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Development and characterization of new materials incorporating phase change materials (PCM) for termal energy storage (TES) applications in buildings

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PhD Thesis

Development and characterization of new materials incorporating phase change materials (PCM) for thermal energy storage (TES) applications in buildings

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Development and characterization of new materials incorporating phase change materials (PCM) for thermal energy storage (TES) applications in buildings

Memòria presentada per optar al grau de Doctor per la Universitat de Lleida redactada segons els criteris establerts en l’Acord núm. 19/2002 de la Junta de Govern del 26 de febrer de 2002 per la presentació de la tesis doctoral en format d’articles.

Programa de doctorat: Enginyeria i Tecnologies de la Informació

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Lleida, 15 d’Abril de 2013.

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Resum

Actualment, la demanda d'energia per satisfer el confort tèrmic en edificació és un dels majors reptes per a les administracions. Per tant, l'eficiència dels diferents sistemes d'emmagatzematge d'energia s’està investigant intensament per la comunitat científica. Una alternativa viable és l'ús de materials de canvi de fase (PCM). Les parafines han estat molt utilitzades com PCM per la seva alta capacitat d'emmagatzematge de calor (al voltant de 100-130 $kJ \cdot kg^{-1}$) i la seva baixa temperatura de fusió la qual és molt estable. A més, el consum d'energia i les oscil·lacions de la temperatura internes d'edificis es poden reduir quan un PCM s'incorpora en evolvents.

L'objectiu principal d'aquesta tesi és el desenvolupament de nous materials que continguin PCM basant-se en l'estudi del procés per obtenir la correcta introducció del PCM dins el material. A més, les propietats termofísiques d'aquests nous materials s'han de conèixer i per tant caracteritzar a nivell de laboratori. Aquesta tesi doctoral se centra en els treballs publicats en revistes científiques amb alt factor d'impacte indexats al camp de l’Energia els quals reflecteixen treball realitzat. D'altra banda, aquesta tesi conté una revisió de l'estat de l'art destacant els requisits per a un PCM i llista tots els tipus de PCM disponibles al mercat i utilitzats en investigació.

D'altra banda, un nou concepte de material compost que incorpora PCM ha estat desenvolupat en aquesta tesi. Aquest compost té la matriu polimèrica, i inclou un residu del procés de reciclatge de l’acer. D'aquesta manera s'obtenen làmines denses que es poden modelar. La fabricació d'aquest material podria considerar-se un mètode per a la reutilització d'aquest residu. D'altra banda, aquest tipus de residus conté òxids de metalls pesants que augmenten les propietats d'aïllant acústic de la làmina aconseguint millorar el resultat final de la solució constructiva. A més, el comportament termofísico dels materials compostos utilitzats en edificis és difícil de caracteritzar i l'anàlisi tèrmica dels PCM és un pas necessari per al disseny dels mateixos. Les dues primeres caracteritzacions termofísiques estudiades en aquesta tesi es van realitzar mitjançant corbes calorimètriques que és una de les tècniques més potents disponibles actualment. tres estudis més van ser van realitzar amb dispositius desenvolupats per diferents grups d'investigació a Espanya per tal de mesurar les propietats termofísiques dels materials compostos o materials multicapa que incorporen PCM.

Resumen

Hoy en día, la demanda de energía para satisfacer el confort térmico en edificación es uno de los mayores desafíos para las administraciones. Por lo tanto, la eficiencia de los diferentes sistemas de almacenamiento de energía está siendo intensamente investigado por la comunidad científica. Una alternativa viable es el uso de materiales de cambio de fase (PCM). La parafina ha sido muy usada como PCM debido a su alta capacidad de almacenamiento de calor (alrededor de 100-130 $kJ \cdot kg^{-1}$) y a su baja temperatura de fusión la cual es muy estable. Además, el consumo de energía y las oscilaciones de la temperatura internas se pueden reducir cuando un PCM se incorpora en envolventes de edificios.

El objetivo principal de esta tesis es el desarrollo de nuevos materiales que contengan PCM basándose en el estudio del proceso para obtener la correcta introducción del PCM. Además, las propiedades termofísicas de estos nuevos materiales se debe conocer y por tanto caracterizar a nivel de laboratorio. Esta tesis doctoral se centra en los trabajos publicados en revistas científicas con alto factor de impacto indexados en el campo de Energía los cuales reflejan el trabajo realizado. Por otra parte, esta tesis contiene una revisión del estado del arte destacando los requisitos para un PCM y lista todos los tipos de PCM comercializados y utilizados en investigación.

Por otra parte, un nuevo concepto de material compuesto que incorpora PCM ha sido desarrollado en esta tesis. Este compuesto tiene la matriz polimérica, e incluye un residuo del proceso de reciclaje de acero. De este modo se obtienen láminas densas moldeables. La fabricación de este material podría considerarse un método para la reutilización de este residuo. Por otra parte, este tipo de residuos contiene óxidos de metales pesados que aumentan las propiedades de aislante acústico de la lámina consiguiendo mejorar el resultado final de la solución constructiva. Además, el comportamiento termofísico de los materiales compuestos utilizados en edificios es difícil de caracterizar y el análisis térmico de los PCM es un paso necesario para el diseño de los mismos. Las dos primeras caracterizaciones termofísicas estudiadas en esta tesis se realizaron mediante calorimetría diferencial de barrido que es una de las técnicas más potentes disponibles actualmente. tres estudios más fueron realizaron con dispositivos desarrollados por diferentes grupos de investigación en España con el fin de medir las propiedades termofísicas de los materiales compuestos o materiales multicapa que incorporan PCM.

Summary

Nowadays, energy demand to satisfy thermal comfort in buildings is one of the major challenges for governments and administrations. Therefore, energy storage system efficiency is being studied by the international scientific community. A feasible alternative is the use of phase change materials (PCM). Paraffin waxes have been used as PCM because of their high heat storage capacity (around 100-130 kJ·kg^{-1}) and their low and stable melting temperature. Furthermore, the energy consumption and indoor oscillations temperature may be reduced when PCM is incorporated in building envelopes and the thermal inertia increment when PCM is combined with thermal insulation was widely studied.

The main objective of this thesis is the development of new materials containing PCM based on the study of process to get the correct PCM introduction. In addition, thermophysical properties of these new materials must be characterized. In order to perform the characterization, it was used several developed devices. This PhD thesis is based on papers published in scientific journals with high impact factor in the Energy field and one patent that reflect the work performed.

This thesis contains a review of the state of the art highlighting the requirements order to a certain PCM and lists and sorts all PCM available in the market and used in research. On the other hand, a new concept of composite material incorporating PCM is developed in this thesis. This composite has polymeric matrix and includes one waste from the steel recycling process obtaining mouldable dense sheets. The manufacture of this material is considered a way to reuse the waste. Furthermore, this waste contains heavy metals oxides which add acoustic insulation properties to the final constructive system. One patent and two papers are the main result.

Moreover, thermophysical behaviour of composite materials used in buildings envelopes is difficult to characterize. In addition, PCM thermal analysis is a necessary step of building design as well as it will be a key point in the final thermal results of the envelope. The first two thermophysical characterizations studied in this thesis were performed using differential scanning calorimetry which is one of the most powerful techniques. Three more studies were performed using devices developed by different research groups in Spain in order to measure thermophysical properties of composite materials or multilayered materials incorporating PCM.

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Chapter I: Introduction

1. Introduction

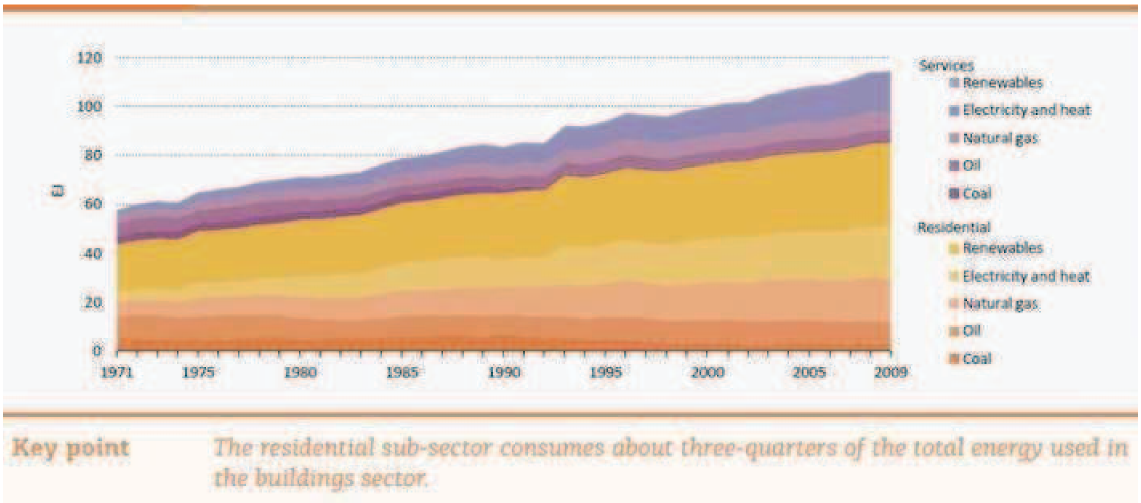
1.1. Energy consumption in buildings

The buildings sector, including the residential and services sub-sectors, consumes approximately 34% of global final energy use, making it responsible for almost 15% of total direct energy-related CO_2 emissions from final energy consumers [1][2]. Total energy consumption in the buildings was around 115 exajoules (EJ) in 2009.

In addition, 60% reduction in CO_2 emissions will be needed in the buildings sector by 2050 compared to today's level if the goal of limiting global temperature rise to 2 ºC must be achieved. Most of these savings will come from the decarbonisation of the electricity used in the buildings sector, incorporation of more efficient systems for indoor conditioning, use of better materials for building envelopes, etc.

Energy demand increment for building sector rises up to 50% in recent years due to rapid growth in number of world's population, households, floor building area, and developed area in our planet which increases electricity demand for electricity-consuming devices and new products. Moreover as Figure 1 shows, the total energy consumption in the buildings sector grew 1.8% a year between 1971 and 2009.

The residential sub-sector requires the largest share of energy, around 75% of total energy consumption in buildings, although the services sub-sector has increased its share since 1990. Moreover, CO_2 emissions follow a slower trend than energy consumption, 0.4% and this fact is due to the mix of energy used. Clean energy technology implementation will make possible to achieve the international environmental goals: energy demand reduction and related greenhouse-gases which will lead to sustainable development under less environmental impact while energy security will be enhanced. In that direction, electricity and renewables are the main energy sources used by the sector, accounting for about 60% of total buildings' energy consumption (Figure 2). Indoor conditioning of buildings (space heating, cooling heating and water heating) takes over 65 EJ of total energy consumption in building sector (2009) being the 57%. Consequently, new policies have been proposed by the European Union recently [3]. The governments are being pushed to create new regulations to construct more sustainable buildings [4].



Key point *The residential sub-sector consumes about three-quarters of the total energy used in the buildings sector.*

Figure 1. Global energy consumption in buildings by energy source divided in residential sub-sector and services sub-sector [1].

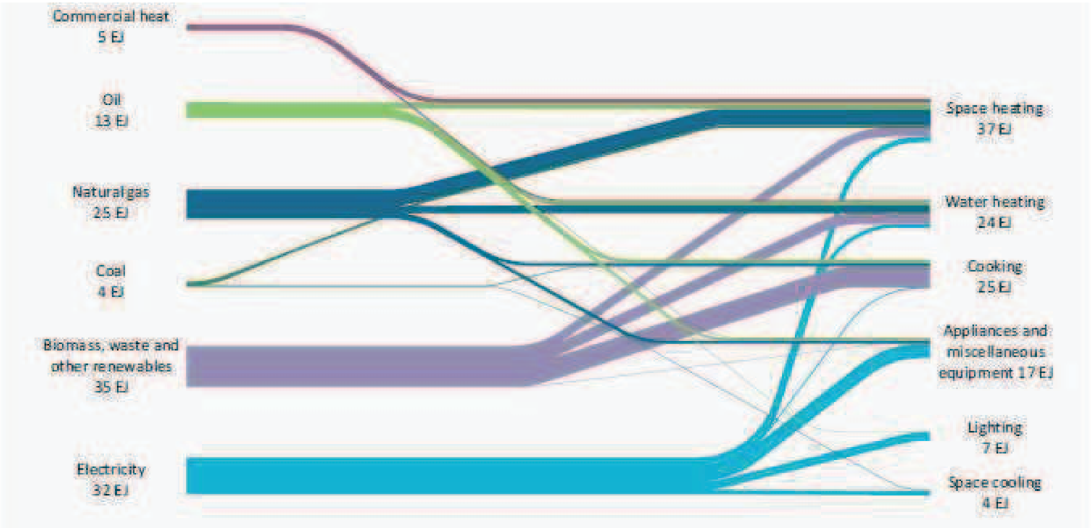


Figure 2. Energy consumption flow for the building sector in 2009 divided into energy source used and where the energy is consumed: space heating, water heating, cooking, lighting, and space cooling [1].

Moreover, Figure 3 shows the global energy consumption distribution divided in commercial and residential building sectors and groups all the others sectors as *other*. Residential sector spends annually $2.43 \cdot 10^{13}$ kWh, commercial sector spends $8.42 \cdot 10^{12}$ kWh, and $6.48 \cdot 10^{13}$ kWh are spent in the others sector as industrial, transport, etc.

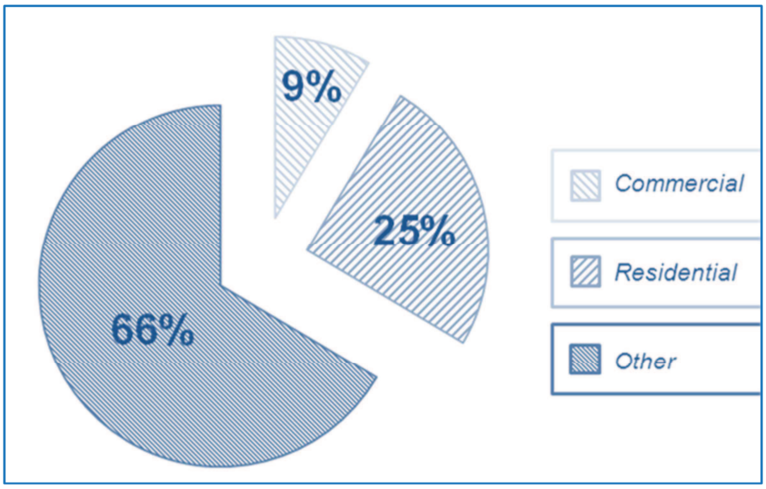
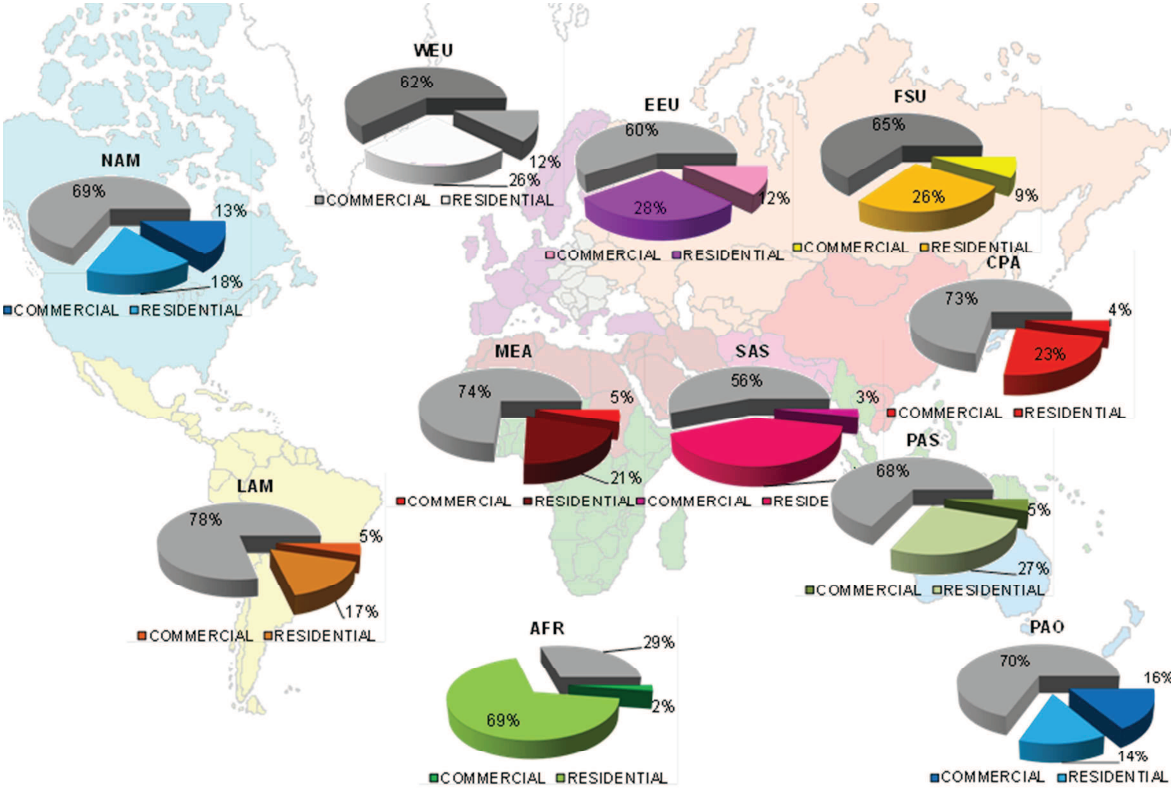


Figure 3. Distribution of total energy consumption in the world divided by commercial subsector, residential subsector and other sectors. [Source: created from data of the International Energy Agency (IEA – 2012)].

Global energy consumption distribution divided by world zones and classified as residential subsector, commercial subsector and other sectors are presented in Figure 4. There are several differences between energy consumption distributions depending on the zone considered: zones from the Organisation for Economic Cooperation and Development (OECD) present a similar consumption in residential and commercial subsectors. However, in world zones with the lowest gross domestic product - GDP as Africa - AFR, Latin America - LAM, PAS, MEA, and SAS present commercial energy consumption lowest than 5% of total zone energy consumption.

This effect is shown because these countries compute a low number of commercial buildings. Additionally, the energy consumption increment in the residential sub-sector is directly related to population and household growth is closely related to the increase in age of buildings, buildings type, house size, income growth, climatic conditions, increase in appliance ownership, and overall energy efficiency improvements while energy consumption within services sub-sector is more related to economic activity, growth in floor area, building types, age of buildings, climatic conditions, and energy efficiency improvements consuming in OECD countries almost four times more energy per capita than non-OECD countries.



NAM – North America
LAM – Latin America and Caribbean
WEU – Western Europe
EEU – Central & Eastern Europe
FSU – Former Soviet Union
MEA – Middle East & North America

SAS – South Asia
PAS – Other Pacific Asia
CPA – Centrally Planned Asia & China
AFR – Sub-Saharan Asia
PAO – Pacific OECD

Figure 4. World zones energy consumption distribution divided by commercial and residential subsectors and others for 2010 [1].

Buildings are usually refurbished rather than being replaced. More than 50% of building built now in OECD countries will be still available in 2050. This value rises up to 75% for developed countries. However, refurbishment rarely takes into account energy efficiency enhancement and it might be considered by policy makers because energy efficiency in buildings only will reach or will increase through this way. The refurbishment rate of residential sub-sector building stock in OECD countries is slightly slow. Then, decrement of heating and cooling demand under ambitious CO_2 reduction scenarios is reticent. Furthermore, services sub-sector buildings are less restrained because they are replaced or refurbished more often than residential buildings [1].

1.2. Thermal energy storage

Thermal energy storage (TES) will play a key role in the successful application of thermal heating and cooling technologies. Meanwhile, the International Energy Agency (IEA) suggests energy storage as a possible solution for the energy problems described, often focusing on materials and systems for building applications [5]. Thermal energy can be stored following three processes: as sensible heat, as latent heat or as thermochemical energy. Furthermore, TES systems can be charged with heat (or cold) and hold energy over time by shifting demand over time to reduce peak loads and facilitating the greater use of renewable energy by storing the energy produced so it can coincide with demand.

In 1983, Abhat et al. [6] proposed a first classification of substances used for thermal energy storage materials stating those utilized as PCM which was useful and widely used. This classification is shown in Figure 5 and recommended differentiate between materials for sensible heat storage, latent heat storage and thermochemical storage. This thesis here presented is focused in latent heat storage – PCM, using solid-liquid phase change from commercial paraffin.

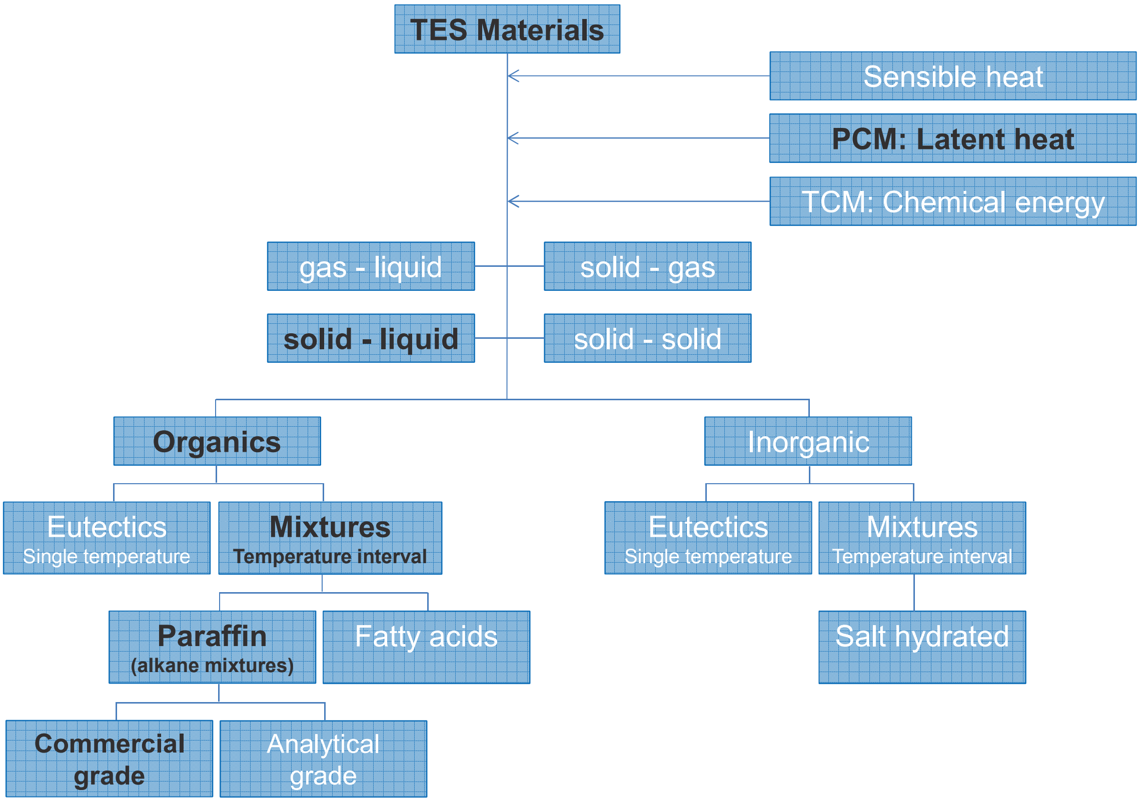


Figure 5. Classification of substances used as PCM for thermal energy storage [6].

1.2.1. Thermal energy storage as sensible heat

The heat transferred to a storage medium leads to a temperature increase of that medium. The heat stored in this process is known as sensible heat [7]. Then, the energy stored by one substance or material as sensible heat is analyzed when it is subjected to temperature changes taking into account its specific heat. Figure 6 shows the thermophysical behaviour observed for one material or substance storing energy as sensible heat. The most common material used to store energy as sensible heat is water which has a specific heat capacity of 4.18 $kJ \cdot kg^{-1} \cdot K^{-1}$. Sensible heat storage has two main advantages: it is cheap and without the risks derived from the use of toxic materials.

Heat capacity is given from content of material used, volume or mass. Sensible heat is often used with solids like stone or brick, or liquids as water (high specific heat).

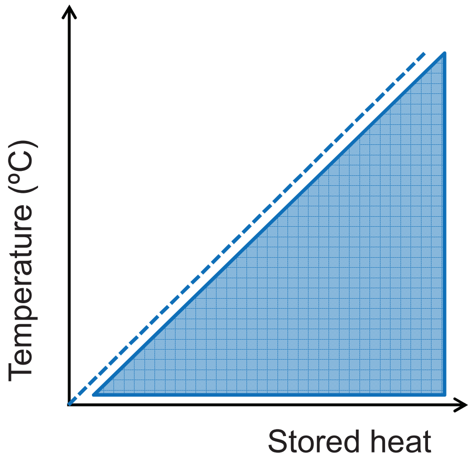


Figure 6. Thermal energy storage profile vs. temperature when heat is stored as sensible heat.

1.2.2. Thermal energy storage as latent heat – phase change materials

Thermal Energy Storage (TES) proposes phase change material (PCM) as materials capable of storing a high quantity of energy as latent heat during the phase change. PCM are presented as an option to increase the thermal mass of the building envelopes and building systems. Such materials have been extensively studied in the past by renowned researchers [8],[11]. Among all materials, those that have high storage density for small temperature range are considered PCM [12] and PCM are classified as different groups depending on the material nature.

Conventional profile when one PCM is submitted to a temperature increment is shown in Figure 7. A temperature increment produces a temperature increase on the material evaluated. Then, the temperature remains constant during the phase change occurring but heat stored is increased. Further transfer of heat results as sensible heat again when the phase change is finished.

1.2.3. Thermochemical energy storage

Thermochemical materials (TCM) are materials which can store energy by a reversible endothermic/exothermic reaction/process and the resulting reaction products are easily separated (usually a gas–solid system or a liquid–solid system). First of all, it is performed the charging process: applying heat, the material reacts and it is separated in two parts: A + B. Then, storing process takes place: the heat is stored because the products are easily separated and the storage could be complete at low temperature. Finally, the discharging process is performed: as a reversible reaction, when products A + B are placed together and under the suitable pressure and suitable temperature conditions to react, the energy is released again. This process is shown in Figure 8.

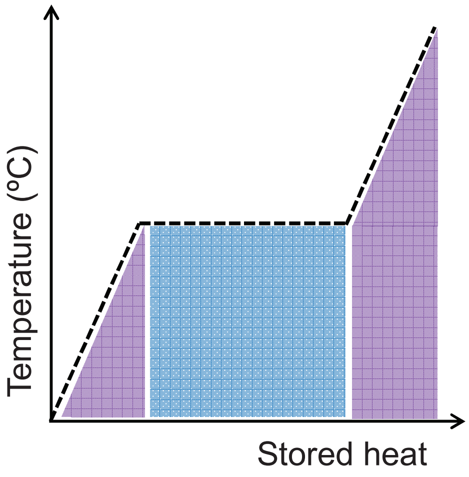


Figure 7. Thermal energy storage profile vs. temperature when heat is stored as latent heat.

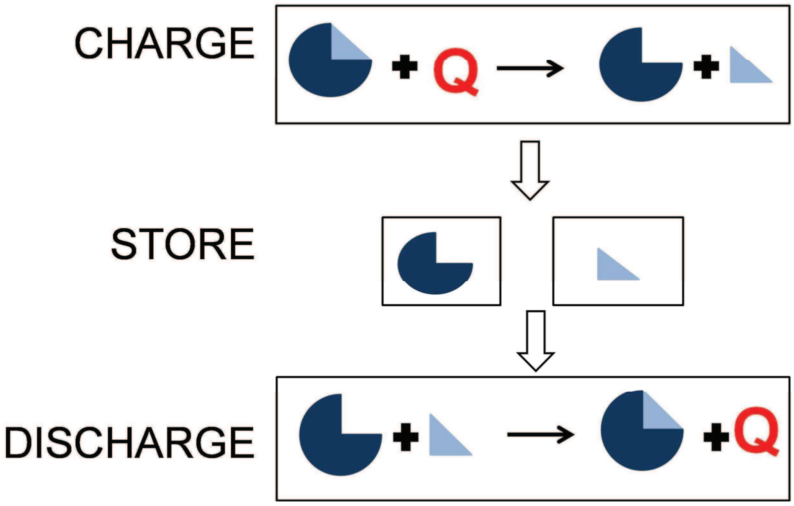


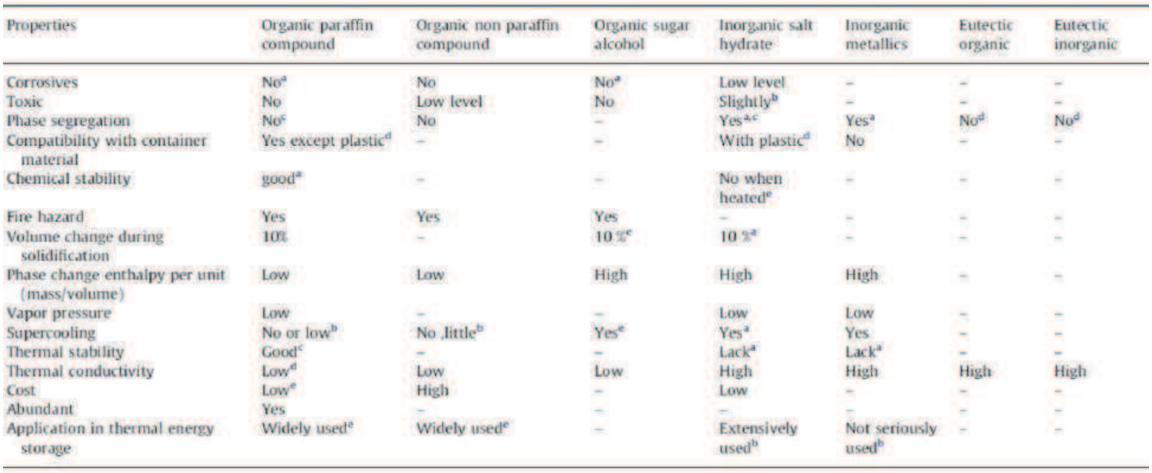
Figure 8. Steps followed by TCM to store energy.

1.3. Thermal energy storage incorporating phase change materials in building applications

1.3.1. Materials

PCM are divided in three groups of materials: organics, inorganics and eutectics. Al-Abidi at al. [13] classified them as Table 1 shows stating that there are some exceptions, for example, some of organic materials properties are flammability, varying level of toxicity, and instability at high temperatures, and some metallic materials have a low heat of fusion per unit weight and a high heat of fusion per unit volume.

Table 1. Properties of different groups of PCM [13].



Properties	Organic paraffin compound	Organic non paraffin compound	Organic sugar alcohol	Inorganic salt hydrate	Inorganic metallics	Eutectic organic	Eutectic inorganic
Corrosives	No[a]	No	No[a]	Low level	–	–	–
Toxic	No	Low level	No	Slightly[b]	–	–	–
Phase segregation	No[c]	No	–	Yes[a,c]	Yes[a]	No[d]	No[d]
Compatibility with container material	Yes except plastic[d]	–	–	With plastic[d]	No	–	–
Chemical stability	good[a]	–	–	No when heated[e]	–	–	–
Fire hazard	Yes	Yes	Yes	–	–	–	–
Volume change during solidification	10%	–	10 %[e]	10 %[a]	–	–	–
Phase change enthalpy per unit (mass/volume)	Low	Low	High	High	High	–	–
Vapor pressure	Low	–	–	Low	Low	–	–
Supercooling	No or low[b]	No ,little[b]	Yes[e]	Yes[a]	Yes	–	–
Thermal stability	Good[c]	–	–	Lack[a]	Lack[a]	–	–
Thermal conductivity	Low[d]	Low	Low	High	High	High	High
Cost	Low[e]	High	–	Low	–	–	–
Abundant	Yes	–	–	–	–	–	–
Application in thermal energy storage	Widely used[e]	Widely used[e]	–	Extensively used[b]	Not seriously used[b]	–	–

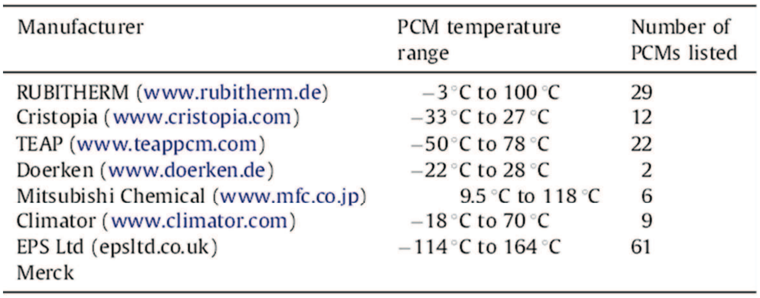
Furthermore, certain conditions should be fulfilled by the PCM when selecting it [14],[15]: melting point of PCM must be closed to the selected work temperature range, it must own high specific heat in order to provide sensible heat, and high thermal conductivity (solid and liquid state) to support charging and discharging processes in storage system used. Additionally, PCM must not change volume during phase change transformation and it must not emit vapours allowing conventional containers use as well as high latent heat is required in order to reduce final container volume. Moreover, it must melt congruently with minimum subcooling and it must be chemically stable.

Additionally, new developments in PCM are meaning new applications such as PCM embedded in building materials like bricks, insulation, wall boards, flooring, etc. Moreover, researchers and companies are focused on reducing costs of PCM, developing thermal energy storage systems incorporating PCM as well as improving the number of cycles that can be achieved by emerging storage technologies. PCM are well suited to cooling application because of the low temperature phase change required for release of energy.

One commercial PCM option is paraffin or paraffin waxes. This class of material is cheaper than other organic and inorganic PCM and they have moderate thermal storage densities (around 200 $kJ{\cdot}kg^{-1}$ or 150 $MJ{\cdot}m^{-3}$). Furthermore, they are chemically inert and stable with no phase segregation and they do not present subcooling or it is negligible. However, they have low thermal conductivity (around 0.2 $W{\cdot}m^{-1}{\cdot}K^{-1}$) and it limits their applications. Regarding salt hydrates, the main limitations are: their chemical instability when they are heated because they can lose easily some water content every heating cycle and then, the thermophysical properties change completely. Furthermore, some salts are chemically aggressive against structural materials but they have higher heat conductivity in comparison with organic materials. Finally, salt hydrates have a relatively high degree of subcooling.

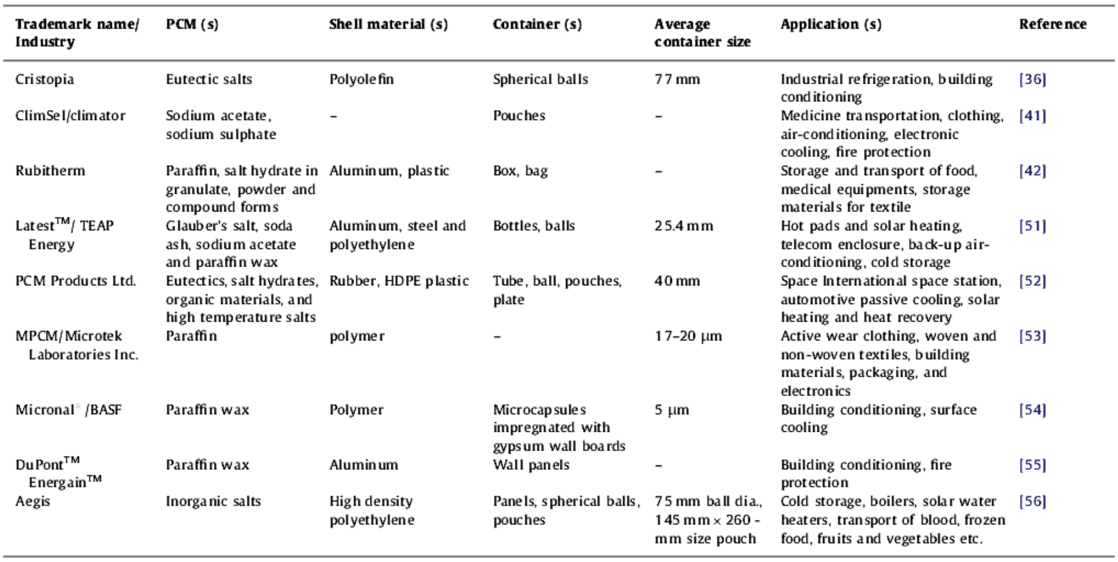
Agyenim et al. [16] enumerated the commercial PCM manufacturers in the world in 2010 (Table 2) and Salunkhe et al. [17] listed encapsulated PCM available in the market in 2012 (Table 3) and the main application.

Table 2. List of PCM manufacturers available in the market [16].



Manufacturer	PCM temperature range	Number of PCMs listed
RUBITHERM (www.rubitherm.de)	−3 °C to 100 °C	29
Cristopia (www.cristopia.com)	−33 °C to 27 °C	12
TEAP (www.teappcm.com)	−50 °C to 78 °C	22
Doerken (www.doerken.de)	−22 °C to 28 °C	2
Mitsubishi Chemical (www.mfc.co.jp)	9.5 °C to 118 °C	6
Climator (www.climator.com)	−18 °C to 70 °C	9
EPS Ltd (epsltd.co.uk)	−114 °C to 164 °C	61
Merck		

Table 3. List of manufacturers of encapsulated PCM and their main specifications [17].



Trademark name/ Industry	PCM (s)	Shell material (s)	Container (s)	Average container size	Application (s)	Reference
Cristopia	Eutectic salts	Polyolefin	Spherical balls	77 mm	Industrial refrigeration, building conditioning	[36]
ClimSel/climator	Sodium acetate, sodium sulphate	–	Pouches	–	Medicine transportation, clothing, air-conditioning, electronic cooling, fire protection	[41]
Rubitherm	Paraffin, salt hydrate in granulate, powder and compound forms	Aluminum, plastic	Box, bag	–	Storage and transport of food, medical equipments, storage materials for textile	[42]
Latest$^{\text{TM}}$/ TEAP Energy	Glauber's salt, soda ash, sodium acetate and paraffin wax	Aluminum, steel and polyethylene	Bottles, balls	25.4 mm	Hot pads and solar heating, telecom enclosure, back-up air-conditioning, cold storage	[51]
PCM Products Ltd.	Eutectics, salt hydrates, organic materials, and high temperature salts	Rubber, HDPE plastic	Tube, ball, pouches, plate	40 mm	Space International space station, automotive passive cooling, solar heating and heat recovery	[52]
MPCM/Microtek Laboratories Inc.	Paraffin	polymer	–	17–20 μm	Active wear clothing, woven and non-woven textiles, building materials, packaging, and electronics	[53]
Micronal$^{®}$ /BASF	Paraffin wax	Polymer	Microcapsules impregnated with gypsum wall boards	5 μm	Building conditioning, surface cooling	[54]
DuPont$^{\text{TM}}$ Energain$^{\text{TM}}$	Paraffin wax	Aluminum	Wall panels	–	Building conditioning, fire protection	[55]
Aegis	Inorganic salts	High density polyethylene	Panels, spherical balls, pouches	75 mm ball dia., 145 mm × 260 - mm size pouch	Cold storage, boilers, solar water heaters, transport of blood, frozen food, fruits and vegetables etc.	[56]

1.3.2. Thermophysical properties determination

The thermophysical properties required from PCM to be used as TES material are tangible and have to be taken into account during the material selection step. PCM must have low density variation but high density and they should not present subcooling. Furthermore, from the thermophysical point of view, PCM must present phase change temperature suitable for the desired application, high thermal conductivity supporting the heat transfer and high enthalpy of phase change which will provide high thermal energy storage capacity. Also, PCM should be stable from the chemical point of view, should not present nor segregation neither corrosion/degradation of container materials and they must not be inflammable. Finally, they must be cheap and abundant.

The most common TA methods to analyse the thermophysical properties of PCM are listed in Table 4 [18]. DSC is the most powerful technic concerning melting and solidification point determination, as well as energy involved in different processes analysis. Among studies where researchers used DSC [19] to analyse thermophysical properties of PCM, Flaherty [20] et al. characterized hydrocarbons and natural waxes, Giavarini et al [21] characterized petroleum products and Salyer [22] measured thermophysical properties of paraffin. However, Gibbs et al [23] mentioned that there is considerable uncertainty about thermophysical properties provided by manufacturers and it is therefore advisable to use DSC to obtain more accurate values. Analysis of uncertainty of DSC measurements and manufacturers available properties of PCM are also studied in this PhD thesis analysing different types of PCM (paraffin and salt hydrate) and applying different DSC modes.

Table 4. Common TA techniques with their related methods, their abbreviation and the measured property [18].

TA Measurement Technique	Method	Abbreviation	Output Property
Differential Thermometry	Differential Thermal Analysis	DT/ DTA	Temperature difference
Differential Scanning Calorimetry	---	DSC	Heat Flow difference
Thermogravimetry	Thermogravimetric Analysis	TG/ TGA	Mass change
Themomechanometry	Thermomechanical Analysis	TM/ TMA	Deformation
Thermoacoustimetry	Thermoptometric Analysis	TO/ TOA	Optical properties
Exchanged/Evolved Gas Measurement	Exchanged/Evolved Gas Analysis	EGM/ EGA	Gas exchange
Thermoelectrometry	Thermoelectrical analysis	TE/ TEA	Electrical properties
Thermoacoustimetry	Thermoacoustimetric analysis	TO/ TOA	Acoustic properties
Thermomanometry	Thermomanometric Analysis		Pressure
Thermomagnetometry	Thermoagnetic Analysis		Magnetic properties

Nevertheless, Yinping et al. [24] reviewed the above-mentioned conventional methods of PCM analysis and points out their limitations that are the following:

- Small sample size is analysed (1–10 mg) and PCM thermophysical behaviour depends on of the sample mass.

- The analysis instrumentation is complex and expensive.
- Phase change cannot be visually observed using some of techniques listed in Table 4.

For that reasons, Yinping et al. [24] developed a simple method for determining phase change temperature, subcooling, enthalpy, specific heat, and thermal conductivity in solid and liquid phases known as T-History method. Temperature–time curves are represented and PCM results must be compared with a reference results (water is the most common reference material used).

However, before T-history development and validation, other authors had proposed methods for measuring PCM thermophysical properties. Actually, T-history could be inspired by one these methods. The method proposed by Vlasov et al. [25] consists in heating a solid sample until it is completely melt and record its inner temperatures when phase changing. This method is able to analyse thermal diffusivity in the liquid and solid phase, thermal conductivity in the liquid and solid phase and latent heat during the phase change. Moreover, Carré and Delaunay [26],[27] designed one method based on guarded hot plate device which allows the simultaneous measurement of the thermal conductivity, the specific heat and the latent heat of PCM as well as of other complex fluids. Furthermore, Demirel et al. [28] proposed one method proposed to test the thermal performance of encapsulated heat storage materials in large non stirred samples using two water baths.

On the other hand, it is important to note that the thermophysical properties of materials which will compose the final constructive systems used as building envelope or walls (multilayered materials or composites materials) must also be known and knowledge is a key point for the building design step itself. For that important reason, several research groups started developing new devices to measure thermophysical properties of macro-samples of materials used in envelopes. Some of these devices were used in this thesis to measure thermal properties of new materials developed during this PhD as well (Chapter V).

1.3.3. Building applications

Buildings can use the latent heat from PCM by two different concept systems: passive latent heat energy storage systems (LHES) or by using active LHES systems [29] which use a mechanical ventilation source.

It is well known that several ways of bulk encapsulation of PCM were available in the market and were investigated in the past but these methods were inadequate to deliver heat to the building after the PCM was melted [29]. However, the walls and ceilings of a building offer large areas for passive heat transfer within every zone of the building [14]. The application of PCMs in building can have two different goals: using natural heat that is solar energy for heating or night cold for cooling and using manmade heat or cold sources [29]. Passive LHES systems design uses available heat energy interactions in order to maintain the comfort conditions in buildings and minimize the usage of mechanically assisted heating or cooling systems [14]. There are several ways to use PCM in passive systems and some of them are listed below [29],[30]:

- PCM trombe wall is the first example. It consists of a thick masonry wall on the south side of a house. A single or double layer of glass or plastic glazing is mounted about four inches in front of the wall's surface. Solar heat is collected in the space between the wall and the glazing. The outside surface of the wall is of black colour that absorbs heat, which is then stored in the wall's mass. Heat is distributed from the trombe wall to the house over a period of several hours.
- PCM wallboards [31], which are cheap and widely used in a variety of applications, making them very suitable for PCM encapsulation. Kedl et al. [32], Salyer et al. [33], used paraffin wax impregnated wallboard for passive systems. Shapiro et al. [34] investigated methods for impregnating gypsum wallboard and other architectural materials with PCM.
- PCM shutter was studied by Buddhi et al. [35] where the thermal performance of a test cell (1 m x 1 m x 1 m) with and without PCM. The passive system concept is based on shutter-containing PCM placed outside of window areas. During daytime they are opened to the outside the exterior side is exposed to solar radiation, heat is absorbed and PCM melts. At night we close the shutter, slide the windows and heat from the PCM radiates into the rooms.

- PCM building blocks with impregnated PCM. There are several studies of thermal performance of PCM block made with cement, gypsum, concrete, etc. [30],[36][39].
- Tyagy et al. [14] also reviewed three more ways to use LHES as passive systems: air-based heating system, floor heating, and ceiling boards.

On the other hand, mostly active floor system can be used for off peak storage of thermal energy in buildings. Thus, peak loads may be reduced and shifted to night-time when electricity costs are lower. These active systems are described in next points:

- Floor heating: An electrical under floor heating system having paraffin wax (melting point, 40 ºC) as the PCM was proposed by Farid and Chen [40]. Moreover, Nagano et al. [41] presented a floor air conditioning system with latent heat storage in buildings.
- Ceiling boards: Ceiling boards are the important part of the roof, which are utilized for the heating and cooling in buildings. Bruno et al. [42] developed a system, which stored coolness in PCM in off peak time and released this energy in peak time. In addition, Kodo and Ibamoto [43] made an effort to reduce the peak load of air conditioning system using the PCM in the ceiling board.
- Kaygusuz and Ayhan [44] investigated solar heat pump system with storage part using microencapsulated PCM for residential heating.
- Systems which collect coolness and store it from ambient air during night and relived to the indoor ambient during the hottest hours of the day are known as free-cooling and it is used as part of air conditioning [45].

1.4. Methods followed for reuse and valorise of electrical arc furnace dust (EAFD)

One way to produce steel is to refine iron in an electric arc furnace (EAF), in which heat is supplied by arcs through the molten metal between carbon electrodes. This process is used primarily for refining steel scrap and direct reduced iron and high temperatures are reached by the arc plasma and some volatiles are generated which have to be removed from the melted metal vessel producing a dust. This dust is known as electrical arc furnace dust (EAFD). Millions of tons of EAFD are generated worldwide, and the amount of EAFD generated is expected to increase because this is the first used process to obtain steel.

EAFD has a complex composition, and X-ray diffraction (DRX) analyses and scanning electron microscopy (SEM) confirmed that the major components of EAFD are iron oxide, zinc oxide and zinc ferrite as well as sodium chloride and potassium chloride. Besides, arsenic oxides are frequently found in EAFD composition. Since EAFD contains hazardous metals, such as lead, cadmium and arsenic, its treatment is a costly and time consuming problem for steel manufacturers. The most common process to deal with EAFD is moving this dust to an offsite processor for its landfill or recycling. Moreover, EAFD is categorized as hazardous waste in most of the industrialized countries and classified by the European Waste Catalogue as hazardous residue being necessary its treatment previous the final disposal. The main processes followed in this dust treatment previous landfill are the following:

- Stabilization/solidification technologies complete with Portland cement is the cheapest alternative but some problems regarding metal dissolution arise from the elevated pH in the leachate. This process is the less used [46].
- Encapsulation methods of toxic metals. These methods are not commercially interesting, as they involve important investments and there is no metal recovery.
- Acid based extraction processes can dissolve metals of interest but it is required high amount of acids to neutralize the medium. Then, acid-based extractions of EAFD are not readily commercialized.
- Pyrometallurgical processes are used to remove lead and zinc from EAFD by fuming and then condensing the metals in relatively pure form. However, with pyrometallurgical processes there is no recycle of iron to the electrical arc furnace process [47][48].
- Caustic based processes in which the leaching and dissolving steps employ simple chemistry that takes advantage of the amphoteric nature of zinc, lead, 25 tin, arsenic, selenium and aluminium can be used to treat EAFD [49].

The process of incorporating EAFD as filler into a polymer matrix, in order to obtain a composite formulation is the followed in this PhD thesis to obtained a dense sheet with acoustic insulation properties to be used as one layer of constructive systems. The acoustic insulation properties will come from the heavy metal oxides EAFD have in its composition. These metals are bulky atoms which will lead with noise waves preventing or hindering the progression of those waves.

However, in previous studies it was described the use of EAFD as filler of polymeric materials to obtained composite formulation than can yield a mouldable heavyweight sheet useful for acoustic insulation in automotive industry [50],[51]. The composite formulation also uses barite ($BaSO_4$) and/or calcium carbonate ($CaCO_3$) as fillers. This technique has the limitation that only EAFD generated in the manufacture of high quality steels can be used, because the resulting EAFD has lower zinc, lead and arsenic contents and presence of these elements in higher concentration in EAFD from carbon steel industries make impossible its use as polymer filler for automotive application because products obtained thereof will overpass the limits required for automotive components. On the other hand, this previous study used mineral oil as lubricant agent during mixing process. The novelty of the composite dense sheet developed in this PhD thesis is the use paraffin wax (RT-21 from Rubitherm) as lubricant agent during mixing process (plasticizer). Furthermore, PCM can store energy because their high storage capacities due to the latent heat of phase change.

Thereby, the new material developed in this PhD thesis addresses the problem of obtaining an economically and feasible alternative treatment of large amounts of EAFD, regardless the origin of the latter. This is achieved by means of a stabilizing integration of EAFD into a new valuable composite formulation that e.g. can be used massively in the building industry. This material was patented in 2012 [52] and this patent is part of the PhD thesis here presented.

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Chapter IV: Development of new materials incorporating PCM

4. Development of new materials incorporating PCM

4.1. Introduction

Although the situation in the world economy since 2009 remains uncertain, global primary energy demand rebounded by a remarkable 5% in 2010, pushing CO_2 emissions to a new high [1].

Furthermore, another point to consider is that 30-40% of total energy consumption in developed countries comes from the private sector (housing and offices) [2]. The building sector is focusing on developing new concepts, new materials and advanced systems to minimize the energy consumption significantly by improving its energy efficiency.

There are several methods to introduce phase change materials in constructive systems. The most easy-going is to introduce the PCM without encapsulation but this method difficult to control: PCM leakage is the most important drawback. On the other hand, PCM impregnation [3] in porous building materials as gypsum, plaster, gypsum board, cement, mortar [4], etc. is the most useful method because allows high PCM content introduction in these material matrixes listed above.

Therefore, in almost all cases PCM has to be encapsulated for technical use, as otherwise the liquid phase would be able to flow away from the location where it is applied. Encapsulation is a containment method which comprises the inclusion of PCM in some form of package such as tubes, pouches, spheres, panels or other receptacle [5]. The use of microcapsules is a solution of leakage drawback [6] and the final aspect of them is as powder [7]. Then, they must be incorporated in most of building materials easily but the final cost of building material is increased with this method because the microcapsules manufacture process is expensive.

During this thesis, new materials were developed based on polymer composite used as shape stabilized PCM. The material developed incorporates Electrical Arc Furnace Dust (EAFD). One way to produce steel is to refine iron from steel scrap in an electric arc furnace [8]. Very high temperatures are generated in the arc plasma and volatile species are effectively removed from the metal as a brown dust. This dust, named EAFD, is a brown powder containing heavy metals and it is classified as hazardous waste in most of the industrialized countries, requiring a treatment previous its landfill. For this reason, the process of incorporating EAFD as a filler into a polymer matrix, in order to obtain a composite formulation that can yield a mouldable heavyweight sheet useful for increase acoustic insulation in constructive systems is a feasible method to valorise this waste and to achieve one way to encapsulate/stabilize PCM.

The development process of new composite materials incorporating PCM and EAFD to be used as dense sheet in building envelopes is described in in three parts: one patent and two peer reviewed papers presented below.

4.2. Patent: Waste removal of EAFD by means of its stabilization integrating it into a building material - PCT/ES2012/070564

This patent explains the development of one composite material with polymeric matrix incorporating PCM and EAFD. This new dense sheet is proposed as alternative to reuse the electrical arc furnace dust which is a hazardous waste being isolated as well as valorised. Furthermore, the present invention obtains an economically feasible alternative treatment of large amounts of EAFD. Figure 13 shows the dense sheet developed from the laboratory scale to manufactured material.

Figure 13. Composite dense sheet based on polymeric matrix incorporating PCM and EAFD.

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I	**Título de la invención**	`INERTIZACIÓN DE POLVO DE ACERÍA MEDIANTE SU INTEGRACIÓN ESTABILIZANTE EN UN MATERIAL DE CONSTRUCCIÓN`

The main claims of this invention are:

- ✓ The provision of a composite formulation obtainable by mixing a set of materials comprising the following ingredients, in the stated amounts, expressed as weight by weight percentages in respect to the total weight of the formulation: (i) one or more polymers able to form a solid polymer matrix, in an overall amount of 10-25%; (ii) one or more organic phase change materials (PCM), and (iii) EAFD, in 40-80%.

- ✓ The composite formulation of the present invention allows the incorporation of high amounts of EAFD, thus making an important contribution to waste removal of this toxic by-product.
- ✓ Dense sheet solid materials obtained by extrusion, or by calendaring, or by hot pressing (typically at a temperature of about 150 ºC) is one of the most important part of this invention.
- ✓ The sheet must be 1-5 mm thick being 2 mm the preferred thickness. The sheet of solid material of the present invention simultaneously has good acoustic insulating properties and thermal energy storage properties. This fact, together with its relatively good mechanical properties, makes it useful for being incorporated into building materials: floors, roofs, and particularly wall panels.

4.3. Paper 2: Development and characterization of new shape-stabilized phase change material (PCM) - polymer including electrical arc furnace dust (EAFD), for acoustic and thermal comfort in buildings

The composite material developed in this thesis incorporates PCM and EAFD. The EAFD is an industrial waste which was characterized in this paper with different physicochemical characterization technics: X-ray diffraction, X-ray fluorescence, SEM, density and specific surface were analyzed, and particle size distribution was quantified. Paraffin wax is added with two functions: on one side as lubricant agent to promote a correct mixing between the inorganic filler and the polymeric matrix. Moreover, paraffin acts as phase change material (PCM) due to their high thermal energy storage (TES) capacity as latent heat from the phase change. This composite material is a dense sheet able to be used as one layer of constructive systems. Final composite material was characterized mechanically, thermally and acoustically. Moreover, formulation limits were established. During this study, a new composite material varying the PCM and EAFD contents to demonstrate that manufacturing this material is a suitable treatment for EAFD to valorise this residue and to achieve one way to encapsulate/stabilize PCM was developed.


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Development and characterization of new shape-stabilized phase change material (PCM)—Polymer including electrical arc furnace dust (EAFD), for acoustic and thermal comfort in buildings

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The main contributions to the state-of-the-art from this study can be summarized in the following points:

- ✓ Composite formulation limits:
    - PCM content: It was confirmed that for composites with PCM content lower than 10% in weight, the effect of the storage by the phase change is not appreciable. Furthermore, it was observed after 60 days that those samples with more than 20 % wt of PCM were sticky. Then, PCM stabilization was not achieved. This effect was also observed after 100 days with sample containing 15 % wt PCM. Therefore the concentration limits for the PCM are from 10 to 15% wt.

    - Matrix content: the matrix percentage limits were established between 15–20 % wt because high polymer content improves mechanical properties, does not affect thermal and acoustic properties but increase the cost of the composite.

    - EAFD content: maximum EAFD content as possible in order to increase the waste valorisation.

- ✓ It is feasible to introduce EAFD in a polymer matrix using paraffin wax PCM as lubricant, in this case RT-21.

- ✓ The PCM phase change occurs at a 20–21 ºC, it is not modified when introduced in the new material. Within this operational temperature, the used PCM is adequate to be used around thermal comfort temperatures.

- ✓ The material developed in this thesis is able to encapsulate PCM and the valorisation of EAFD obtaining 3 mm dense sheets able to be used in combination with other materials as constructive systems in buildings.

4.4. Paper 3: Use of PCM–polymer composite dense sheet including EAFD in constructive systems

Furthermore, two formulations of this dense sheet were evaluated being different composite materials containing EAFD and PCM and varying the polymeric matrix. Obtained results were compared with a commercial dense sheet made by TEXSA.

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Use of PCM–polymer composite dense sheet including EAFD in constructive systems

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The main contributions to the state-of-the-art from this study can be summarized in the following points:

- ✓ New shape stabilized PCM materials developed in this thesis were compared by using two different polymeric matrix: the first one has EPDM matrix and the second one has EVA/EXACT (1:3) matrix. This characterization was compared with a commercial dense sheet available in the market: Texsound.

- ✓ From the physical and mechanical point of view, properties required are not restrictive because they are not structural. Even so, EPDM material is the densest and it showed a moderate porosity compared with the other dense sheets characterized, the highest strength and the lowest elongation were obtained for EVA/EXACT (1:3) formulation and the lowest strength and the highest elongation was observed for Texsound samples.

- ✓ DSC analyses showed that the formulation made with EPDM is the material which can store more latent heat.

- ✓ From the point of view of stability, the commercial material (Texsound) is the material with less mass loss but three dense sheets analyzed have similar behaviour. Furthermore, both developed materials are stable below 100 ℃.

- ✓ The effective thermal conductivity (κ_{eff}) of the multilayered construction system (gypsum board/dense sheet/gypsum board) was also evaluated and the results showed that both new material constructive systems, composed with EPDM and EVA/EXACT (1:3), are more thermal insulating than the commercial material ones, being the one containing EVA/EXACT (1:3) dense sheet the more insulating multilayered system.

- ✓ The better results were obtained for EPDM matrix composite mainly in frequencies below 3500 Hz. Acoustic results reveal that ductile matrix in polymer composites leads to a better acoustic behaviour especially in frequencies above 3500Hz. All materials exhibit quite noble acoustic properties, around 35dB of insulation, in the overall frequencies studied.

Use of PCM–polymer composite dense sheet including EAFD in constructive systems

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Abstract

The overall energy consumption is increasing significantly in recent years and the energy consumption in building sector represents over 30% of the total global ones in developed countries. Thermal energy storage (TES) using phase change materials (PCM), which are materials able to store high amount of energy as latent heat during the phase change, is suggested as a possible solution for this drawback. The authors developed materials able to encapsulate/stabilize PCM in addition to isolate an industrial residue from the steel recycling process, electrical arc furnace dust (EAFD), which is a hazardous dust, producing dense sheet materials suitable for multilayered constructive systems. In this paper the physical, mechanical, thermal and acoustical characterization of two new materials is presented. One material has a polymeric matrix (a mixture (1:3) of polyethylene-co-vinyl acetate copolymer - EVA and ethylene-octene copolymer), and the other matrix is ethylene propylene diene monomer rubber - EPDM). The results are compare with the obtained for one commercial dense sheet material available in the market, Texsound commercialized by TEXSA (Spain). The new dense sheet materials developed in this paper have similar acoustic properties and improved thermal properties compared to the results obtained for the commercial material (Texsound).

Keywords: Phase Change Materials (PCM), Shape stabilized PCM, Thermal Energy Storage (TES), Electrical Arc Furnace dust (EAFD), polymeric matrix, acoustic properties, thermophysical properties, mechanical properties.

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1. Introduction

The overall energy consumption is increasing significantly in recent years. Since this growth is directly proportional to the increase in CO_2 emissions and greenhouse gases, among other pollutants, governments from developed and emerging countries are emphasizing to stop or to moderate the global energy consumption. Consequently, new policies have been proposed by the European Union recently [1]. Furthermore, the governments are being pushed to create new regulations to construct more sustainable buildings due to the oil price increase and the climate change is a global concern [2].

Meanwhile, the International Energy Agency (IEA) suggests energy storage as a possible solution for the problems described above [3], often focusing on materials and systems for building applications. The energy consumption in houses and offices has continued growing up during the past decade and it represents over 30% of global energy consumption in developed countries [2,4].

Thermal Energy Storage (TES) proposes phase change material (PCM) as materials capable of storing high energy amount as latent heat during the phase change. Such materials have been extensively studied in the past by renowned researchers [5-8].

For this study, the authors developed materials able to encapsulate/stabilize PCM [9]. The first one has a polymeric mixture as matrix: EVA (polyethylene-co-vinyl acetate - copolymer) and EXACT (ethylene-octene copolymer), and was characterized by the authors [10,11]. The second one has an elastomeric matrix (EPDM - ethylene propylene diene monomer rubber).

Electrical arc furnace dust (EAFD) is a residue from the steel recycling process. Since EAFD contains hazardous metals, such as iron or zinc as well as manganese, lead, cadmium, chromium, and arsenic, its treatment is a costly and time consuming problem for steel manufacturers [12-14]. The most common ways to deal with EAFD is shipping it to an offsite processor for landfill or if possible, as raw material for zinc recovery process [9]. There are also references that consider incorporation of this dust in concrete [15-17]. EAFD is categorized by the European Waste Catalogue as hazardous residue being necessary its treatment previous the final disposal. Therefore, the fact of incorporating this filler in a polymeric matrix becomes the isolation of this residue. For this reason, the process of incorporating EAFD as a filler into a polymer matrix, in order to obtain a composite formulation that can yield a mouldable heavyweight sheet useful for acoustic insulation in automotive industry, has been described in previous studies by Niubó et al. [18,19]. The presence of elements such as lead, chromium, cadmium and/or mercury in the EAFD make impossible its use as polymer filler for this application because products obtained thereof overpass the limits required for automotive components. Thus, this treatment process is not suitable neither for incorporating large amounts of EAFD, or for other grades of EAFD. Moreover, most of the reported formulations consist on a polymer matrix having thermoplastics rubbers such as EPDM, EVA, LLDPE and mineral fillers above 60 phr (parts per hundred parts of resin). Therefore, the EAFD incorporation into polymeric matrix to make dense sheet for building systems appears as a good choice in order to reuse and isolate this dust.

The composites formulated have a specific density above 7 $kg \cdot m^{-2}$ which is directly related with their acoustic insulation capabilities [20,21].

As a result and taking into account the EAFD properties, it was incorporated in the formulation of the composite materials developed in this paper. The EAFD used in this study was provided by CELSA Barcelona (plain-carbon steel industry). In addition to isolate an industrial residue, these new materials aim to encapsulate or stabilize PCM in order to facilitate their introduction in constructive systems. The phase change material (PCM) used to manufacture both new materials was a paraffin, with a phase change at 21 ℃ and its melting enthalpy of 100 $kJ \cdot kg^{-1}$. It also acts as a manufacturing lubricant that facilitates the polymer-filler mixture. Therefore, the new materials can work as thermoregulators storing high amounts of energy at a temperature close to the inner comfort temperature required for building applications. Furthermore, PCM can smooth the inner temperature fluctuation in buildings as Castell et al. studied [22] and reduce the energy consumption in buildings sector [23].

The main objective of this paper is to characterize the thermal, acoustic and mechanical properties of the two new materials developed in this study which were formulated and manufactured with EAFD and PCM in order to enhance the acoustic insulation and to increase thermal inertia for constructive systems, respectively. Furthermore, they are both compared with a dense sheet material available in the market which by using the same methodology.

2. Materials and characterization

2.1. Materials

Two different polymeric matrixes have been used in order to be compared to a commercial sample. The first one was a mixture of polyethylene-co-vinyl acetate copolymer (EVA) with

18% content of vinyl acetate, EVA Alcudia PA-538 from Repsol YPF, with a melt flow index (MFI) of 2 g·10min^{-1} (190 ºC at 2.16 kg load) and a density of 937 kg/m^3, and an ethylene based plastomer resin Exact 8201 from Exxon Mobil Chemical, with a MFI of 1.1 g·10min^{-1} (ASTM D 1238) and density 882 kg/m^3. The second one was an elastomeric matrix made with EPDM. This rubber material has a density of 1230 kg·m^{-3} and due to its high density, EPDM acts reflecting the acoustic waves. Thereby, the matrix will increase the acoustic properties of the final material. Their compositions are listed in Table 1.

Table 1. Composition of the materials under study

		EPDM	EVA/EXACT (1:3)	Texsound
PCM	(% wt)	12	10	0
EVA 18	(% wt)	0	4.4	0
EXACT	(% wt)	0	13.3	0
EPDM	(% wt)	16.7	0	0
EAFD	(% wt)	71	72	0
Zn stearat	(% wt)	0.3	0.3	0
TEXSOUND	(% wt)	0	0	100

As shown in Table 1, both composite materials developed in this study differ from each other in their matrix. Note that the amount of EAFD and PCM are approximately the same. The small difference between these percentages is due to the manufacturing process. The EAFD used was provided by CELSA Barcelona. The composition of this dust was characterized in previous studies [9-11]. On the other hand, the PCM used to manufacture the new materials was RT-21 commercialized by Rubitherm. This PCM has 21 ℃ as melting point and its phase change enthalpy is 100 kJ·kg^{-1}.

Both materials were manufactured at large scale (150 kg, approx.). A Banbury mixer was used to manufacture the material and a homogeneous mixture was achieved. The material was laminated with a two-roll mill at room temperature. This is the critical point of the manufacture: the EVA/EXACT (1:3) matrix presents few problems during ambient temperature lamination because it is slightly rigid. Due to this reason, researchers decided to try manufacturing one dense sheet using EPDM as matrix because it is a widely used elastomer with softer properties and these two manufactured new materials are compared in this study. Furthermore, the obtained results were compared with the results obtained for a commercial material characterized following the same essays and experiments. Thus, the advantages and inconveniencies presented for both new materials may be shown and compared with one material available actually in the market.

2.2. Physical characterization

In order to be used as dense sheet in a constructive system, the density, the thermophysical properties and the acoustic properties have to be determined. However, the required mechanical properties for these dense sheet materials must be high enough to guarantee the structural stability of the material.

ρ_{He} is the density measured through a Helium pycnometer (densimeter) and ρ_{bulk} density was calculated by determining the mass and volume of the samples under study. The open porosity was calculated following Eq. 1 where P_O (%) is the open porosity [24]:

$$P_o(\%) = \frac{\rho_{\text{bulk}} - \rho_{\text{real}}}{\rho_{\text{bulk}}} \cdot 100$$ **Eq. 1**

The thermomechanical analysis (TMA) measurement consist on evaluating the deformation of the material (compressive deformation) when it is subjected to a temperature gradient. TMA/SDTA841e device from Mettler Toledo was used to perform the experiments. The samples were subjected to a heating/cooling rate of 2 K·min^{-1} from 5 °C to 40 °C under a N_2 atmosphere flow of 50ml ·min^{-1} applying 0.1 N compressive strength.

Using the obtained results and following the Eq. 2 may be calculated the expansion coefficient of the material, where α is expansion coefficient, L is the length, T is the temperature in each instant and L_o is the starting length.

$$\alpha = \frac{dL}{dT} \cdot \frac{1}{L_0}$$ **Eq. 2**

This coefficient is the expansion magnitude (or contraction) per unit of length resulting from one temperature degree change for the material studied, and it is also known as expansivity.

It is expected that the softness of the materials will change with the temperature, as well as the volume of PCM after melting, and the results will show which the impact of these changes is.

The tensile strength test was carried out through Zwick Roell tensile testing machine under a constant displacement speed of 100 mm/min. The composites stiffness was analysed evaluating the maximum tensile strength σ_{max}, and maximum elongation ε_{max}.

2.3. Thermal characterization

Because one of the main objectives of the developed materials is to improve the thermal inertia of a constructive system, the PCM incorporated in the formulation of the new materials has to be carefully studied. Therefore, the materials will be evaluated by Differential Scanning Calorimetry – DSC which is one of the most powerful technics to analyse the latent heat from the PCM. Moreover, the amount of humidity and the amount of PCM incorporated in the formulations will be analysed by thermogravimetrical analysis– TGA, because the materials were manufactured and the precise compositions are not carefully known. Furthermore, it is necessary to evaluate the thermal behaviour of the dense sheets under study when they are placed in a multi-layered material. Due to this reason, the dense sheets were placed between two drywall layers and the effective thermal conductivity of the multi-layered constructive system was measured. The details of each analysis will be described during the next sections.

The thermophysical properties were evaluated by differential scanning calorimetry (DSC), which is able to determine the melting enthalpy and the phase change temperature of the material analysed. Furthermore, the analysis were performed using hermetically sealed crucible to avoid evaporation, applying a 0.5 ºC·min^{-1} dynamic mode between 10–40 ºC and cycling three times each sample since this mode is widely used for PCM thermophysical analysis [25]. The equipment used was a DSC 822e device from Mettler Toledo under N_2 atmosphere flow of 80 ml·min^{-1} and the amount of sample used was around 40 mg while the equipment precision is ± 0.3 ºC for temperature and ± 1 kJ·kg^{-1} for enthalpy results. A new methodology developed by the authors to analyse composite materials by DSC was used [26].

The weight loss evolution over the time was studied through a thermogravimetrical device developed at University of Barcelona [27]. This device consists on a sample inside an alumina crucible that hangs from an analytical balance OHAUS-Explorer, connected to a computer which records the weight loss/gain over time while the sample is subjected to a temperature ramp. The sample is placed into an insulated furnace. The temperature is measured by thermocouples type *k* and the signal is recorded using a datalogger.

The main difference between this equipment and other calorimetric equipment as TGA/DTA is the sample amount allowed (up to 1 g) and the sample heterogeneity. The experiments were performer between room temperature and 600 ºC.

The effective thermal conductivity (κ_{eff}) of the materials under study was analysed with the Conductimeter device [28,29]. The multi-layered samples consist on a dense sheet (EPDM, EVA/EXACT (1:3) or Texsound) placed between two pladur® layers (gypsum precast combined with cellulose). The sample size was 30x30 cm, the dense sheet thickness was 0.3 cm and the pladur® layer ones was 1.5 cm.

This Conductimenter device is homemade equipment developed by University of Barcelona researchers following the standard UNE-EN 12664 [30], in order to measure effective thermal conductivity - κ_{eff}. The κ_{eff} of the samples is calculated by the thermal gradient achieved due to the power supplied from the hot plate and the cold temperature regulated by the thermostatic water bath connected to the cold plate. The measurements are performed under steady-state conditions.

According to the standard [30], the effective thermal conductivity (κ_{eff}) is calculated following Eq. 3 where ϕ is the heat flux which is the electrical power of the hot plate, e is the thickness of the sample, S is the surface of the sample, and ΔT is the temperature gradient between both sample surfaces.

$$\kappa_{\text{eff}} = \frac{\phi \cdot \text{e}}{\text{S} \cdot \Delta \text{T}}$$ **Eq. 3**

2.4. Acoustical characterization

An experimental device developed following the UNE-EN-ISO140 standard [31] was used to evaluate the airborne sound insulation and plot the insulation index (dB) vs. frequency (from 100 to 5000 Hz). This device was decribed in previous studies [11]. The level of noise was registered in each chamber. L_e and L_r are the noise recorded in the emitter and receiver chamber, respectively. L_e is calculated from the average of six measurements as shown in Eq.4.

$$\text{L}_\text{e} = 10 \times \log \frac{1}{6}\left(10^{\frac{\text{L}_1}{10}} + 10^{\frac{\text{L}_2}{10}} + ... + 10^{\frac{\text{L}_\text{i}}{10}}\right)$$ **Eq. 4**

Noise in the receiver chamber must to be corrected considering the background noise L_b and following the Eq. 5 where L_r' is the corrected noise level recorded in the receiver chamber.

$$L'_r = 10 \times \log\left(10^{\frac{L_r}{10}} - 10^{\frac{L_b}{10}}\right) \qquad \textbf{Eq. 5}$$

Moreover, the difference between the two levels was the acoustic insulation index *D* (dB) and it is calculated following the Eq. 6 where L_e is the noise recorded in the emission chamber.

$$D = L'_r - L_e \qquad \textbf{Eq. 6}$$

The acoustic insulation index *D* was used to compare the acoustic properties of the different formulations using the same device and experimental conditions. Sample size used in the experiments performed was 30x30 cm.

3. Results and discussion

3.1. Physical characterization

The bulk and real density results of the materials and the open porosity (calculated following the Eq. 1) are shown in Table 2. The results obtained with the density study show which is the densest material and hence the expected material with better acoustic insulating properties as it was studied by Yanai et al. [20] who conclude that the highest the density, highest the acoustic insulation properties are.

Table 2. Density and porosity results of dense sheet materials under study

Samples		EPDM	EVA/EXACT (1:3)	Texsound
Bulk density (ρ_{bulk})	(g/cm^3)	2.7	2.0	2.3
Real density (ρ_{He})	(g/cm^3)	2.12	1.90	1.95
Porosity (P_o)	(%)	27.4	5.3	17.9

As shown in Table 2, the EPDM is the densest material followed by the commercial material (Texsound). Consequently, results show that EPDM material is expected to have high acoustic insulation properties comparing to the other materials analysed. Moreover, the porosity was calculated and the results show that the less porous material is the EVA/EXACT (1:3) material (5.3%) and the most porous material is the EPDM (27.4%). This contributes to greater tortuosity of the materials because of the porous and leads to a higher acoustic wave dispersion and thus higher noise absorption.

The expansion coefficient was calculated with the results obtained from the experiments performed with TMA. Figure 1 presents the graphical representation of the instantaneous expansion coefficient vs. temperature during the heating process.

Therefore, the results demonstrate that during the heating process around 21 ℃ a phase change takes place producing changes in the expansion coefficient results. Additionally, EPDM and Texsound are affected having a falling value of the expansion coefficient (contraction) at temperatures above 35 ℃ approx. while the EVA/EXACT (1:3) material is stable inside this temperature range. This behaviour was obtained because both materials (EPDM and Texsound) are more elastic and softer.

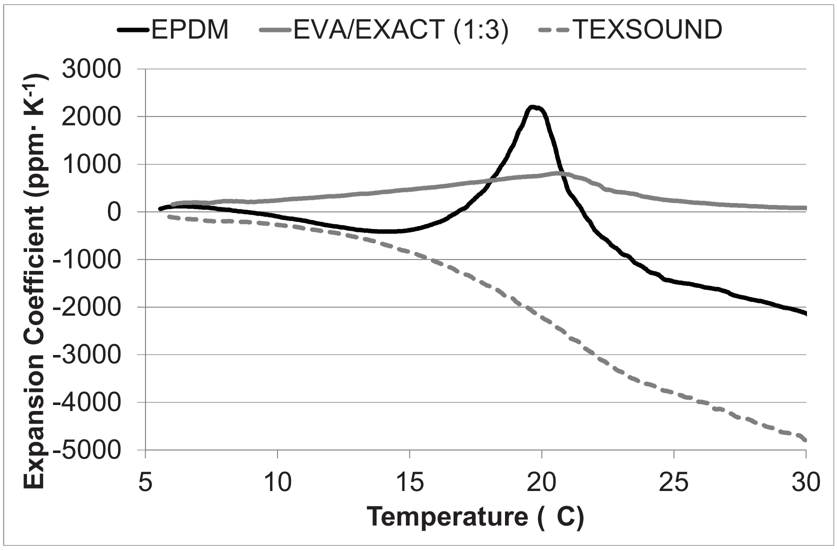

Figure 1. Expansion coefficient profile vs. temperature for the three samples under study

Furthermore, tensile strength test was done on three samples of each material at room temperature conditions (around 20 ℃) and the results of the mechanical properties average are listed in Table 3.

Table 3. Tensile strength properties of dense sheet materials under study

		EPDM	EVA/EXACT (1:3)	Texsound
Maximum strength: σ_{max}	(MPa)	2.0 ± 0.1	3.4 ± 0.2	0.4 ± 0.0
Maximum elongation: ε_{max}	(%)	437	37.5	575

The highest strength was obtained for EVA/EXACT formulation and the lowest elongation. However, the lowest strength and the highest elongation were observed from Texsound samples. Since the dense sheet mechanical properties required are not structural and then, they are not restrictive, materials should not be discarded.

3.2. Thermal characterization

The thermal characterization results performed by DSC are listed in Table 4 where the study of energy involved in phase change and peak temperatures are presented. The melting peak temperature for both materials is around 21 ℃ as i t was expected because it is the melting point of paraffin incorporated. Moreover, the melting enthalpy obtained in both cases is higher than 10 kJ·kg^{-1} otherwise the PCM effect would not be observed. Furthermore, melting enthalpy values shows that there is around 18% wt of paraffin in EPDM material and around 12 %wt of paraffin in EVA/EXACT (1:3) ones.

Table 4. Melting temperature and melting enthalpy obtained for the materials under study during the heating process

Samples		**EPDM**	**EVA/EXACT (3:1)**	**Texsound**
Melting Temperature	(℃)	22.4 ± 0.1	21.5 ± 0.5	No phase change
Melting Enthalpy	(kJ·kg^{-1})	18 ± 0	12 ± 1	

The thermo-gravimetrical results are shown in Figure 2. The results show that Texsound has fewer changes in the material and it decomposed with effervescence effect. It is completely stable during the heating process between 50 ℃ and 250 ℃. Thermal decomposition starts at this temperature leading to a total mass loss of 21.3% at 600ºC.

The mass loss showed by the materials developed is slightly different because these materials contained PCM. The mass loss below 100 ℃ was attributed to moisture of the samples. The mass loss between 100 ℃ and 300 ℃ is in accordance with the PCM incorporated during the manufacturing process regardless Texsound because this material has not got PCM in the formulation. Furthermore, sample moisture has also effect during first part of this temperature range. Then, the mass loss between 300 ℃ and the end of the experiment is due to the polymer decomposition. This decomposition doesn’t seem finished at 600 ºC for Texsound.

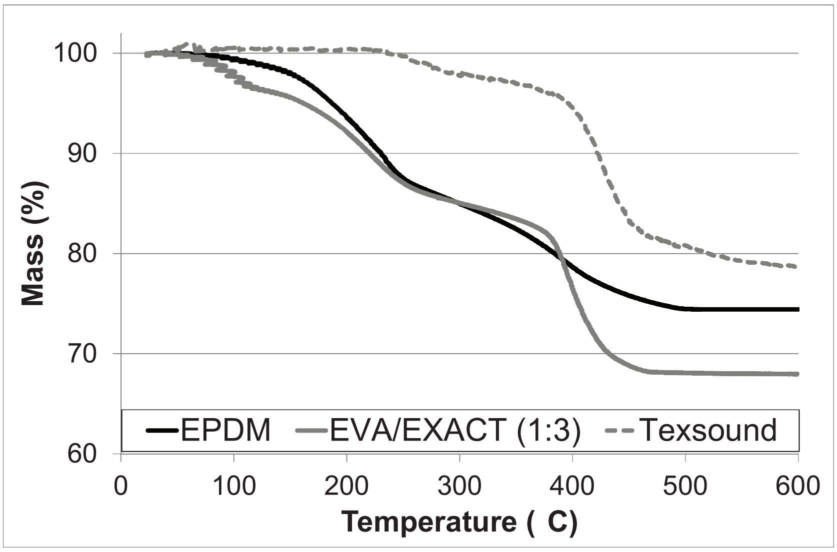

Figure 2. Mass loss (%) vs. Temperature of the materials under study

On the other hand, inorganic compounds are materials remaining in the crucible at the end of the experiment. The remaining filler content is rather in concordance with the EAFD percentage introduced and slight differences are due to the manufacturing process. The details of the mass loss process are listed in Table 5. All dense sheets under study have similar mass loss behaviour being analyzed between 50ºC and 600 ºC. However, Texsound is the material with less mass loss.

Table 5. Mass loss process details from the materials under study

	EPDM	EVA/EXACT (3:1)	Texsound	
Mass loss at 100 ℃	0.0%	2.0%	0.0%	Moisture
Mass loss 100 – 300 ℃	15.0%	15.0%	2.3%*	PCM
Mass loss 300 – 600 ℃	24.5%	32.0%	21.3%	Polymer degradation

* Texsound: there is not PCM included, and then 2.3% mass loss is due to the volatilization of lubricant and dispersant contained in this material

The effective thermal conductivity (*κeff*) measurements were performed under steady state conditions. The cold and hot surface temperatures recorded at this stage were used to calculate *κeff* of the sample following Eq.2. Table 6 presents the effective thermal conductivity of the 3 different multi-layered constructive systems evaluated.

Table 6. Temperature conditions and calculated effective thermal conductivity of materials under study

		EPDM	EVA/EXACT (3:1)	Texsound
Room temperature	(℃)	20.8	20.9	21.6
Sample mean temperature	(℃)	28.8	26.5	25.8
Effective thermal conductivity: κ_{eff}	(W/m·K)	0.21	0.18	0.24

The effective thermal conductivities (κ_{eff}) obtained were around 0.2 $W \cdot m^{-1} \cdot K^{-1}$. The constructive system with the lowest κ_{eff} is the EVA/EXACT (1:3) one; then, this is the most insulating constructive system measured (25.0% more insulating than the commercial dense sheet constructive system). This fact is due to higher EAFD and polymeric matrix content in EVA/EXACT (1:3) formulation. Anyhow, the constructive system made with EPDM dense sheet is also 14.3% more insulating than the wall system made with the commercial material.

3.3. Acoustic characterization

Figure 3 shows the acoustic insulation index (D), in dB vs. frequency (Hz), measured from 400 Hz to 5000 Hz for the developed dense sheets. In this figure is also shown the results obtained for commercial material (Texsound) which was analysed to compare its acoustic behaviour as dense sheet for constructive systems.

Rather the acoustic behaviours for materials under analysis are very similar, the results show that the materials developed in this paper have an acoustic insulation index higher than commercial material in low frequencies (from 1000 Hz of frequency). The scale up of the cabins lead to an inaccuracy in the results of acoustic insulation far below of 400-1000 Hz of frequency, which makes not relevant conclusions obtained in this area. EPDM composites exhibit an acoustic insulation until 3000 Hz similar to commercial composite, but at higher frequencies EPDM and EVA/EXACT (1:3) composites present less acoustic insulation compared to the commercial material (over than 3500 Hz). If materials developed in this work are compared, best results are obtained for the composite containing EPDM in the matrix than the homologue with EVA/EXACT at frequencies above 3500 Hz. These results behaviors may come from the obtained mechanical properties, because the EPDM matrix shows less rigidity, more flexibility and therefore it leads to an increment in damping the acoustic wave at high frequencies. This is in agreement with Texsound mechanical and acoustic results.

recorded. The main limitations of this equipment are the sample condition requirements: small size, purity and homogeneity [3]. These are huge limitations because many samples are mixtures of different components.

5.2.1. Paper 4: New methodology developed for the differential scanning calorimetry analysis of polymeric matrixes incorporating phase change materials

Under this PhD thesis, a new material was developed incorporating PCM (Chapter IV) but this new material has a polymeric matrix and filler which interfere in DSC signal of PCM. For that reason, a new methodology was developed for DSC measurement in order to enhance the DSC curve and to improve the obtained PCM results. This methodology is based on subtracting the matrix DSC signal from the composite DSC signal removing the matrix effect in the final results.

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New methodology developed for the differential scanning calorimetry analysis of polymeric matrixes incorporating phase change materials

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The main contributions to the state-of-the-art can be summarized in the following points:

- ✓ New experimental methodology to analyse composite materials containing PCM by DSC was designed and tested. This methodology consists on subtracting DSC matrix signal from the composite ones as Figure 14 shows. Thereby, the PCM signal is clearer and the phase change peak is acuter.

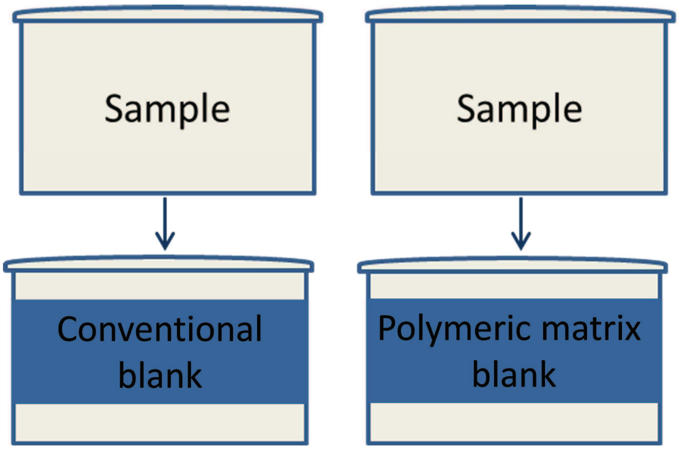

Figure 14. Sample and blank scheme used for developed DSC methodology.

- ✓ Improvements in the signal and, hence, accurate curve evaluation has been achieved. This enhancement is shown in the results as Figure 15 remarks. This figure shows without subtracting the matrix signal (a) and subtracting the matrix signal inside the DSC crucible (using this crucible as the blank instead of empty crucible which is the common procedure).

- ✓ Results of three successive measurements when using the polymeric matrix as blank are in agreement ensuring repeatability between experiments.

- ✓ This new DSC methodology is strongly recommended in any case where the matrix signal has to be isolated from any other DSC signal from another material component.

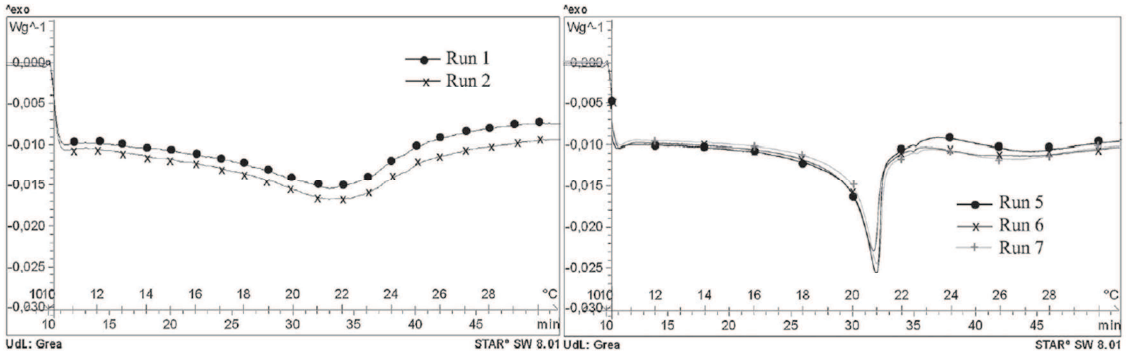

Figure 15. DSC profiles of the composite material with conventional blank subtracted (left), DSC profile of heating process of composite sample which contains PCM using different types of blank (right).

New methodology developed for the differential scanning calorimetry analysis of polymeric matrixes incorporating phase change materials

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New methodology developed for the differential scanning calorimetry analysis of polymeric matrixes incorporating phase change materials

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Abstract
Nowadays, thermal comfort needs in buildings have led to an increase in energy consumption of the residential and service sectors. For this reason, thermal energy storage is shown as an alternative to achieve reduction of this high consumption. Phase change materials (PCM) have been studied to store energy due to their high storage capacity. A polymeric material capable of macroencapsulating PCM was developed by the authors of this paper. However, difficulties were found while measuring the thermal properties of these materials by differential scanning calorimetry (DSC). The polymeric matrix interferes in the detection of PCM properties by DSC. To remove this interfering effect, a new methodology which replaces the conventional empty crucible used as a reference in the DSC analysis by crucibles composed of the polymeric matrix was developed. Thus, a clear signal from the PCM is obtained by subtracting the new full crucible signal from the sample signal.

Keywords: phase change materials (PCM), differential scanning calorimetry (DSC), thermal energy storage (TES), thermophysical properties, blank, polymer matrix

1. Introduction

It is well known that energy demand to satisfy thermal comfort in buildings is one of the major challenges for governments and administrations. The energy consumption by indoor thermal conditioning has grown considerably due to the increase of cooling/heating systems in the market. The increase in energy consumption, CO_2 emissions and fuel prices is pushing for new policies on sustainability and energy efficiency in buildings.

Therefore, energy storage system efficiency is being studied by the international scientific community. A feasible alternative to these systems is the use of phase change materials (PCM). PCM are suitable to store thermal energy due to their good heat storage capacity when phase change occurs. They have been extensively studied since 1980 [1–4].

Paraffinic materials can be used as PCM because their heat storage capacity is around 130 kJ kg^{-1} and their melting temperature ranges from 15 to 30 °C [5–8]. This temperature range is accepted by most countries as thermal comfort conditions for buildings. Consequently, PCM can be incorporated in construction systems. These materials increase the building envelope's thermal inertia and, when combined with thermal insulation, the energy consumption and temperature oscillations can be reduced [9].

The thermal behaviour of composite materials used in building envelopes is difficult to characterize (large size and heterogeneity). Moreover, PCM thermal analysis is a necessary

5.3.2. Paper 7: Improvement of the thermal inertia of building materials incorporating PCM. Evaluation in the macroscale

University of Barcelona researchers developed two devices to measure the thermal effective conductivity of multilayered materials or composite materials used in building envelopes as well as to see the PCM effect as a time delay of thermal stabilization of samples under temperature gradient. These two devices were used to analyze two type or matrixes used in buildings: gypsum and ordinary Portland cement incorporating both PCM and the obtained results were compared with samples without PCM.

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Improvement of the thermal inertia of building materials incorporating PCM. Evaluation in the macroscale

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The main contributions to the state-of-the-art can be summarized in the following points:

- ✓ Gypsum materials and ordinary Portland cement materials containing 0% wt, 5 % wt and 15 %wt of PCM were characterized comparing the results. Samples at the macro scale (300 x 300 x 30 mm) which contain microencapsulated PCM were evaluated (see Figure 18).

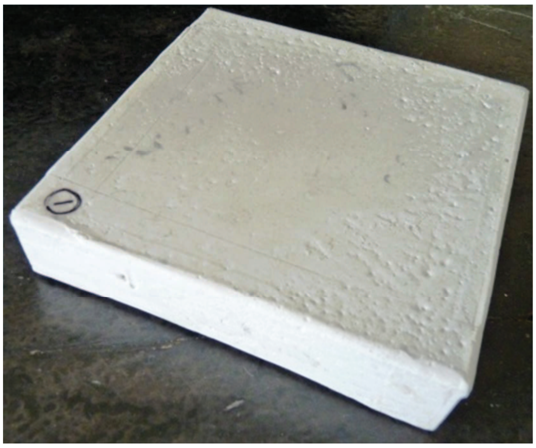

Figure 18. Samples analyzed in this study (in this case, gypsum + microencapsulated PCM samples).

- ✓ These measurements were performed by two devices: the Conductimeter device (shown in Figure 19) and the T–t curves device (shown in Figure 20).

Figure 19. Conductimeter device: cold plate, data-loggers, insulation, and energy supply.

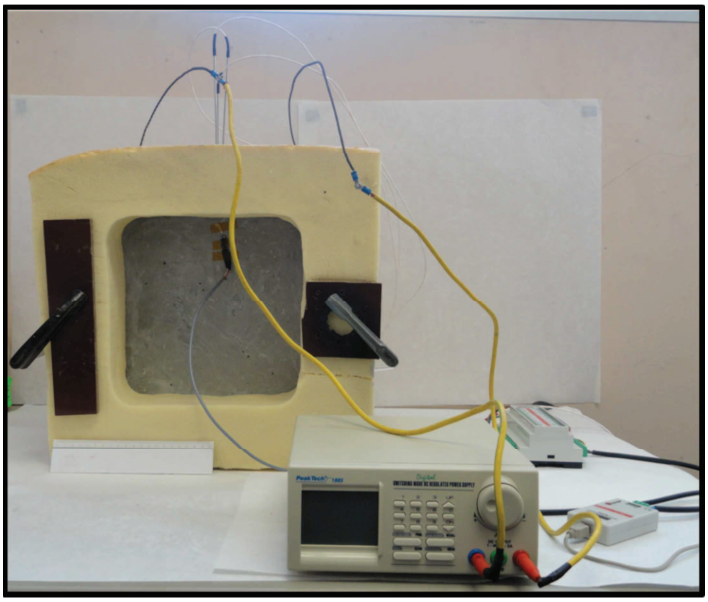

Figure 20. T-t curves device: temperature sensors, energy supply, and data-logger.

- ✓ Effective thermal conductivity was analyzed with Conductimeter device showing the differences between samples incorporating PCM and samples without PCM.

- ✓ Temperature-time curves were obtained with T-t curves devices showing the PCM effect of samples under study. This curves note the time delay of thermal stabilization between samples containing or not PCM.

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Improvement of the thermal inertia of building materials incorporating PCM. Evaluation in the macroscale

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HIGHLIGHTS

- ▶ The materials thermophysical characterization is a key point during building design.
- ▶ Authors developed two devices able to characterize materials at the macroscale.
- ▶ The thermal conductivity was measured and the temperature-time response curves were recorded.
- ▶ The materials tested and compared have a gypsum or Portland cement matrixes.
- ▶ The materials analysed incorporated 5%wt and 15%wt of PCM.

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ABSTRACT

The energy demand by the private sector for buildings HVAC systems has increased significantly, driving the scientific community to find different alternatives to reduce this high energy demand. Phase change materials (PCMs) are presented as materials with high thermal energy storage (TES) capacity due to the latent heat stored/released during phase change, able to reduce the energy demand of buildings when incorporated to construction materials. The analysis of the construction materials and their thermophysical properties are a key step in the building design phase. Even though the thermal characterization of real samples might be helpful, it is not always possible and it is usually costly. Therefore, the authors have developed two devices able to characterize effective thermal conductivity of real materials at macroscale and to register the temperature–time response curves produced by the inclusion of PCM in the constructive system for thermal inertia increase. The materials tested have a gypsum or Portland cement matrix which incorporates 5 wt% and 15 wt% of microencapsulated PCM (DS5001 Micronal®). Comparing the results, it was demonstrated that the PCM addition produces a reduction in the thermal conductivity of the samples. Furthermore, to incorporate 5 wt% PCM in Ordinary Portland cement matrixes is more beneficial than to add this PCM amount in gypsum matrixes, from the thermal properties point of view. However, the benefit from extending the PCM addition up to 15 wt% is better for gypsum samples than for Ordinary Portland cement matrixes.

1. Introduction

It is well known that energy consumption has grown recently worldwide due to the increase of private demand and industrial consumption. Actually, the energy consumption in the building sector is between 20% and 40% of the total demand in the European Union and other developed countries [1]. A possible alternative to reduce this high energetic demand is the use of thermal energy storage (TES) systems which incorporate materials with a high capacity to store energy as sensible heat storage (SHS), latent heat storage (LHS) or thermochemical heat storage (TCHS) [2].

Phase change materials (PCMs) are materials that have the ability to store energy due to their latent heat produced during the phase change [3]. These materials have been extensively studied as an alternative to be implemented in constructive envelopes for building applications [4–6]. The use of a latent heat storage system using phase change materials (PCMs) is an effective way of storing thermal energy and has the advantages of high-energy storage density and the isothermal nature of the storage process as was studied by Sharma et al. [7]. PCM combined with thermal insulation can reduce the energy consumption of the building and hence smooth the temperature oscillations [8]. Furthermore, the different applications which the phase change method of heat

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5.3.3. Paper 8: Comparison of three different devices available in Spain to test thermal properties of building materials including phase change materials

Limitation of thermophysical characterization of materials containing PCM used as part of building envelopes guided different research groups to develop their own equipment to test different thermal properties. Three devices developed in three Spanish Universities are compared in this study as inter-laboratory test and one Journal paper was published:

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Comparison of three different devices available in Spain to test thermal properties of building materials including phase change materials

Camila Barreneche[a,b,1,2], Alvaro de Gracia[a,1], Susana Serrano[a,1], M. Elena Navarro[b,2], Ana María Borreguero[c,3], A. Inés Fernández[b,2], Manuel Carmona[c,3], Juan Francisco Rodriguez[c,3], Luisa F. Cabeza[a,*]

The main contributions to the state of the art resulting of this study are the followings:

- ✓ Samples analysed in this paper have in their formulation phase change materials (PCM) and gypsum. They were made at the University of Lleida at same time and were sent to different laboratories to be tested by other universities, independently.

- ✓ Paraffin PCM was introduced in the gypsum matrix following three procedures:
  - Microencapsulated PCM: Micronal® DS5001 from BASF was mixed with the gypsum in dry state and then the gypsum bock was manufactured.
  - PCM suspension: A suspension with the needed water and PCM (RT 21 from Rubitherm) in liquid state was produced, and it was used as liquid suspension for the manufacture of the gypsum block.

  - Impregnation: Dry gypsum blocks were impregnated with liquid RT-21 from Rubitherm.

- ✓ Density and porosity of samples under study were analysed in order to control the sample hardening.

- ✓ The effective thermal conductivity was evaluated with the three devices while total heat accumulated and specific heat were evaluated with the equipment developed at the University of Lleida and equipment developed at the University of Castilla-La Mancha.

- ✓ Results obtained for all samples under study and using different devices were compared and trends on thermophysical properties analysed were provided. The comparison of the obtained results was used in order to verify the suitability of the different home-made devices for the composite materials thermal characterization.

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Comparison of three different devices available in Spain to test thermal properties of building materials including phase change materials

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HIGHLIGHTS

- ▶ Thermal properties of building envelopes were analysed in an inter-laboratory test in Spain.
- ▶ Tested materials were gypsum blocks containing PCM and made by three different ways.
- ▶ The effective thermal conductivity, the total amount of heat accumulated, and the specific heat were measured.
- ▶ The conductivity and Cp results were Blank < Suspension < Microencapsulated < Impregnated.
- ▶ The conductivity did not decrease with impregnated PCM due to the PCM filling gypsum pores.

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ABSTRACT

Thermal properties of materials used in building envelopes must be analysed in order to evaluate the thermal response of the constructive system. This thermal characterisation is a key point during the design phase of a building. However, thermal characterisation of constructive systems at laboratory scale is difficult to be carried out under real environment conditions. In this paper, three devices developed by three different research groups in Spain were used to compare in an inter-laboratory test the performance, capabilities and thermal properties of construction systems at lab scale. Tested materials were gypsum blocks containing phase change materials (PCMs) and made by three different ways: using microencapsulated materials Micronal® DS5001, a suspension water/PCM and impregnation with RT21. The effective thermal conductivity, the total amount of heat accumulated, and the specific heat were measured using these homemade devices. *k* results followed same trend but there was a drift between them due to the samples porosity and thickness. Moreover, the *k* decreased when adding PCM but this behaviour was not followed by impregnated samples; due to the PCM filling gypsum pores instead of air. The Cp results followed same trend $Cp_{Blank} < Cp_{Suspension} < Cp_{Microencapsulated} < Cp_{Impregnated}$ but a gap between results was observed due to different amount of incorporated PCM.

1. Introduction

A substantial increase in global energy consumption has been recorded in recent years. There is a high concern for the exhaustion of fossil fuels energy resources and how their use can impact the environment. In developed countries, the buildings contribution (private and offices consumption) to total energy consumption is between 20% and 40% [1].

Thermal properties of materials used in building envelopes must be analysed during the design phase to evaluate the thermal response of the building. Several researchers have studied the thermal behaviour of building insulation materials in situ [2–4]. However, the thermal properties of these constructive systems are poorly characterised at laboratory scale with samples sizing several cm. Therefore, it is important to test the materials that will be used in the construction of building envelopes before implementing them. This type of characterisation is difficult to reach

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5.3.4. Conclusions

- ✓ The higher PCM content in gypsum samples, the lower the effective thermal conductivity measured except for Impregnated PCM samples. The increase of the impregnated sample conductivity was due to the air substitution by the liquid PCM, decreasing the gypsum porosity.

- ✓ Cp average was estimated with the results obtained with the devices from Unviersity of Lleida and University of Castilla-La Mancha and results followed the same trend: $Cp_{Blank} < Cp_{Suspension} < Cp_{Microencapsulated} < Cp_{Impregnated}$ but higher values were observed for samples analysed at University of Castilla-La Mancha.

- ✓ The thermal properties of real materials used for building applications can properly be measured by the different home-made devices described in this paper since the obtained results were consistent and in the range of those values found in literature.

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Chapter VI: Conclusion and recommendations for future work

6.1. Conclusions and achievements of the thesis

6.2. Recommendation for future work

6. Main conclusions of the thesis and recommendation for future work

6.1. Conclusions and achievements of the thesis

This thesis presents the development and characterization of new materials. The incorporation of a waste from the refinement of steel of electric arc furnaces in polymeric matrixes to be used in building envelopes was success. This residue known as EAFD contains heavy metals oxides which can improve the acoustic behaviour of materials. New material has noble acoustic properties close to commercialized materials or even better acoustic insulation properties. On the other hand, it is important to remark that new materials incorporate PCM enhancing thermal behaviour of building envelopes as well. Reviewing the state of the art, paraffin is presented as one of the most studied PCM for building applications because of their thermophysical properties. For this reason, the PCM used in this thesis was paraffin wax PCM. In summary, the main achievements and conclusions of present PhD thesis are the following:

- ✓ A state of the art review of materials available in the market to be used as PCM and studied PCM used for building applications was complete in order to have the existing knowledge in this filed.

- ✓ Development of new materials incorporating at least 10% wt PCM using different materials as matrix: polymer mixtures, gypsum, gypsum board and ordinary Portland cement.

    - One material was patented which was developed during this PhD thesis. This material is able to stabilize PCM and to isolate EAFD which is a toxic waste from steel recycling process.
    - Two polymeric materials (EVA/EXACT (1:3) and EPDM) were used as matrix of this new material. Properties were analysed and compared also with commercial material (Texsound):

The EPDM material is the densest and it showed a moderate porosity compared with other dense sheets characterized

The highest strength and the lowest elongation were obtained for EVA/EXACT (1:3) formulation.

DSC analyses showed that the EPDM is the material which can store more latent heat.

From the point of view of stability, the commercial material (Texsound) is the material with less mass loss but three dense sheets analyzed have similar behaviour.

The measured effective thermal conductivity (κ_{eff}) showed that both new material constructive systems are more thermal insulating than the commercial material ones and similar acoustic behaviour was obtained for the polymer composites developed. Therefore, materials developed in this PhD thesis are competitive with material available in the market.

- ✓ Difficulties on thermophysical characterization at laboratory scale at microscale were solved by developing new methodology for DSC analysis in order to separate PCM DSC signal and matrix signal.

    - This methodology consists on introducing the polymeric matrix in the crucible used as blank and then subtracting this blank curve from the sample curve removing the interference produced by the polymeric matrix.
    - This new DSC methodology is now available to clarify one DSC signal which has high interest for the research when analyzing materials presenting matrix interferences in DCS signal.

- ✓ DSC operating modes were compared when common PCM are characterized (paraffin and salt hydrate).

  - The recommended DSC operation for both PCM groups analyzed, organic and inorganic, is the slow dynamic mode (0.5 K $\min^{-1}$). This analytical procedure is time saving and less laborious when analyzing DSC curves since there is no doubt in selecting integration limits.

- ✓ Thermophysical characterization of samples at macroscale was evaluated by using different developed devices at several universities in Spain.

  - Thermophysical properties of multilayered sample were analysed using developed equipment which simulates real thermal conditions. Furthermore, the results presented in this paper during the dynamic experiment can be used to validate numerical models and hence, predict the thermal behaviour of different building envelopes containing PCM under daily temperature oscillations.

    Samples of wood + gypsum board (with and without PCM) were tested and measured results demonstrate that the addition of impregnated PCM in gypsum board increases slightly the U-value of the sample and average heat storage capacity is increased in 30% and therefore the thermal inertia of the tested building envelope.

  - Thermophysical properties comparison of ordinary Portland cement and gypsum matrixes incorporating both PCM was performed using a Conductimeter device and registering the temperature time curves during cooling process.

    Results from both materials demonstrated that the PCM addition produces a reduction in the effective thermal conductivity of the samples.

    Due to the PCM incorporation in those materials, extra time is needed to stabilize the sample temperature compared to the reference (without PCM).

- The improvement in the thermal behaviour of gypsum board samples due to the addition of PCM was analysed using three different devices developed by three Spanish Universities.

  Thermophysical properties of macroscaled gypsum samples incorporating PCM by three different processes were analyzed.

  The higher the amount of PCM, the lower the effective thermal conductivity measured except for Impregnated samples whose porous are filled with PCM moving the air located inside.

  The average Cp was estimated finding same trend $Cp_{Blank} < Cp_{Suspension} < Cp_{Microencapsulated} < Cp_{Impregnated}$ but higher values were observed for samples analysed with the C.R. device due to the differences in porosity percentage.

6.2. Recommendation for future work

PCM available in the market and previously studied for use in buildings were listed at the beginning of this thesis. Its introduction as database (see Figure 10) through the CES Selector software was the first step but the analysis of the data taking into account the following points is recommended:

- ✓ The thermophysical properties in some cases are quite different depending on the font used. Is this due to standardization lack when measuring thermophysical properties or is due to the material itself?
- ✓ PCM group classification taking into account its nature, is the spread of data related to this classification?
- ✓ Classification according phase change temperature ranges or phase change enthalpy required: criteria for selecting PCM.
- ✓ Introduction in the database of details from other technical materials used to store thermal energy as latent heat: microencapsulated PCM, slurries, emulsions, etc.

The use of other polymers as dense sheet matrixes and the introduction of other PCM type into polymeric matrix must be studied. Also, trying to incorporate PCM into polymer matrices at lower temperatures (without polymer fusion) could be a procedure to achieve more PCM input and achieve optimized material.

To control the porosity when PCM is incorporated in porous ceramic materials is an important issue. The procedure to control this parameter must be studied as well as thermophysical properties characterization of new samples made under these conditions could be interesting in order to compared again same devices used in interlaboratory test presented in this PhD thesis (Paper 8). This new study must help to highlight the differences between systems developed in research centres are minimal.

To test other parameters of materials used as building envelopes is needed. The measurement of volatile compounds which are released to the environment when these new materials are introduced in building systems must be measured. This type of analysis is often complicated but highly recommended as future work.

The fire reaction test of materials incorporating organic PCM is also recommended as it is well known that this type of PCM increase the flammability of materials.

Annex: Journal Publications and Conferences

Papers published in Peer review Journals:

E. Oró, L. Miró, C. Barreneche, I. Martorell, M. M. Farid, L. F. Cabeza. Corrosion of metal and polymer containers for use in PCM cold storage. Applied Energy, DOI 10.1016/j.apenergy.2012.10.049, 2013.

J. Giro-Paloma, G. Oncins, C. Barreneche, M. Martínez, A. I. Fernández, L. F. Cabeza. Physico-chemical and mechanical properties of microencapsulated phase change material. Applied Energy, DOI 10.1016/j.apenergy.2012.11.007, 2013.

E. Oró, C. Barreneche, M.M. Farid, L.F. Cabeza. Experimental study on the selection of phase change materials for low temperature applications. Renewable Energy 57, 130-136: 2013.

L.F. Cabeza, C. Barreneche, L. Miró, J.M. Morera, Esther Bartolí, A.I. Fernández. Low carbon and low embodied energy materials in buildings: a review. Renewable & Sustainable Energy Reviews, DOI 10.1016/j.rser.2013.03.017i, 2013.

C. Barreneche, A. Gil, F. Sheth, A.I. Fernández, L.F. Cabeza. Effect of d-mannitol polymorphism in its thermal energy storage capacity when it is used as PCM. Submitted to Solar Energy SE-D-13-00159.

A. Gil, C. Barreneche, P. Moreno, C. Solé, A.I. Fernández, L.F. Cabeza. Thermal behaviour of d-mannitol when used as PCM: comparison of results obtained by DSC and in a thermal energy storage unit at pilot plant scale. Submitted to Applied Energy APEN-D-12-01812.

L.F. Cabeza, C. Barreneche, L. Miró, M. Martínez, A.I. Fernández, D. Urge-Vorsatz. Affordable construction towards sustainable buildings: embodied energy in building materials. Submitted to Current Opinion in Environmental Sustainability COSUST-D-12-00093R1.

S. Serrano, C. Barreneche, L. Rincón, D. Boer, L.F. Cabeza. Optimization of three new compositions of stabilized rammed earth incorporating PCM: Thermal properties characterization and LCA. Submitted to Buildings & Environment BAE-S-12-01055-2-1.

A. Solé, L. Miró, C. Barreneche, I. Martorell, L.F. Cabeza. Review of the T-history method to determine thermophysical properties of phase change materials (PCM). Submitted to Renewable and Sustainable Energy Reviews, RSER-D-13-00284 .

Other Paper published in Journals:

A. Solé, X. Fontanet, C. Barreneche, I. Martorell, A. I. Fernández, L. F. Cabeza. Parameters to take into account when developing a new thermochemical energy storage system. Energy Procedia 30, 380-387: 2012.

S. Serrano, C. Barreneche, L. Rincón, D. Boer, L. F. Cabeza. Stabilized rammed earth incorporating PCM: optimization and improvement of thermal properties and life cycle assessment. Energy Procedia 30, 461-470: 2012.

C. Barreneche, A. Solé, L. Miró, I. Martorell, A.I. Fernández, L.F. Cabeza. New methodology developed for DSC to analyze composite materials incorporating phase change materials (PCM). Usercom Journal 37 (Mettler Toledo): 2013.

DSC analysis using two operation methods for organic and inorganic phase change materials (PCM). L. Miró, A. Solé, C. Barreneche, I. Martorell, A. I. Fernández, L. F. Cabeza. Submitted to Usercom (Mettler Toledo): 2013.

Papers submitted to Peer review Journals:

C. Barreneche, M. Niubó, E. Oró, L.F. Cabeza, A.I. Fernández. New material from rubber crumbs with acoustic insulation properties suitable for highway sound barriers applications. Submitted to Journal of Hazardous Materials HAZMAT-D-13-00789.

A. Solé, X. Fontanet, C. Barreneche, A.I. Fernández, I. Martorell, L.F. Cabeza. Requirements to consider when choosing a suitable thermochemical material. Submitted to Solar Energy, SE-D-12-00936.

Conference contributions

C. Barreneche, A.I. Fernández, A. Castell, L.F. Cabeza. PCM in building envelops for energy efficiency: experimental results and new concepts. PALENC 2010, 3rd International Conference on Passive & Low Energy Cooling for the Buit Environment. Rhodes island (GREECE), 2010. Oral presentation.

A. de Gracia, A. Gil, C. Barreneche, M.M. Farid, L.F. Cabeza. New equipment for testing thermal mass of composite materials. ISSE 2011 - International Symposium on Sustainable Systems and the Environment. Sharjah (UNITED ARAB EMIRATES), 2011. Oral Presentation.

A. de Gracia, C. Barreneche, M.M. Farid, A.I. Fernández, A. Castell, L.F. Cabeza. Dynamic thermal response of composite materials.ISES Solar World Congress 2011, Kassel (GERMANY), 2011. Oral presentation.

V. Safari, C. Barreneche, A. Castell, A. Basatni, L. Navarro, L.F. Cabeza, F. Haghighat. Volatile organic emission from PCM building materials. Innostock 2012 -

The 12th International Conference on Energy Storage. Lleida (SPAIN), 2012. Poster presentation.

C. Barreneche, A. Gil, P. Moreno, C. Solé, L.F. Cabeza. Thermal behaviour of d-mannitol when used as PCM: comparison of results obtained by DSC and in a pilot plant storage tank. Innostock 2012 - The 12th International Conference on Energy Storage. Lleida (SPAIN), 2012. Oral presentation.

M.E. Navarro, C. Barreneche, T. Castillo, A.I. Fernández, L.F. Cabeza. Improvement of the thermal inertia of building materials incorporating PCM. Evaluation in the macroscale with T-t comparative curves. Innostock 2012 - The 12th International Conference on Energy Storage. Lleida (SPAIN), 2012. Oral presentation.

C. Barreneche, A. de Gracia, S. Serrano, M.E. Navarro, A.M. Borreguero, A.I. Fernández, M. Carmona, J.F. Rodríguez, L.F. Cabeza. Comparison of three different equipments available in Spain to test thermal properties of building materials including phase change materials. Innostock 2012 - The 12th International Conference on Energy Storage. Lleida (SPAIN), 2012. Poster presentation.

C. Barreneche, L. Miro, A. Solé, A.I. Fernández, L.F. Cabeza. New methodology for DSC analysis of PCM included in polymeric matrixes. Innostock 2012 - The 12th International Conference on Energy Storage. Lleida (SPAIN), 2012. Poster presentation.

C. Barreneche, A. Gil, C. Solé, A.I. Fernández, L.F. Cabeza. Influence of polymorphism in the thermal energy storage capacity of d-mannitol. Innostock 2012 - The 12th International Conference on Energy Storage. Lleida (SPAIN), 2012. Poster presentation.

J. Giro-Paloma, G. Oncins, C. Barreneche, M. Martínez, A.I. Fernández, L.F. Cabeza. Physico-chemical and mechanical properties of microencapsulated phase change material. Innostock 2012 - The 12th International Conference on Energy Storage. Lleida (SPAIN), 2012. Oral presentation.

S. Serrano, C. Barreneche, A. de Gracia, A.I. Fernández, L.F. Cabeza. Optimization and improvement of rammed earth incorporating PCM. Innostock 2012 - The 12th International Conference on Energy Storage. Lleida (SPAIN), 2012. Poster presentation.

E. Oró, L. Miró, C. Barreneche, I. Martorell, M.M. Farid, L.F. Cabeza. Corrosion of metal and polymer containers for use in PCM cold storage. Innostock 2012 - The 12th International Conference on Energy Storage. Lleida (SPAIN), 2012. Poster presentation.

A. Solé, X. Fontanet, C. Barreneche, A.I. Fernández, I. Martorell, L.F. Cabeza. Recomendaciones para caracterizar correctamente los materiales termoquímicos. XV Congreso Ibérico y X Congreso Iberoamericano de Energía Solar - CIES 2012. Vigo (SPAIN), 2012. Oral presentation.

C. Barreneche, A.I. Fernández, J.M. Chimenos, A. Castell, L.F. Cabeza. Valorización del polvo de acería de hornos de arco eléctrico mediante su incorporación en matrices poliméricas con materiales de cambio de fase para el almacenamiento de energía térmica en edificios. XII Congreso Nacional de Materiales y XII Congreso Iberoamericano de Materiales. Alicante (SPAIN), 2012. Oral presentation.

C. Barreneche, A. Gil, C. Solé, M. Martínez, A.I. Fernández, L.F. Cabeza. Influencia del polimorfismo del d-manitol en su uso como material de cambio de fase (PCM). XII Congreso Nacional de Materiales y XII Congreso Iberoamericano de Materiales. Alicante (SPAIN), 2012. Oral presentation.

S. Serrano, C. Barreneche, L. Rincón, A.I. Fernández, L.F. Cabeza. Mejora de la inercia térmica de un muro de tapia mediante la adición de materiales de cambio de fase. XII Congreso Nacional de Materiales y XII Congreso Iberoamericano de Materiales. Alicante (SPAIN), 2012. Oral presentation

S. Serrano, C. Barreneche, L. Rincón, D. Boer, A. Castell, L.F. Cabeza. Stabilized rammed earth incorporating PCM: optimization and improvement of thermal properties and life cycle assessment. SHC 2012 - International Conference on Solar Heating and Cooling for Buildings and Industry. San Francisco (UNITED STATES), 2012. Poster presentation.

A. Solé, X. Fontanet, C. Barreneche, A.I. Fernández, I. Martorell, L.F. Cabeza. Parameters to take into account when developing a new thermochemical energy storage system. SHC 2012 - International Conference on Solar Heating and Cooling for Buildings and Industry. San Francisco (UNITED STATES), 2012. Oral Presentation.

C. Solé, S. Serrano, L. Navarro, C. Barreneche, L. Rincón, L.F. Cabeza. Laboratory and pilot plant experiments with rammed earth walls. COINVEDI 2012 - 2nd International Conference on Construction and Building Research, Valencia (SPAIN), 2012. Oral presentation.

C. Barreneche, A.I. Fernández, L.F. Cabeza. New shape stabilized PCM polymer including solid waste for acoustic and thermal comfort in buildings. Annex 23 & Annex 25 Joint Workshop - ECES IA - International Energy Agency, Auckland (NEW ZEALAND), 2012. Oral presentation.

Conference Papers submitted in 2013:

C. Barreneche, M.E. Navarro, M. Niubó., L.F. Cabeza, A.I. Fernández. Characterization of two new shape stabilized phase change material (PCM) including electrical arc furnace dust (EAFD) with polymeric matrix used as dense sheet for building applications. International Conference on Sustainable Energy Storage in Buildings, Dublin (IRLAND). Oral presentation.

C. Barreneche, M.E. Navarro, S. Serrano, L.F. Cabeza, A.I. Fernández. New database on phase change materials for thermal energy storage in buildings to help PCM selection. ISES Solar World Conference 2013, Cancun (MEXICO). Oral presentation.

A. Solé, C. Barreneche, L. Miró, I. Martorell, A.I. Fernández, L.F. Cabeza. Corrosion test of salt hydrates and vessel metals for thermochemical energy storage. SHC International Conference on Solar Heating and Cooling for Buildings and Industry 2013. Freiburg (GERMANY).