect” structure remains to be explained.

5. Conclusions

Based on structural data, it is currently assumed that commercial magnesium stearate consists of either crystalline hydrates (di- or tri-hydrate or a mixture thereof) or a poorly crystallised anhydrate. This proves insufficient to account quantitatively for the results of thermal analyses presented here and taken from the literature. The reversible change from one structure (hydrates) to the other (anhydrate) is triggered by a surprisingly small change in the water content, with the anhydrate phase still containing a substantial amount of water, about 1 mpm. The weight losses measured under dry gas at 130–140 °C are always smaller than expected, except possibly for one material (MgSte E) among those investigated by Wada and Matsubara [7]. Various assumptions have been considered to tentatively reconcile the structural and gravimetric points of view. The idea that an inert fraction of the materials does not participate in the reaction with water vapour or that the crystalline hydrates are under-stoichiometric phases (which is equivalent to a certain extent) offers a partially satisfactory explanation only.

For the first time, to the author’s knowledge, partial and total heat loss values have been presented that are in agreement with the general rule that the enthalpy of dehydration of hydrates is commensurate with the enthalpy of vaporisation or sublimation of water. They are at variance with the data reported the literature [7]. But it is also observed, that the extraction of about 1 mol of residual water from the so-called anhydrate (rotator phase) is accompanied by a steadily increasing enthalpy change when the fusion temperature is approached. This might suggest that the final steps of the dehydration and the beginning of the fusion process overlap to some extent.

Commercial magnesium stearate appears as more complex material than currently believed, and the present paper has not succeeded in fully clarifying the relation between its thermal and structural properties. A systematic comparison of accurate new experimental data with values extracted from the literature has revealed the limits of our present understanding of the hydration–dehydration process of magnesium stearate. Contrary to current ideas, the problem does not find its roots primarily in the material purity and drying process. Indeed, the same conclusions could be reached starting from two products from different origins, hydration and crystallisation states as well as from literature data (when numerical values of reasonable accuracy could be read from the published figures).

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