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Review on the methodology used in thermal stability characterization of phase change materials

Gerard Ferrer [a,1], Aran Solé [a,1], Camila Barreneche [a,b,2], Ingrid Martorell [a,1,3], Luisa F. Cabeza [a,*,1]

[a] GREA Innovació Concurrent, Edifici CREA, Universitat de Lleida, Pere de Cabrera s/n, 25001 Lleida, Spain
[b] Department of Materials Science & Metallurgical Engineering, Universitat de Barcelona, MartíiFranqués 1-11, 08028 Barcelona, Spain

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ABSTRACT

In general, PCM are classified in organic and inorganic groups or families. First group mainly encloses paraffin, fatty acids, and sugar alcohols. Inorganic are mostly represented by salt hydrates, salt solutions, and metals. Eutectics and mixtures are also being formulated to obtain a desired phase change temperature. One of the most important PCM requirements is being stable after a number of repeated melting/freezing cycles, which is known as cycling stability. A PCM should present the same or almost the same thermal, chemical and physical properties after a repeated number of freezing and melting cycles. Thermal cycling tests results and detailed tests procedures are classified by PCM type in this review. Moreover, the parameters that must be considered in order to perform cycling stability tests are highlighted depending on the importance they have on the following four issues: the choice of the equipment to perform the cycling tests; the selection of the techniques to characterize the PCM before and after thermal cycling test and to follow the PCM thermal degradation; the definition of the number of cycles to perform; and finally, the choice of the heating rate and thermal cycling method (pyramid, or dynamic, or others) to perform the tests. It is mandatory to conclude that, based on the literature reviewed, no common standard for thermal cycling stability tests is available at the moment.

Contents

* Corresponding author.
E-mail addresses: cbarreneche@ub.edu (C. Barreneche), lcabeza@diei.udl.cat (L.F. Cabeza).
[1] Tel.: +34 973 003576; fax: +34 973 003575.
[2] Tel.: +34 934021298.
[3] Serra-Hunter, fellow.

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1. Introduction

Current trends in energy supply and use are patently unsustainable – economically, environmentally and socially [1]. Energy policies are focusing on achieving net zero buildings and on reusing waste heat from the industry. Then, fossil fuel and electricity consumption can be decreased and consequently, CO_2 emissions too. Furthermore, the use of renewable energies is pushing to design new technologies implementing them as a primary source. One huge field implementing waste heat utilization and solar energy is thermal energy storage (TES).

One way of storing heat is by using the latent heat of phase change of a substance, usually from solid to liquid, as it can provide high energy densities. Then, when this stored heat is needed, it can be released by leaving the material temperature decrease, becoming a solid again. Materials used for this purpose are known as phase change materials (PCM). PCM are being implemented in different systems, active or passive, and for several applications, cold storage, building comfort, medium and high temperatures [1–5].

In general, PCM are classified in organic and inorganic. First group mainly encloses paraffin, fatty acids, and sugar alcohols. Inorganic are mostly represented by salt hydrates, salt solutions, and metals [3,6]. Eutectics and mixtures are also being formulated to obtain a desired phase change temperature. All these materials present advantages and disadvantages, as exposed in Table 1.

Moreover, to overcome some of these disadvantages, composites, shape-stabilized or form-stable PCM are being formulated and developed. Composites are mainly thought to enhance thermal conductivity, increase cycling stability, and prevent leakage and corrosion [7–10]. In addition, the combination of nucleating agents with PCM is presented as a solution to decrease subcooling.

The main requirements from the material point of view are, of course, high phase change enthalpy and a suitable phase change temperature, depending on the application in which the PCM needs to be implemented. Furthermore, a PCM is suitable for applications if it is stable after a number of repeated melting/freezing cycles, that is to say, if it has a proper cycling stability. Sometimes it is also called long term stability [5]. This stability encloses thermal, chemical and physical properties, which should remain constant or almost constant after a cycling stability test. Chemical stability is usually studied by infrared spectroscopy (FT-IR) [11]. Another concept is thermal stability. A thermal stability test is useful to ensure that the PCM is stable at a constant established working temperature. The maximum temperature the PCM can stand is known as the degradation temperature. Thermal stability can be studied in an oven or with TGA [4]. The present review is focused on the thermal cycling stability.

Table 2 reviews the importance given to thermal cycling stability as mentions in different published articles. As shown, and despite the relevance given to these parameters, not much data is available in these publications.

Table 1
Advantages and disadvantages of organic and inorganic PCM.

	Organic	Inorganic
Advantages	Non-corrosive Low or no subcooling Cycling stability	Higher phase change enthalpy Higher conductivity Non-flammable
Disadvantages	Lower phase change enthalpy Lower thermal conductivity Flammable	Subcooling Corrosive Phase separation Lack of cycling stability
Price (€/kg)	6.5–13	3–8

Table 2
Review on the properties listed in the literature.

References	Mention on thermal stability	Mention on thermal cycling stability	Mention on thermal cycles	Cycle range	Data availability	Data presented
[12]	+++	+++	+++	1000–5000	+	SEM Images, DSC data,TGA data
[13]	+	++	++	1000–5000	+	NDA
[14]	+++	++	++	NDA	–	NDA
[15]	+	+	+	NDA	–	NDA
[16]	++	+++	+++	5–100	++	SEM Images, DSC data,TGA data
[17]	+	–	–	NDA	–	NDA
[18]	–	–	–	NDA	–	NDA
[19]	++	++	++	NDA	–	NDA
[20]	+	+	+	NDA	–	NDA
[21]	+	++	++	NDA	++	SEM Images, DSC data,TGA data
[22]	+++	+++	+++	1000–5000	+++	SEM Images, DSC data,TGA data
[10]	+++	+++	+++	1000–5000	+++	SEM Images, DSC data,TGA data
[23]	+++	++	++	5–5000	+++	Particle Size distribution
[24]	++	+	+	NDA	–	NDA

NDA: no data available