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Crossed analysis by T-history and Turbiscan for the characterization of PCM with Glauber salt

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1. Abstract

The Glauber salt (sodium sulfate decahydrate) is a low-cost Phase Change Material (PCM) with promising characteristics. It offers economic and environmental advantages since it can be recovered as a waste product from the lead battery disposal. However, sub-cooling and phase segregation problems [1] require the addition of appropriate additives capable to reduce the melting temperatures as well as the latent heat [2]. These mixtures are dispersions, heterogeneous systems, for which the T-history method [3] seems to be more suitable respect to the traditional DSC, due to the major and more significant sampling. On the other hand, these systems are not thermodynamically stable and need more detailed information on the kinetics of destabilization.

With this aim, the authors propose the analysis by using Turbiscan, an instrument commonly used in the pharmaceutical and cosmetic sector since it allows identification of slow and not visible phenomena that precede the dispersion destabilization [4]. Also the integration of the characterization by this method could provide further information on the effectiveness of the additives addition and on the method of samples preparation.

Keywords: PCM, Glauber salt, T-History, Turbiscan, Stability.

2. Introduction

The dispersions based on Glauber salt can be very interesting for applications in the building sector, thanks to the high latent heat of fusion and the temperature at which this transition occurs. As for other hydrated salts, however, sub-cooling and phase segregation problems appear, and in all the experiments suitable additives are used. For example, tetraborate

decahydrate (borax) is often used as a nucleating agent, while fumed silica, bentonite, or polymeric gels are used as a thickener. Since the samples are dispersions, their degree of instability could compromise the reproducibility of the thermal properties over the time. One method to test the stability is the comparison of the thermal properties after several cycles of cooling and heating [5]. This procedure allows the detection of performance degradation during the time but it is not able to detect the phenomena involved in destabilization processes. The analysis of thermal properties and stability is carried out by using a particular sample made of a mixture of sodium sulfate / bentonite / borax and water in excess compared to the stoichiometric value required for the formation of Glauber salt. This precaution has the function of limiting the formation of the anhydrous salt. Bentonite is preferred to other thickeners thanks to the good price-performance ratio while the borax is chosen as a nucleating agent because of the results obtained in different studies. The percentages by weight are 60% water, 5% bentonite, 31% sodium sulfate, 4% borax. Each sample was prepared by sonication in order to reduce the diameter of powder particles in water.

3. Methodology

3.1 Thermal analysis

T-history is the adopted method and the experimental system is similar to that one described in the original procedure with the difference of using a refrigerated thermostat as cooling chamber, as suggested by Stanislava et al. [6]. As regards applications in the building sector, a more limited temperature range (10-40 °C) than the original one (10-70 °C) has been chosen, four continuous cycles of cooling and heating on the sample have been performed to ensure the reproducibility of the measurements and to get a first assessment of its stability. For the presentation of the obtained results, reference to the method of Marin et al. [7] has been made, but the representation shows the trend enthalpy-temperature, in the examined range, instead of the enthalpy of solidification curve. In fact, PCM do not have homogeneous composition and, therefore, they have rather a wide solidification range. The curve has been obtained by considering the changes in enthalpy on small temperature ranges according to eq. (1).

$$\Delta h_p(T_i) = \left(\frac{m_w \cdot c_{pw}(T_i) + m_t \cdot c_{pt}(T_i)}{m_p} \right) \cdot \frac{I_i}{I_i'} \cdot \Delta T_i - \frac{m_t}{m_p} \cdot c_{pt}(T_i) \cdot \Delta T_i \qquad (1)$$

where m_w, m_t and m_p is the mass of water, test and PCM respectively [kg]; c_{pw}, c_{pt} is the specific heat of water and test material [kJ/kg K]; ΔT_i is the temperature range [°C] with medium value T_i, to whom corresponds the enthalpy variation $\Delta h_p\ (T_i)$ [kJ/kg]; I_i is the integral with respect to

time of the difference in temperature between PCM and environment; I_i' is the integral with respect to time of the difference in temperature between water and environment.

The latent heat of solidification was calculated as $[\Delta h_p(T_i) - \Delta h_p(T_f)]$ where T_i is the initial temperature of solidification obtained as the maximum value reached after sub-cooling and T_f is the final temperature, calculated according to [8] as a point of inflection on the cooling curve of PCM. The specific heat of fluid state (C_{pl}) and solid state (C_{ps}) were calculated in reference to the article of Marin [7] as the gradients of the two straight lines. To simplify the comparison among the cycles, the effect of sub-cooling was not included, however its extension is reported for each test.

3.2 Analysis of stability

Turbiscan is a tool used in the study of the stability of concentrated dispersions [9]. It is able to distinguish the phenomena due to the migration of particles (sedimentation, creaming) from those ones due to the change in particle size (flocculation and coalescence). The instrument is made of a light source at 880 nm which passes through the sample over its entire length. It is equipped with two detectors, one for transmitted light (T, transmission) and the other one for the light backscattered (BS, baskscattering). The frequency of scan is programmable and the transmission and backscattering profiles are obtained for each scansion. The superposition of the profiles is indicative of stability while their deviation across the time increases with the instability of the dispersions. The TSI (stability index) can be determined by using the comparison of the scans at a given time.

4. Experimental results

4.1 Thermal analysis

Figure 1 shows the trend of enthalpy in relation to temperature. The curves obtained during the four cycles are reproducible, the values of the examined samples are shown in Table 1. In the comparison, the heat lost by sub-cooling was negligible (2-3 °C) and not taken into account.

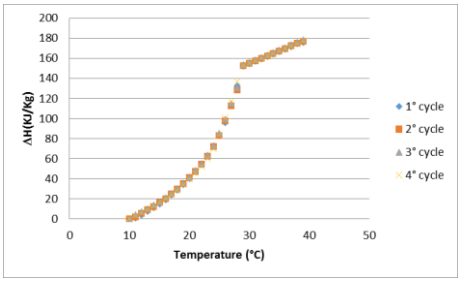

Figure 1. Enthalpy in relation to temperature for four cooling cycles.

Table 1. Thermal parameters determined for each cooling cycle, medium values and percentage errors. T_i, T_{fin} initial and final temperature of solidification, ΔT solidification interval, ΔH enthalpy variation, C_{pl} and C_{ps} specific heat for the liquid and solid phase.

	T_{in} (°C)	T_{fin} (°C)	ΔT (°C)	ΔH (kJ/kg)	C_{pl} (kJ/kg K)	C_{ps} (kJ/kgK)
1	28.06	21.15	6.91	84.21	2.43	3.96
2	28.50	20.20	8.30	98.33	2.47	4.06
3	28.50	20.18	8.32	98.62	2.44	3.97
4	28.00	20.18	7.82	95.92	2.43	3.80
Medium value	28.27	20.43	7.84	94.27	2.44	3.95
Max	28.50	21.15	8.32	98.62	2.47	4.06
Min	28.00	20.18	6.91	84.21	2.43	3.80
Error	0.25	0.48	0.71	7.21	0.02	0.13
Error %	0.88	2.37	9.00	7.64	0.82	3.29

4.2 Analysis of stability

The sample was stored for 24 hr at 40 °C, the maximum temperature in the considered range in which the phenomena of destabilization should be more evident. The dispersion is opaque, thus it is in backscattering regime, being the transmission equal to zero along the entire height of the cell containing the sample. The phenomenon becomes more visible by observing the Delta backscattering reported in Figure 2 where each scan is subtracted from the initial one used as a reference.

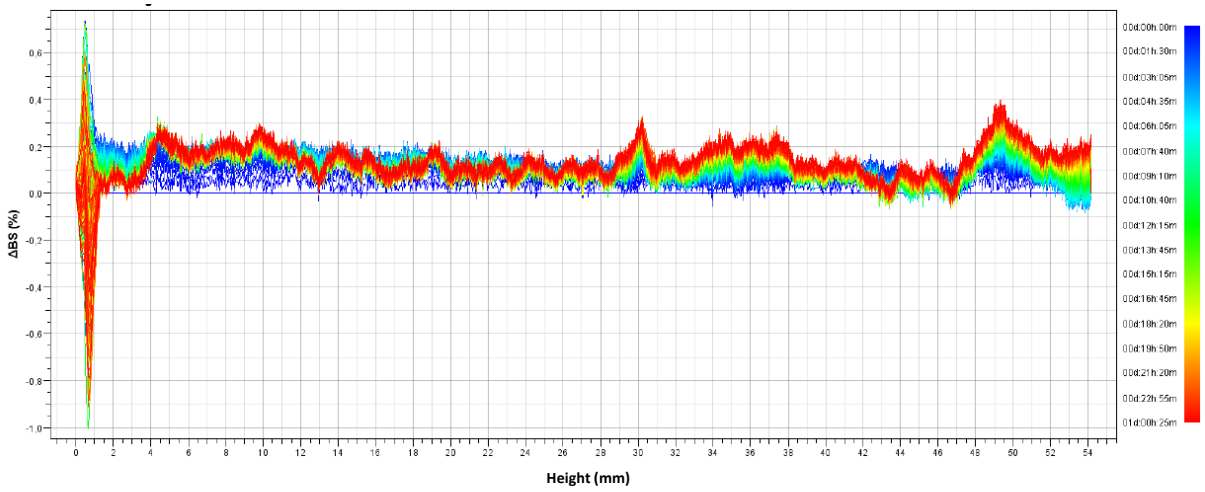

Figure 2. Delta BS of the sample.

The results show that despite the sample in the four cooling cycles appear stable, actually it is subject to phenomena of flocculation which could lead to sedimentation and, therefore, to phase separation. The visual homogeneity is apparent and the sample shows different values of BS corresponding to areas of inhomogeneity along the height. The progressive destabilization of the sample is slow but visible in the TSI graph reported in Figure 3.

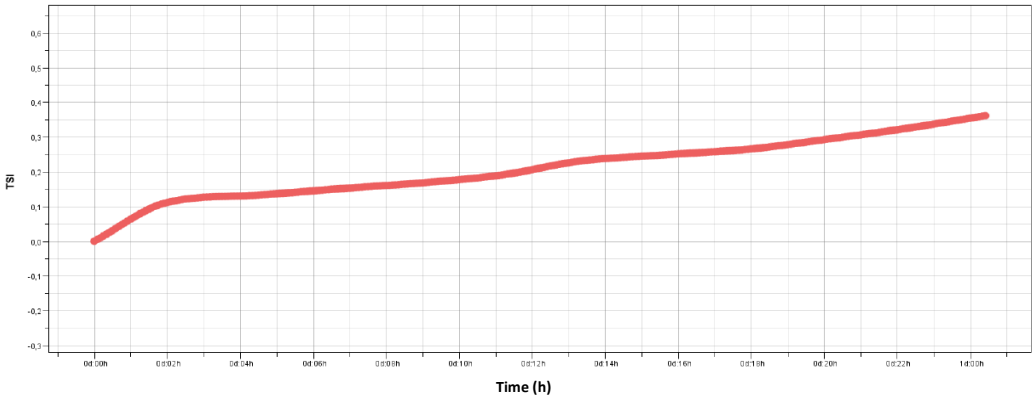

Figure 3. TSI, global destabilization of the sample during the time.

5. Conclusions

The experimental analysis underlines the importance to study PCM dispersions in fluid state as the properties are variable in time due to thermodynamic instability. In order to investigate this problem, two complementary methods are applied by considering both the thermal and the stability aspects. The thermal analysis, obtained by the T-history, shows the reproducibility of the characteristics after four cooling cycles, on the other hand the stability analysis, carried out

by Turbiscan, reveals a progressive long-term destabilization of the sample. For this reason, the application of Turbiscan is very useful to investigate the kinetic behavior of the system and to individuate the opportune additives in relation to the observed phenomenon of destabilization. The method can be used to verify the effectiveness of the selected composition.

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6. References

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