

**UTILIZATION OF FORM-STABLE PHASE
CHANGE MATERIALS IN BUILDING
APPLICATIONS UNDER HOT WEATHER
CONDITIONS**

BY

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A Dissertation Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

CIVIL ENGINEERING

DECEMBER 2022

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

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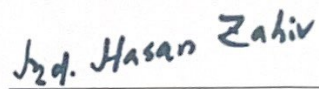

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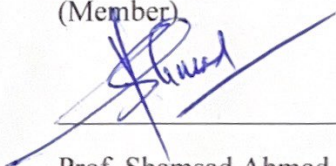
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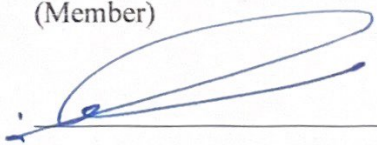



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Dedicated to my dear parents, my affectionate wife, my adorable siblings
and my beloved daughter and son, for their patience, endless love,
encouragement and support.

ACKNOWLEDGMENTS

In the Name of Allah the All-Merciful, the Ever Merciful. All perfect praise be to Allah, the Lord of the worlds, for guiding me and granting me patience, knowledge, courage, and health, to complete this research successfully.

I would like to express my love and gratitude to my dear parents, my lovely wife, my brothers and sisters, my blessed kids (Sham and Omar) and all my relatives for their support, encouragement, prayers and infinite patience, without them it would be difficult for me to achieve my educational goals. May Allah reward you all.

I would also like to express my heartfelt gratitude to my advisor Dr. Salah U. Al-Dulaijan for allowing me to complete my Ph.D. dissertation under his supervision. I also would like to thank my esteemed Co-Advisor Dr. Hasan Zahir and my admired committee members, Prof. Mohammad Maslehuddin, Prof. Shamsad Ahmed and Dr. Dr. Mesfer M. Al-Zahrani for their ideas, continuous guidance, suggestions and constructive comments during my research journey.

Acknowledgement is also due to King Fahd University of Petroleum & Minerals and the Civil Engineering department for giving me the opportunity to complete my Ph.D. degree and providing me the facilities and materials that I need.

Finally, I acknowledge the Kingdom of Saudi Arabia for providing me Ph.D. scholarship and for all other facilitations.

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LIST OF ABBREVIATIONS

BIPV	Building-Integrated Photovoltaics.
CNT	Carbon Nanotubes.
DSC	Differential Scanning Calorimetry.
EDS	Energy-Dispersive X-ray spectroscopy.
E	Energy storage efficiency.
E_{eff}	Efficient energy per unit mass of PEG.
ExP	Expanded Perlite.
ExPP	Expanded Perlite/Polyethylene Glycol Composite.
FE-SEM	Field Emission Scanning Electron Microscopy.
FTIR	Fourier Transform Infrared.
HFMT	Heat Flow Meter Temperature.
HDPE	High-Density Polyethylene.
HVAC	Heating Ventilation and Air Conditioning.
LHES	Latent Heat Energy Storage.
LHTES	Latent Heat Thermal Energy Storage.
LHS	Latent Heat Storage.

NZEB	Net Zero Energy Building.
OA	Oil Ash.
OAP	Oil ash/Polyethylene Glycol Composite.
PCM	Phase Change Materials.
PEG	Polyethylene Glycol.
R	Impregnation Ratio.
SC	Scoria.
SCP	SC/PEG composite.
SCPC	Cement coated scoria/polyethylene glycol composite.
SEM	Scanning Electron Microscopy.
TES	Thermal Energy Storage.
TCHS	Thermochemical Heat Storage.
TEM	Transmission Electron Microscopy.
TGA	Thermogravimetric Analysis.
UV-VIS	Ultraviolet-visible.
XPS	X-ray Photoelectron Spectroscopy.
XRD	X-ray Diffraction.

ABSTRACT

Full Name : [KHALED OWN MOHAISEN]
Thesis Title : [UTILIZATION OF FORM-STABLE PHASE CHANGE
MATERIALS IN BUILDING APPLICATIONS UNDER HOT
WEATHER CONDITIONS]
Major Field : [CIVIL ENGINEERING]
Date of Degree : [December 2022]

Phase change materials (PCMs) have received significant attention for their use in energy saving applications. However, their utilization in buildings, especially under hot weather conditions is limited. The components of PCMs melt during the daytime and then they solidify during the nighttime. This phase change process decreases the internal temperature during the daytime and increases the temperature during nighttime. PCMs store heat from solar and other sources as latent heat within a temperature range, resulting in a significant conservation of energy required for air conditioning (AC). As such, the use of PCMs is highly desirable in the Kingdom due to the prevailing extreme weather conditions. The interest around the use of PCMs is increasing over the last decade, due to the need for conserving energy and natural resources. Several PCMs have been developed for several applications, such as solar water heating, thermal insulation, low temperature food applications, etc. However, not much research has been done on their use in the buildings. The construction industry requires such a technology to decrease energy consumption and to improve internal building comfort. PCMs can be used to conserve and store energy, or to control the fluctuation in the indoor temperature.

PCMs can be utilized in many structural and non-structural elements, such as walls, blocks, partitions plaster, etc. of a building. The use of PCMs in buildings will significantly decrease the energy that is generally required for cooling and heating. Among the PCMs, organic PCM has high demand for building applications due to its easy availability, desired temperature ranges and non-toxic properties. However, two drawbacks of organic PCMs, are leakage during melting and solidification process at day and night times, and low thermal conductivity that will affect its efficiency, are limiting their use in buildings. Consequently, there is a need to develop carriers that can be used to overcome these disadvantages. Some work has been conducted on the use of form stable PCMs in buildings. However, it has been concentrated in the cold weather conditions using manufactured and high cost materials. The feasibility of utilizing this emerging technology in the hot weather conditions, such as in the Arabian Gulf, is yet to be assessed. Consequently, the main goal of this study was to develop form-stable PCMs for the hot weather conditions of the Kingdom. In addition, indigenous natural and industrial waste materials can be used to develop a form stable PCM with better conductivity and encapsulation to prevent leakage problems.

In this study, several supporting materials were investigated to develop a form stable phase change material (FS-PCM). The thermal and physico-chemical properties of the selected materials was evaluated utilizing a wide array of analytical techniques. Among the materials investigated, ExPP/CNT (0.5%) exhibited the best performance, indicating that it is a viable material for thermal energy storage system. Further, the developed ExPP composite is a promising PCM for TES in energy-efficient buildings due to its remarkable ability of rapid energy storage/release combined with good chemical stability and thermal

reliability. Further, ExPP does not have leakage problems, super cooling is minimized and all other properties that play a crucial role in maintaining building comfort are superior. However, it has low thermal conductivity which limits its application as an energy storage system. Compared to other PCM composites, the developed ExPP/CNT (0.5%) PCM offers greater enthalpy, superior storage capacity, and minimum super cooling. The structural properties and the pore network of ExPP/CNT (0.5%) composite prevents the leakage of liquid PEG during service.

To utilize PCMs in building applications, cement coated scoria/PEG particles (SCPC) were characterized and utilized for the first time to improve the thermal performance of concrete. Porous volcanic scoria was successfully employed as supporting material to develop a FS-PCM used in concrete. The absorption capacity SC was found to be 47% using a vacuum impregnation technique. Moreover, the XRD and FTIR results showed that SCP indicating that the developed SCP was formed without any chemical reactions during the preparation process. Additionally, the compressive strength results show that up to 80% replacement of SCPC by SC in concrete can be deployed as a structural concrete in buildings. Moreover, the thermal performance analysis shows that concrete panels containing SCPC has a maximum temperature reduction of 5.49 °C and 3.88 °C for the heating and cooling cycles, respectively. Which reflects the higher thermal inertia of concrete containing SCPC. Thus, the prepared SCPC concrete has a function of reducing the energy consumption by decreasing the temperature and shifting the loads away from the peak periods. Therefore, SCPC can be used to enhance the thermal storage of concrete in buildings.

ملخص الرسالة

الاسم الكامل: خالد عون عوض محيسن

عنوان الرسالة: استخدام مواد متغيرة الحالة والمستقرة الشكل في تطبيقات البناء في ظل ظروف الطقس الحار

التخصص: الهندسة المدنية

تاريخ الدرجة العلمية: ديسمبر 2022

حظيت مواد تغيير الحالة (PCMs) باهتمام كبير لاستخدامها في تطبيقات توفير الطاقة. ومع ذلك ، فإن استخدامها في المباني ، خاصة في ظل ظروف الطقس الحار ، محدود. تذوب مكونات PCM خلال النهار ثم تتصلب أثناء الليل. وخلال هذا التغير تقوم بامتصاص وإطلاق الطاقة مما يساعد على بقاء المباني باردة أثناء النهار في الصيف وتقليل الحاجة للتبريد. تخزن PCMs الحرارة من الطاقة الشمسية وغيرها من المصادر كحرارة كامنة ضمن نطاق درجة حرارة معينة ، مما يؤدي إلى الحفاظ على الطاقة المطلوبة لتكييف الهواء (AC) . إن استخدام مثل هذه المواد أمر مرغوب فيه للغاية في المملكة بسبب الظروف الجوية القاسية السائدة. فقد زاد الاهتمام باستخدام مواد PCM بشكل حاد خلال العقد الماضي ، بسبب الحاجة إلى الحفاظ على الطاقة والموارد الطبيعية. تم تطوير العديد من أنظمة PCM لاستخدامها في العديد من التطبيقات المختلفة ، مثل تسخين المياه بالطاقة الشمسية ، والعزل الحراري ، وتطبيقات الأطعمة ذات درجات الحرارة المنخفضة ، وما إلى ذلك. ومع ذلك ، لم يتم القيام بالكثير من الأبحاث على استخدامها في المباني. إن استخدام هذه التكنولوجيا في عملية البناء يساعد على تقليل استهلاك الطاقة وتحسين الراحة الداخلية للمبنى. ويمكن أيضا استخدام PCMs للحفاظ على الطاقة وتخزينها ، أو للتحكم في تقلبات درجة حرارة المبنى الداخلي للحصول على الراحة الداخلية في المباني.

يمكن استخدام PCMs في العديد من العناصر الهيكلية وغير الهيكلية للمبنى ، مثل الجدران والأسقف والفواصل وما إلى ذلك. سيؤدي استخدام PCMs في المباني إلى تقليل الطاقة المطلوبة بشكل عام للتبريد والتدفئة. من بين أنظمة PCM المختلفة ، هناك طلب كبير على PCM العضوي لتطبيقات البناء نظراً لسهولة توفره ونطاق درجة الحرارة المطلوب وخصائصه غير السامة. ومع ذلك ، هناك عيبان لاستخدام PCM العضوي ، وهما مشاكل التسرب أثناء عملية الذوبان والتصلب في أوقات النهار والليل والتوصيل الحراري المنخفض الذي سيؤثر على كفاءته ، مما يحد من استخدامه في المباني. لذلك، هناك حاجة ماسة لتطوير مواد PCM يمكن استخدامها للتغلب على هذه العيوب. تم إجراء بعض الأعمال على استخدام نماذج PCM مستقرة في المباني. ومع

ذلك ، فقد تركز معظم هذا العمل في ظروف الطقس البارد باستخدام مواد مصنعة وعالية التكلفة. وحيث لم يتم بعد تقييم جدوى استخدام هذه التكنولوجيا الناشئة في ظروف الطقس الحار ، كما هو الحال في الخليج العربي. وبالتالي فإن الهدف الأساسي من هذه الدراسة هو تطوير مواد PCMs ذات الشكل المستقر لاستخدامها في ظروف الطقس الحار في المملكة. بالإضافة إلى ذلك، يمكن استخدام المخلفات الصناعية والمواد الطبيعية لتطوير شكل مستقر من مواد ال PCMs للتغلب على مشاكل التسرب.

في هذه الدراسة، تم فحص العديد من المواد الداعمة لتطوير شكل مستقر من ال PSMs لتصبح مستقرة الشكل (FS-PCM). وقد تم تقييم الخصائص الحرارية والفيزيائية والكيميائية للمواد المختارة باستخدام مجموعة واسعة من التقنيات التحليلية. من بين المواد التي تم تحليلها، أظهرت مادة ExPP/CNT(0.5%) أفضل أداء، مما يشير إلى أنها مادة قابلة للتطبيق لنظام تخزين الطاقة الحرارية. علاوة على ذلك فإن مادة ExPP المطورة تعد مادة واعدة للاستخدام في أنظمة تخزين الطاقة الحرارية في المباني، وذلك لاستجابتها السريعة لتخزين/إطلاق الطاقة المخزنة مع الحفاظ على الاستقرار الكيميائي والقدرة الحرارية. حيث لا تعاني مواد ExPP من مشاكل التسرب، بالإضافة إلى كفاءة جميع الخصائص الأخرى التي تلعب دوراً هاماً في الحفاظ على الراحة الحرارية في المبنى. ومع ذلك فإن ExPP لديها موصلية حرارية منخفضة، مما يحد من تطبيقها كنظام لتخزين الطاقة. مقارنة بمركبات PCM أخرى، فإن ExPP/CNT(0.5%) يوفر قدرة أكبر من المحتوى الحراري، وسعة تخزين فائقة. حيث تمنع البنية الهيكلية لمركب ExPP/CNT(0.5%) تسرب ال-PEG أثناء عملية الانصهار والتجمد.

لاستخدام PCMs في المباني، تم تحليل وفحص جزئيات السكوريا المغلفة بالاسمنت (SCPC) واستخدامها لأول مرة لتحسين الأداء الحراري للخرسانة. حيث تم استخدام السكوريا البركانية ذات المسامية المرتفعة كمادة داعمة لتطوير شكل مستقر من مواد FS-PCM تستخدم في الخرسانة. حيث وجد أن قدرة امتصاص السكوريا 47% باستخدام تقنية الحقن الفراغي. علاوة على ذلك، أظهرت نتائج فحص XRD و FTIR أن مواد SCP قد تشكلت بدون أي تفاعلات كيميائية أثناء عملية التحضير. بالإضافة إلى ذلك، تظهر نتائج مقاومة الضغط أنه يمكن استبدال الـ ما يصل حتى 80% من مواد SC بـ SCPC في الخرسانة الإنشائية للمباني. بالإضافة لذلك فإن مواد SCPC لديها القدرة على تخفيض الحرارة بـ 5.49 درجة مئوية و 3.88 درجة مئوية في عمليات التسخين والتبريد، على التوالي. مما يعكس القصور الذاتي الحراري العالي للخرسانة التي تحتوي على مواد SCPC. وبالتالي فإن الخرسانة المحضرة باستخدام مواد SCPC لها القدرة على تقليل استهلاك الطاقة عن طريق خفض درجة الحرارة وبالتالي يمكن استخدامها لتحسين كفاءة استهلاك الطاقة في المباني.

CHAPTER 1

INTRODUCTION

1.1 General

The rising energy demand consumption in the world generally and in the gulf countries especially is rapidly increased, leading to environmental disasters affecting the whole life on the planet. The consumption of energy in the structural sector is expected to be between 20% to 40% of the whole energy demand in developing countries [1]. Higher carbon footprint, increased risk of climate change and higher prices of energy are some of its expected effects. One smart solution used to reduce this consumption is by using energy efficient buildings [2]. This is particularly required in the Kingdom of Saudi Arabia. Under the hot environment of the Kingdom, a modern technology that can store the solar heat, thus decreasing the power required for air conditioning is required. Thermal energy storage systems (TES) incorporate high capacity materials to store energy, this energy can be stored as latent heat storage (LHS), thermochemical heat storage (TCHS) or sensible heat storage (SHS) [1]. The LHS materials are relaying on absorbing heat and then releasing it while transmitting from solid state into liquid state and vice versa. Among TES methods, latent heat thermal energy storage using a phase change material (PCM) is preferred due to high storage density and small temperature change [3].

Phase change materials (PCMs) are used to store energy as LHS systems. In a solid-liquid LHS PCMs acting in a way similar to the SHS materials, while PCMs absorb energy its temperature will increase until it reach its phase transformation temperature, PCM will change its phase from solid to liquid, then it becomes solid again when energy is released

[4]. This process leads to a considerable improvement in the internal building comfort and it will significantly decrease the energy usage. Though the advantages of PCMs in energy conservation have been known, their use has been limited to the cold weather conditions. Consequently, there is a need to develop PCMs for building applications in hot weather conditions.

PCMs mainly divided into three main categories, organic, inorganic and eutectic PCMs. Organic PCMs, such as paraffins, lauric acid and polyethylene glycol (PEG) have been studied due to its wide range of melting temperature, low cost and chemical and thermal stability. Among those different organic PCMs, PEG is an supreme choice due of its high latent heat storage capacity and it has a suitable phase change temperature [5]. However, some drawbacks of PEG, such as leakage, flammability and low thermal conductivity, has limited its use. Low thermal conductivity of PEG reducing the rate of heat transfer. In addition, leakage problems affecting the energy storage system and harm the environment, which limits its use and applications [6].

Several researchers have used good conductive materials, such as graphite/PEG [7–10], graphene/PEG [11–13] and carbon nanotubes/PEG [14,15] to develop PCMs. However, those materials are relatively costly, thus limiting their use in building applications [16]. Moreover, the latent heat of the composite prepared utilizing these materials is very low. Consequently, there is an essential need to develop alternative inorganic low-cost materials that possess high thermal conductivity to be used along with PEG to develop a form-stable PCM.

While several studies have been carried out to develop PCM for building applications, these have been mostly concentrated for cold weather conditions and not many studies have been conducted on the use of PCM in hot weather conditions. Accordingly, there is a need to develop an energy efficient building system, this study aims to develop PCMs to be used under hot weather conditions. Some of the indigenous natural and industrial waste materials, such as perlite [17], scoria [18–20] and oil ash [21–23], having a porous structure with high carbon content, will be used along with PEG to develop a form-stable phase change material. It is anticipated that the developed form-stable PCM will accrue in economic and environmental benefits.

1.2 Significance of Research

High energy consumption is recorded in the Arabian Gulf due to high environmental temperature, especially during summer. Therefore, significant energy consumption is reported due to high cooling demand especially in buildings. Consequently, energy saving methods and techniques need to be developed to enhance the internal building comfort and decrease the energy consumption. The energy storage systems based on PCMs have received significant attention over the last years for its beneficial effect and its use in various applications, especially its use in building applications. PCMs can be used effectively to improve and enhance the thermal performance of buildings and energy savings. Though some studies have been conducted on the use of PCMs in the other part of the world, information is lacking on their use under hot weather conditions, such as in the Arabian Gulf. Therefore, there is a need to conduct a study to assess the performance of PCMs prepared with indigenous natural and industrial

waste materials. Such a study becomes important since there is a great potential of developing thermal efficient construction systems utilizing indigenous lightweight aggregates in combination with suitable PCMs.

1.3 Research Objectives

The objective of the proposed research is to develop energy saving systems utilizing indigenous natural and industrial waste materials along with a suitable PCM for use under local hot weather conditions. The specific objectives are the following:

- i. Assess the possibility of utilizing indigenous natural and industrial waste materials as a carrier to develop a form-stable PCM,
- ii. Evaluate the latent heat capacity and supercooling and discharge properties of the selected PCMs,
- iii. Characterize the properties of developed PCMs,
- iv. Assess the performance of the developed form-stable PCM as part of plaster, mortar and concrete,
- v. Assess the economic and environmental benefits of the developed PCMs, and

Provide recommendations on the avenues of PCM applications.

1.4 Research Methodology

The following work will be conducted to achieve the objectives of the proposed research.

Task 1: Literature review

A thorough review of literature relevant to the subject of the proposed research will be conducted. The proposed literature survey will be helpful in identifying PCMs suitable for the hot weather conditions.

Task 2: Survey of local materials

A survey of local materials, both natural and industrial, will be conducted to identify the possible candidates for the development of energy saving systems using suitable PCMs. Several tests will be carried out to check the suitability of using the selected materials to be used as carrier in PCM. summarize the tests to be carried out on the selected indigenous natural and industrial waste materials.

Table 1.1 Measurements of Weather Conditions

Property	Tests on Carriers	Tests on PCMs
Morphology	Field Emission Scanning Electron Microscopy (FE-SEM)	Field Emission Scanning Electron Microscopy (FE-SEM)
Chemical composition	X-ray diffraction (XRD) Fourier Transform Infrared Spectroscopy (FTIR)	X-ray diffraction (XRD) Fourier Transform Infrared Spectroscopy (FTIR)

	Energy Dispersive X-ray spectroscopy (EDS) X-ray Photoelectron Spectroscopy (XPS)	Energy Dispersive X-ray Spectra (EDS)
Thermal	Thermal Conductivity Thermo-Gravimetric Analysis (TGA)	Thermal Conductivity Thermo-Gravimetric Analysis (TGA) Differential Scanning Calorimetry (DSC)
Microstructure	Particle size distribution	Particle size distribution

Task 3: Preparation and Characterization of a form stable PCMs

Trial tests will be conducted to assess the adequacy and suitability of the prepared form-stable PCMs to be used as energy saving system in building applications. Both the PCMs and carriers will be characterized to evaluate their mineralogical composition, microstructure and thermal properties. Figure 1.1 shows the materials that will be used to prepare the form-stable PCM. Different percentages of carriers and PCMs will be mixed physically by adding ethanol, then sonicated for 30 minutes, and finally stirred overnight to evaporate the ethanol and obtain a form stable PCM. This procedure is outlined in Figure 1.2. and the following points summarize the process of preparing the form-stable PCM:

1. PCM (PEG) and carriers (Perlite, Scoria and Oil Ash) are added to the ethanol solution, as PEG is highly soluble in ethanol and carrier powders are dispersed in ethanol.
2. A physical mixing (No chemical reaction occurs) of PCM and carrier is carried out.
3. Sonication process for 30 minutes is carried out and then the samples are stirred at the room temperature overnight.
4. According to the above process PEG penetrates into porous structure of carriers due to surface tension and capillary pores.

The developed form-stable PCM will be characterized, utilizing analytical techniques listed in Table 3, to assess its adequacy as a phase change material for hot weather applications.

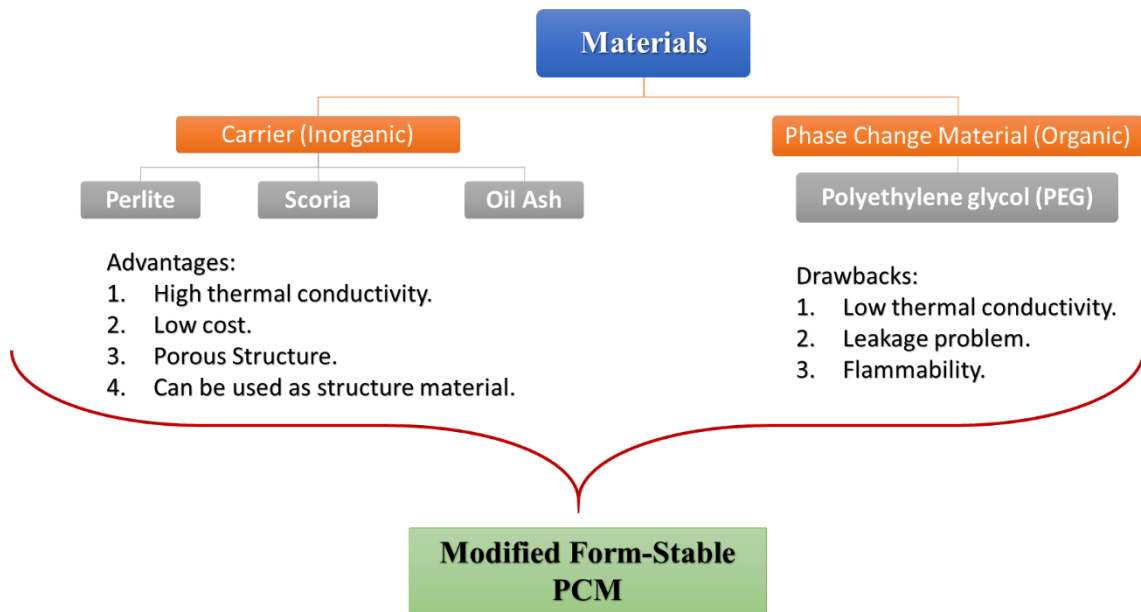


Figure 1.1 Materials proposed to be used to prepare a form stable PCM.

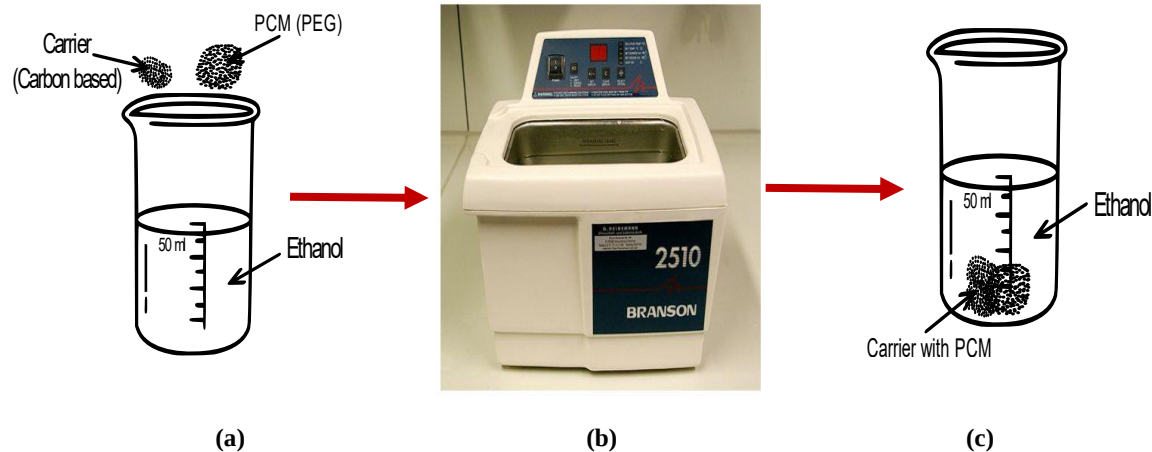


Figure 1.2: Process of preparing a form stable PCM. (a) adding PEG and carrier with ethanol, (b) Sonication process for 30 minutes, (c) stirring the mixture over the night.

Table 1.2: Proposed tests on form stable PCM.

Property	Technique
Morphology	Field Emission Scanning Electron Microscopy (FE-SEM)
Chemical composition	X-ray diffraction (XRD) Fourier Transform Infrared Spectroscopy (FTIR) Energy Dispersive X-ray Spectra (EDS)
Thermal conductivity	Thermal Conductivity Thermo Gravimetric Analysis (TGA) Differential Scanning Calorimetry (DSC)
Stability	Leakage
Compatibility	Between PCM and different metals

Task 4: Evaluation of the form-stable PCM in building applications

The developed form-stable PCMs will be incorporated in selected building materials, such as mortars, plasters and concrete, and the composite system will be evaluated to assess its adequacy to be used in buildings as an energy conservation materials. The composite material will be tested to evaluate its microstructure and mechanical and thermal properties.

Table 1.3 summarizes the tests to be conducted on the composite form-stable PCM.

Table 1.3: Tests to be conducted on the composite form-stable PCM.

Property	Technique
Morphology	Field Emission Scanning Electron Microscopy (FE-SEM)
Chemical composition	Energy Dispersive X-ray Spectroscopy (EDS) XRD
Thermal conductivity	Thermal Conductivity
Mechanical	Compressive strength
Stability	Leakage

Task 5: Data analysis

The experimental data developed in the proposed study will be evaluated to assess the microstructural, mechanical and thermal properties of the developed composite PCM. Additionally, the benefits, such as technical, environmental and energy conservation, accruing out of the use of the developed PCM will be evaluated.

Task 6: Recommendations

Recommendations on the types of PCMs suitable for the local environmental conditions and avenues of their application will be provided.

CHAPTER 2

CHALLENGES OF THE APPLICATION OF PCMs TO ACHIEVE ZERO ENERGY BUILDINGS UNDER HOT WEATHER CONDITIONS

2.1 Abstract

With the global increase in population and temperature, cooling demand has increased tremendously in the building sector, especially in the GCC and African and South Asian countries where temperature can reach 50 °C from mid-May to August. Thermal performance of buildings can be effectively improved by using thermal energy storage (TES) systems based on phase change materials (PCMs). As PCMs melt during the daytime and solidify at nighttime, they can prevent rooms from overheating during daytime in hot months and may also reduce the need for heating during nighttime in the winter. PCMs store heat using their chemical bonds when their phase changes from liquid to solid, and release heat during the melting process, at a constant temperature. While a TES can be used to achieve this, a TES can also be used for other purposes in houses, such as peak shaving or increasing energy efficiency in heating ventilation and air conditioning (HVAC). This paper discusses the use of TES for the storage of sensible heat, latent heat, and thermochemical energy in buildings. Sustainable heating and cooling in buildings employing TES can be achieved with passive building envelope systems, active systems containing PCMs, sorption systems, and seasonal storage systems. This review presents results obtained in earlier studies on the incorporation of PCMs in building materials, the

problems associated with the selection of PCMs, and various methods used to encapsulate PCMs for space heating and cooling applications. Furthermore, this article provides an outline of a range of PCM applications in buildings for decreasing the cooling loads under hot atmosphere conditions, and the parameters influencing the productive and viable use of PCMs under hot weather conditions. Several shortcomings in the application of PCMs, mostly due to the extreme summer weather conditions preventing the PCM from completely solidifying at night and thereby decreasing its effectiveness during the day, were identified. Although sunlight is abundant in the Middle East, the use of solar energy in conjunction with PCM technology for temperature control in buildings is rare. One of the main reasons for the status quo is the small temperature difference between day and night. Hence, the selection of a suitable PCM is crucial and challenging for this type of a hot atmosphere. As a consequence, the current study will fill a scientific gap concerning PCM usage in this vital hot temperature range. Under such extreme environmental conditions, thermal conductivity, density, and the specific heat of the insulation affect the heat flow. Finally, future research opportunities were explored and shortcomings of the technology as of today were discussed.

2.2 Introduction

Currently, researchers are considerably interested in thermal energy storage [24] due to its application in a range of fields, namely desalination, photovoltaic solar cells, solar heating/cooling, petroleum industry as well as the use by armed forces [25]. Particularly noteworthy are the beneficial effects on the energy performance of a building owing to the use of a larger share of renewable energy [26], thereby reducing the demand for energy

based on fossil fuel or peak cooling and heating charges [27]. However, reports on the application of thermal energy storage in the construction of buildings are rare in the literature and determining the type of TES that should be used in a specific building is not straightforward [28]. Storage of thermal energy in the floor, roof, walls [29], and ceilings of buildings can be enhanced by embedding PCMs within certain type of construction materials [30]. These construction materials by using natural convection may directly confine thermal energy [31]. By increasing a building's thermal storage capacity, the indoor air temperature can be kept at the appropriate level for extended periods of time with little variation, improving occupant comfort.[32].

A large amount of the energy is consumed by buildings for lighting, heating, cooling, and air conditioning [33]. Hence, new building materials, structures, and components must be investigated on an urgent basis for energy efficient construction [32]. A recent study by Cui et al. [34] [16] describes work undertaken across the globe on a range of topics involving PCMs, including main building applications, application forms, thermal physical properties, and application effects [34]. Nearly half of the countries evaluating PCMs for building applications are in the Mediterranean climate area. Rahimpour et al. [35] have conducted an extensive study on the use of PCMs in buildings constructed in different cities of Australia.

Hasan et al. have studied the yearly energy performance of a PV (photovoltaic)-PCM system, with paraffin (m.p.38-43 °C) applied as the PCM on the rear of the PV panels, in extremely hot weather conditions prevailing in the UAE [36]. The application of the PCM increases the PV power output due to the cooling produced by the PCM. PV-PCM systems can produce a consistent performance with the enhancement of annual energy yield by

5.9% under hot weather conditions. Fig. 2.1 shows a country-wise breakdown of global research on PCMs [37]. Approximately 114 articles were reviewed, and half of them are from China, the U.S., and Italy. The articles have shown that the use of PCMs in lightweight buildings is highly beneficial in decreasing the HVAC energy demand or shifting that to off-peak hours. Parameters such as the type of PCM and its melting point, pre-cooling/heating, and HVAC temperature setting must be optimized to obtain the best outcome. However, very few studies have been conducted in areas with a hot and harsh climate. Buildings consume 40 percent of the overall energy produced worldwide annually, which also accounts for 1/3rd of the worldwide greenhouse gas productions [38].

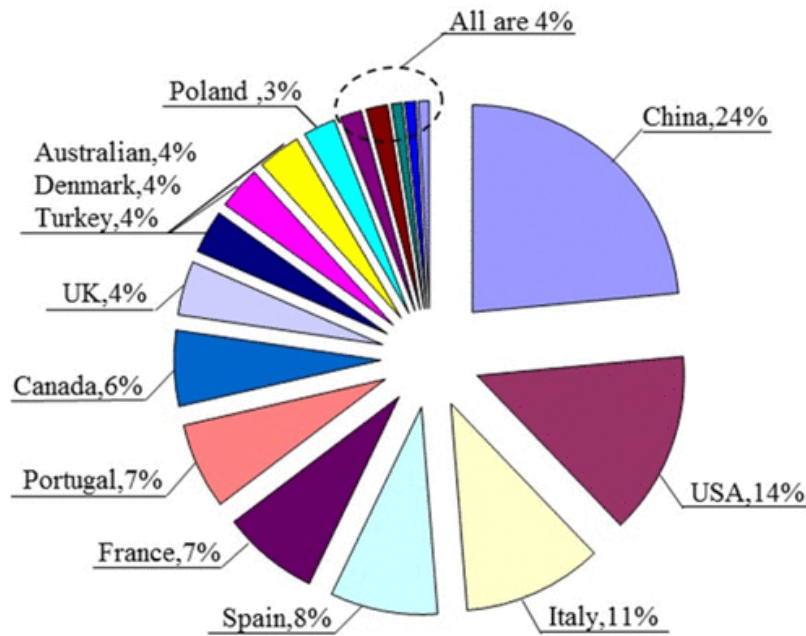


Figure 2.1 Country-wise breakdown of PCM research worldwide [34].

In building construction, PCM layers sandwiched between internal and external surfaces of walls [39] concrete soaked with a PCM [40], gypsum boards impregnated with PCMs [41] or PCM layers randomly mixed with layered PCM-walls may be used [42]. The results

of these experiments show that PCMs are effective in maintaining the indoor comfort level for occupants at the standard specifications. Neeper et al. [43] examined the thermal characteristics of a PCM wallboard exposed to diurnal temperature variations. PCMs can also be used to fabricate interior components, such as heat/ice storage tanks. Another promising use of PCMs is to enhance the energy efficiency of houses. The uses of PCMs have reached the market in many applications, such as refrigeration equipment, distribution and supply of pharmaceuticals, and food logistics. Energy demand for cooling and heating applications is growing across a variety of industries, including construction, commercial refrigeration, textiles, packaging etc. [44]. Increased use of reactive technology associated with PCMs is also expected to increase the global energy conservation efforts owing to the rapidly depleting fossil fuels. Cabeza et al. [45] have thoroughly analyzed all current PCM types along with their descriptions, associated problems, and potential solutions, with regard to their implementation in buildings. Tyagi and Buddhi et.al [46] have focused more attention on how PCMs can be functional in buildings in terms of PCM building blocks. PCM trombe wall, PCM shutters, and PCM wallboards. They have shown that these components have immense potential to lessen the energy demand for cooling and heating [46]. The sources of the articles may vary, depending on the affiliation of the authors. Interestingly, China accounts for more than 17% of the publications. However, GCC or neighboring countries have not published any papers on the subject until 1990, although these countries are located in the sunbelt.

PCMs used in building construction can be divided into three categories, depending on the area of a building they are employed in: PCM windows, PCM roof, and PCM bricks [47]. According to the results of a computer study by Alawadhi [48], the heat flux in indoor

space can be reduced by 17.55 percent when a PCM is embedded in bricks for use in hot climates. Experimental research conducted by Castell et al. [49] compared a passive cooling material (PCM) to two conventional building materials and found that the peak temperature was reduced by PCM by 1°C while reducing daily temperature swings. Using Sierpinski carpet to characterize the geometric shape of the bricks, Principi and Fioretti et al. [50] computed the thermal reaction of a brick wall filled with a PCM in response to changes in ambient temperature. According to Principi and Fioretti et al. [50], enclosing a PCM in bricks is a reliable method of reducing heat-distribution variations through the bricks. Researchers Silva et al. [51] found that PCMs mitigated temperature fluctuations inside buildings, reduced thermal intensity from 10° C to 5° C, and lengthened the period interval by around 3 hours. Using a computer model of a concrete roof with vertical cone frustum holes filled with a PCM, Alawadhi and Alqallaf demonstrated a 39% reduction in heat flux on the roof's interior surface. Field thermal efficiency findings from an experimental PV-PCM system provided by KoSny et al. [52] demonstrate a 30% heating and 50% cooling load reduction.

In this paper, promising recently reported PCMs that can be incorporated in building materials and are capable of operating under hot weather conditions, particularly when the temperature is not much different between the daytime or nighttime are described. The aim of this paper is to provide an overview of a broad range of TES technologies, with a particular emphasis on the configuration of storage technology and the type of building component, i.e., those used in floors, roofs, and walls. Even though there are several promising TES technologies for both commercial and residential buildings, much more work is required, especially in the fields of PCMs and thermochemical storage. Information

on actual successful real-life applications is lacking, with only a very few reports of actual application data, especially for areas with hot weather.

One of the prospective uses of PCMs is to include them in the energy efficiency envelope of houses. The advantages of such applications are a decrease in the total energy use by the air conditioning unit during the summer season, and a time shift in the peak load during the day. Application of PCMs is a positive solution when there is an imbalance between energy supply and demand. Common applications of PCMs for heating and cooling of buildings are in floors, walls, and roofs and/or ceilings. In this review, application of PCMs in areas with hot climatic conditions for all relevant parts of a building structure will be discussed based on published literature. Initially, different types of PCMs and their performance in components used in building construction will be briefly described. The key objective of this review study is to enhance the importance and impact of PCMs, which is essential for (i) energy saving (ii) improving building and/or occupant comfort, (iii) decreasing the greenhouse gas effects, (iv) improving the eco-system, and finally, (v) contributing towards an atmosphere with cleaner air.

2.3 Net Zero Energy Building

According to studies, PCM in walls may greatly reduce radiant heat, which is an important aspect in determining a building's thermal load [53] In order to accomplish NZEB in the future, thermal energy storage (TES) technologies in buildings are becoming more and more common [54]. Utilizing TES systems is an exciting approach that can significantly cut down on the amount of energy that is consumed by the building industry [55]. As TES materials can store heat or cold and release it when needed, they may help bridge the gap

between energy demand and supply. TES is employed in several commercial, industrial, and domestic settings in the event of an energy supply and demand gap [56]. The use of TES systems with phase change materials in commercial and residential buildings has received a lot of attention (PCMs) [57]. Sensible heat, latent heat, or chemical processes are often used to store energy in TES materials [57]. Due to its enormous energy storage capacity and isothermal nature, the PCM latent heat storage technology is very appealing [58]. Radiant floor heating systems' heating capability, interior air temperature, and floor temperature are all significantly impacted by solar radiation [56]. Solar radiation has a significant influence on the conventional air-based management technique and would result in overheating problems, according to Beji et al. [59]. When Zhao et al. [60] analyzed how solar radiation affected heat resistance, they discovered that floors with more thermal mass had a greater ability to regulate heat.

Stritih et al. [61] investigated Slovenia's and Turkey's potential for solar energy using TES. Discussions included the current energy landscape, solar energy potential, and theories and strategies for thermal energy storage in solar applications. Additionally, TES offered the potential for energy savings and a decrease in CO₂ emissions for a variety of solar building applications. A parametric study was carried out by Ramakrishnan et al. [62] to improve PCM performance in naturally ventilated structures. The design of PCM-using buildings was modified to boost interior thermal comfort during the summer and improve the usage of latent heat capacity. The results showed that choosing the best PCM settings was made easier with the use of performance measures. A PCM-based enclosed heat management system was the subject of an experiment conducted by Tyagi et al. [63]. The PCM was chosen because it is readily available within the allowed temperature range and because of

its stable thermal response over time. Following testing using an air conditioning system for storing cold energy, three heating loads were employed to discharge the design system.

Studies on PCM usage in buildings have shown that PCMs may significantly enhance building energy performance [64]. The problem of summertime overheating in houses without air conditioning was investigated by Auzeby et al. [65]. It was thought that the extra heat that PCMs inhaled when the environment was warm and exhaled when the environment cooled was a beneficial passive approach. The findings suggest that PCMs might help residential structures with their overheating issue. To achieve building energy reduction objectives, conducted research on the use of PCMs in gypsum boards [66]. Gypsum boards that have been PCM-impregnated have been shown to effectively increase building thermal performance while using less energy. To determine how well a PCM-integrated wall would work in various cities, a computer simulation was run. It has been shown that it is advantageous to use a PCM whose melting point is near to the level at which the building's inhabitants feel comfortable to lower the peak interior temperature. According to the results of the study, the use of gypsum boards reinforced with PCM contributed to a noticeable decrease in building energy use. Han and Taylor [67] used PCMs embedded in building envelopes to model the inter-building effect and examine the effects of thermal energy on nearby structures. Xu et al. [68] highlighted the potential of PCM flooring for solar-heated buildings and presented instructions for determining the PCM melting point based on the test results. Recent studies of solar radiation's interaction with a floor's enhanced thermal storage have largely focused on gauging the thermal environment and thermal comfort indicators, but these findings fall short from the point of view of solar radiation energy storage. Furthermore, it is difficult to determine how sun

radiation affects PCM flooring in NZEBs. Thus, it is crucial to investigate the PCM floor's performance in a NZEB with solar heating. Solar radiation was the only source of energy used in Entrop et al. [69] testing the effectiveness of a PCM-lined box's insulation against the ambient temperature of a moderately heated room. Lowest nightly air temperature was greater than in the box with a solid concrete bottom, although there was less of a temperature swing within. Lu et al. [70] built a prototype that featured a sunroom and PCM radiant floor heating. Heat was contained in the PCM floor throughout the day even though air had to be pumped into the sunspace.

The simulations were run using various PCM and building network configurations. According to the findings, the control building's yearly HVAC energy consumption might be cut by as much as 17% by using PCM-embedded building envelopes. Pintaldi et al. [71] researched solar cooling control strategies and TES technology. In addition to practical alternatives for solar cooling applications, many ideas for thermal storage systems and media were presented. They also concentrated on PCM uses for high-efficiency solar cooling at melting temperatures between 60 and 250 degrees Celsius.

Thiele et al. [71] performed a daytime thermal assessment of concrete composite wall having microencapsulated PCM. To save expenses and carbon emissions, microencapsulated polymer-modified (PCM) concrete was utilized for the building's outside walls. Maximum heat transmission via a composite wall subjected to solar radiation and diurnal sinusoidal outside temperature may be reduced when PCM is microencapsulated in concrete. This research may serve as a starting point for anyone interested in time-of-use power pricing and the possible advantages of PCM composite walls in a range of climates and seasons.

2.4 Different types of PCMs and their performance as building materials

Typically, a PCM should have a melting temperature in the range of 25 to 50 °C for use in buildings in areas with hot weather. For more than 30 years, many researchers across the globe have conducted studies on PCMs in different temperature ranges [35,72,73]. Hence, reports on various forms of PCMs are available in the literature, and many companies offer certain types of PCMs commercially. Organic, inorganic, and eutectics are the main types of PCMs that can be used in building construction. PCMs with an appropriate phase-change temperature for enhancing the energy efficiency of buildings are available [72]. Three temperature ranges are proposed for buildings: (i) 29-60 °C for hot water applications, (ii) 22-28 °C to enhance the comfort of occupants, and (iii) up to 21 °C for refrigeration applications [72]. PCMs with a phase-change temperature in the range of 15 to 32 °C are also available. Some researchers in this field often propose PCMs that operate outside these temperature ranges. Yet, not many studies have been conducted on PCMs that operate in the temperature range of 25-50 °C, the most suitable range for hot weather conditions.

2.4.1 Organic PCMs

Owing to their high latent fusion heat as well as the non-toxic and non-corrosive nature, organic phase change materials are considered as chemically stable materials. Furthermore, these materials do not suffer from effects due to supercooling. Two types of organic PCMs exist: namely, paraffins and non-paraffins. Low-priced commercial waxes of paraffin or $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ have a reasonable thermal storage density of 120 kJ/kg to 210 kJ/kg [73]. The operating temperature range of paraffins is approximately 20 °C to 70 °C [73].

Furthermore, they have a medium melt vapor pressure, are chemically inert, and do not undergo phase separation. However, there are several major drawbacks of organic-based PCMs that must be overcome. Studies conducted using differential scanning calorimetry (DSC), for example, indicate that technological grade paraffin waxes are not suitable for this purpose, as their thermal performance severely degrades when subjected to 100 thermal cycles [73]. A few paraffins have been used as PCMs [34] and they undergo a major volume change during the phase transformation due to their poor thermal conductivity of about 0.2 W/mK [74]. Metallic fillers and matrix structures can help increase the thermal conductivity. Plastic containers and containers with various geometries have been used to overcome the volume change associated with melting and freezing. These issues must be resolved to successfully apply paraffin PCMs in the construction of houses.

As the thermal conductivity of paraffins and fatty acids is low, a graphite matrix and thin encapsulation can be used to increase the heat transfer [75]. Although these substances can take advantage of the latent heat existing in the solid and liquid states, they must be stabilized or encapsulated for them to be used in active or passive construction methods. Stabilization can be achieved by using microencapsulation techniques [76], stabilization of shape [77], making slurries by the suspension of PCMs in a thermal fluid [78], by directly using PCMs in the wall of a building [20], and impregnating PCMs in material of porous nature, such as gypsum [72].

Alcohols, fatty acids, esters, and glycols [73] are among the suitable non-paraffin organics, and all of them have excellent freezing and melting properties. Owing to their low melting point, lack of supercooling during freezing, and high latent fusion heat, palmitoleic acids

or fatty acid, i.e., $\text{CH}_3(\text{CH}_2)_n\text{COOH}$, have gained attention. During step transformation, they often experience a slight change in the volume. However, the cost of these PCMs is high. Despite this, they display an appropriate phase change, are non-toxic, and have a high nucleation rate. Organic phase change materials have the following advantages: (i) can be used at a wide range of temperatures; (ii) freeze with less supercooling and melt congruently; (iii) they are chemically robust, non-toxic, and non-corrosive, (iv) possess self-nucleating properties without segregation; (v) they are consistent with conventional construction materials; (vi) have a high fusion heat; (vii) they are clean and non-reactive; and (viii) they are recyclable [45]. Natural PCMs have the following disadvantages: thermal conductivity is not very high, volumetric latent heat storage is low, and flame resistance is low (depending on containment).

Nonetheless, reports in the open literature indicate that most studies on ss-PCMs have been conducted using a paraffin as the PCM, although paraffins are not the most suitable choice owing to their higher volume change compared to that of PEG during the phase change process. On the other hand, PEG displays a negligible degree of supercooling, has no odor, has a good chemical stability with no phase segregation, is chemically and thermally stable, is erosion-resistant, can be incorporated directly into carrier-supporting matrices, is nontoxic, and its cost is low. Moreover, PEG has a low vapor pressure and the volume change associated with phase transition is smaller when compared to solid-solid and solid-liquid PCMs [79]. Thus, the use of PEG as the PCM together with porous CaCO_3 for the fabrication of shape stabilized composite PCMs is promising.

2.4.2 Inorganic PCMs

Inorganic PCMs are generally metallic and hydrated salts. Metallic PCMs are not suitable due to their high weight and inappropriate temperature range for applications in building construction. Thus, they are not discussed in this paper. On the other hand, hydrated salts, composed of water and inorganic salts, are of a low cost and readily available, making PCMs based on them cost-effective. Hydration and dehydration associated with the phase change transformation of the salts are similar to freezing and melting. The melting process of salt hydrates takes place in two stages: first, the salt becomes less hydrated followed by the complete removal of water from the hydrated salt making the salt anhydrous [80]. Typical inorganic PCMs have a range of beneficial properties, such as non-flammability, low-cost, ready availability, high thermal conductivity, and high fusion power. The advantages of inorganic PCMs are high volumetric latent heat storage power, rapid change in phase, high heat conductivity, and non-flammability [80]. Demerits of inorganic PCMs are their high-volume transition, supercooling, and segregation. Inorganic PCMs have other disadvantages too, such as the tendency to corrode metals, undergoing isolation due to phase change, and supercooling. Hydrated salts are the substances that are used mostly as inorganic PCMs. Owing to their relatively high thermal conductivity of about 0.5 W/mK, high storage density of about 240 kJ/kg, and relatively low cost compared with paraffin waxes, these salts are ideal for storing thermal energy [73]. Hydrated salts are one of the cheapest materials available for thermal energy storage. However, retaining the latent heat of hydrated salts during cycling is difficult and the storage density capacity decreases owing to the irreversibility of the formation of salts with less hydration, as the hydrated salts can concurrently melt. Inorganic PCMs have the capability of exchanging

heat through direct contact and can be superior in terms of the cost when used as thermal storage media of salt/ceramic-based composites.

As solid-solid PCMs possess larger latent heats, they can be used for applications involving heating processes and space heating [81]. Examples of these PCMs are those based on polyethylene glycol, pentaglycine $\text{CH}_3\text{C}(\text{CH}_2\text{OH})_2$, neopentyl glycol $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})_2$, and pentaerythritol $\text{C}(\text{CH}_2\text{OH})_2$. Furthermore, when cross-linking is present, highly crystalline polymers such as high-density polyethylene (HDPE) provides distinct advantages, with the transformation used to generate 98 percent fusion heat while maintaining the original shape. Nevertheless, some of these PCMs are used as storage media, although only a few solid-solid conversions are identified, with the overwhelming majority occurring at higher, unfavorable temperatures, in the range of 300 °C to 6000 °C [73]. Also, the associated volume change is small, and these materials are readily available at a lower cost. However, hydrated salts suitable for commercial use have an unequal melting problem, which is common among hydrated salts. The melting process periodically allows the salt to release water and convert to its anhydrous form or another salt. Also, anhydrous salts with a high density have a tendency to sink to the bottom of the container. When the anhydrous salts deposit at the bottom, reabsorbing water will become difficult as the temperature reaches the freezing point. This process decreases the total amount of salt during phase change, which also decreases the performance of the materials involved in the phase change. Another problem with hydrated salts is supercooling, which occurs in many salt hydrates owing to the weak nucleating properties [79]. When supercooling occurs, the liquid component of the phase change material does not freeze (solidify) until

the temperatures reach values below the freezing point. This is a critical shortcoming because it influences the transition process associated with temperature change.

2.4.3 Eutectic PCMs

The combination of two or more components with the melting point lower than that of either component is a eutectic [4]. Each component can freeze and melt individually, and a mixture of components that acts as a single substance is formed during the crystallization phase. As the components of the eutectic freeze, they produce a near uniform crystal mixture, which melts simultaneously without any distinction of the two components [82]. Eutectics can be formed by both organic and inorganic compounds, resulting in eutectics consisting of organic, inorganic or organic-inorganic mixtures [73]. Fatty acids form the most investigated organic eutectic mixtures. Researchers have studied several organic eutectics, including those composed of lauric acid and stearic acid [83], myristic acid and palmitic acid/stearic acid [84], capric acid and myristic acid [85], capric acid and lauric acid, and various other organic eutectics [86]. The higher potential to achieve more desired properties, such as a large potential for heat conservation per unit volume or a specific melting point, is one of the benefits of eutectic mixtures. While researchers have paid increased attention to this field in the past decade, eutectic phase change materials for use in latent heat storage systems (LHTS) are not as common as phase change materials based on pure compounds. As a result, the study of eutectic characteristics (physical thermos) has remained a field of advanced study until now, as various combinations are yet to be tested and validated. A system composed of a binary eutectic mixture with a freezing point between 16 and 51 °C, a melting point between 18 and 51 °C, and fusion heat between 120

and 160 kJ/kg has been adapted to produce wallboards enhanced with the eutectic PCM [87].

2.5 Methods of Thermal Energy Storage

A system with a large battery supply and a high charging and discharging capacity is highly sought after. Common, geothermal, regional as well as all of the latent and thermochemical storage methods are well-known (Fig. 2.2). The simplest and most sensitive thermal storage (Fig. 2.2 (a)) is a gradient of temperature on a medium that can be used to store or release heat. Water is the most widely used medium for sensible heat storage. Natural stones (marble, clay, clay/polymer stones, and sandstone) are also commonly used. As industrial practices have become more sophisticated, waste natural stones for use in thermo-electro-mechanical end uses, [types of waste materials with different properties] that were previously ignored have become valuable candidates for use in sensitive heat applications. The most important advantage of this form of heat storage is that it costs less, and it does not use toxic or unsafe products.

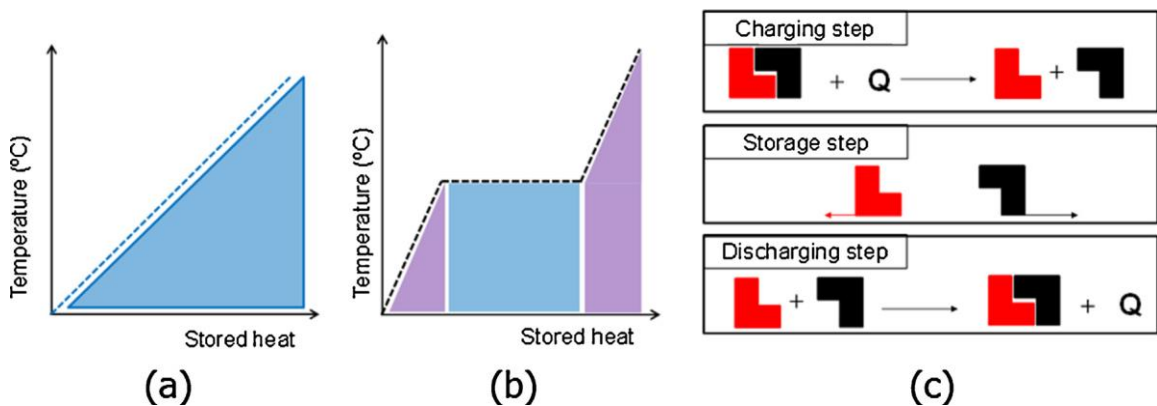


Figure 2.2 Methods of thermal energy storage; (a) sensible heat, (b) latent heat, and (c) thermochemical reaction [88]

Using active or passive technologies in the building sector involves a major disadvantage in terms of the amount of sensible heat storage, which needs more or less energy depending on the demand. In terms of latent heat storage (Fig. 2.2 (b)), the container capacity decreases due to the increase of the storage density. Many studies have been conducted on the use of phase-change products in construction [89]. Grades in PCM are ranked according to the nature of the ingredients (paraffin, fatty acids, salt hydrates etc.). In contrast to ordinary (thermal) materials, which use an endothermic/exothermic method, thermo-chemical materials (TCM) use a reversible endothermic/exothermic reaction (Fig. 2.2 (C)). Heat is added to material A, resulting in the separation of the two components B and C during the charging process. The reaction products can be easily separated and deposited in preparation for discharge. The two are combined and the right amount of energy and pressure is released. Other aspects, including less than adequate performance of essential factors, such as compromising the integrity of the reaction vessel, poor heat transfer, and low mass transfer, must also be factored in. A seasonal storage device is recommended for this kind of process due to the high energy intensity and diminished heat and mass capacity of these types of systems.

2.5.1 Eutectic PCMs

TES as a passive technology is intended to provide thermal comfort with the minimal consumption of electricity [2]. Passive responsive storage is a technique that enables vast quantities of energy to be processed, resulting in thermal efficiency in a structure, due to the use of materials with a high thermal mass in construction. The most widely used components are rammed earth, alveolar bricks, asphalt, or stone [90]. Thick solar walls, also known as Trombe walls (TW), which employ sensible storage, are used to save

electricity in homes [90,91]. Solar water walls are built in the same manner as traditional walls, but the bulk of the material is composed of water tanks that serve as the wall. The body of knowledge on PCM-based passive thermal energy storage has witnessed an enormous increase. PCMs may be incorporated into construction materials in a variety of forms [89], including direct integration, immersion, encapsulation, microencapsulation, and form stabilization. The possibility of leakage from indirect convergence and immersion must also be assessed. A new layer is created as the PCM is encapsulated or incorporated into a new shape-stabilized substrate as part of the wall building method. Wallboards have long been regarded as one of the most successful methods of incorporating PCMs into the walls of a structure. Lee et al. [92] recently emphasized the importance of experimental validation of TW over a long period of time. To cut this time in half, the authors of this paper have introduced a modern testing principle that allows real-time testing of different types of wall structures (Fig. 2.3).

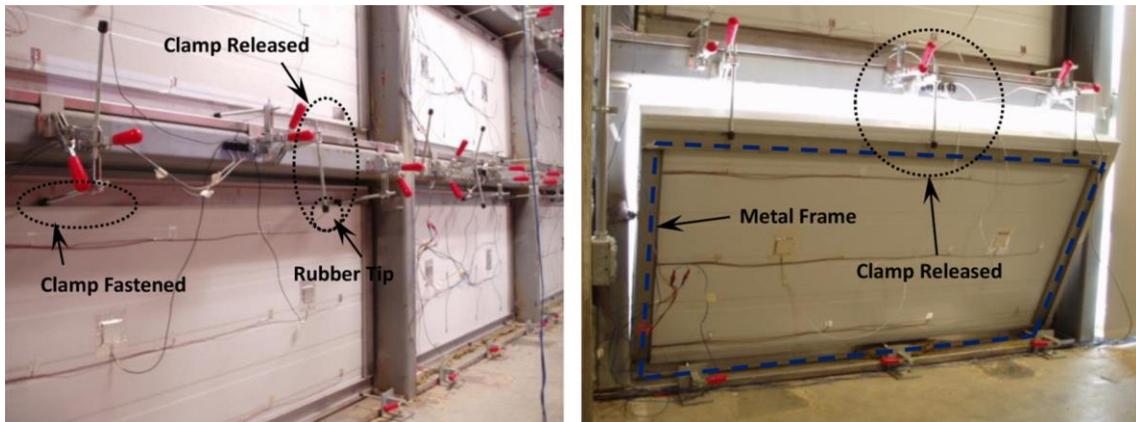


Figure 2.3 PCM containing wallboards [92]

2.5.2 Active Technologies

The use of TES is an attractive and adaptable solution to overcome challenges encountered in a variety of advances or new building applications, such as the incorporation of renewable sources of energy into HVAC in terms of heating and/or cooling spaces, improving the productivity of existing plants, or implementing peak load change strategies [93]. TES may be installed at the top, base, and doors, outside solar facades, hanging ceilings, ventilation system, photovoltaic systems, and water tanks as shown in Fig. 2.4.

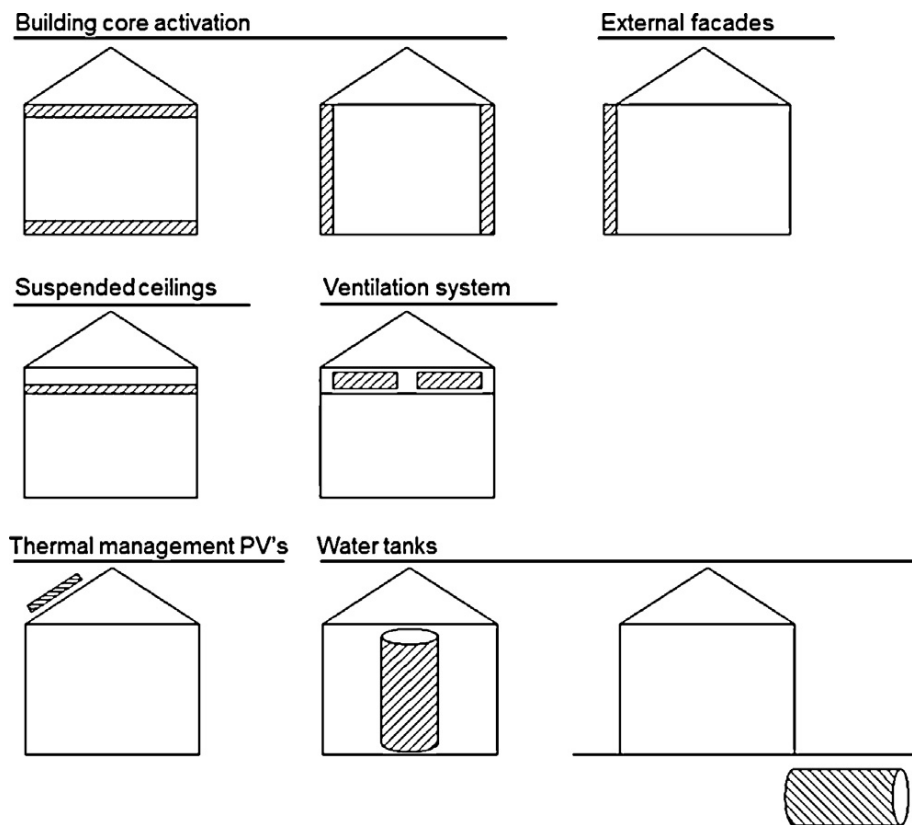


Figure 2.4 Integration of TES into buildings [88].

One of the most important advantages of using TES in active building systems is the ability to cool space without spending for energy by charging the storage system at low nighttime outdoor temperatures and cooling during daytime using the storage system charged at night

[94]. Due to its high energy density and the short distance between the cold source and the application area, PCMs are favored as the medium of storage (for ensuring comfort of occupants). The most challenging drawback of this technology is that the operation of the PCM is totally dependent on atmospheric conditions or may not be practical in the summer months, when temperatures do not reach the required range. These challenges can be overcome by using effective control methods and increasing the thermal conductivity of the PCM. A range of facilities, including thermally activated buildings (TABS) [95], suspended ceilings [96] (Fig. 2.5), exterior facades [97] and ventilating systems [98] (Fig. 2.6), has been used with TES for cooling free of charge.

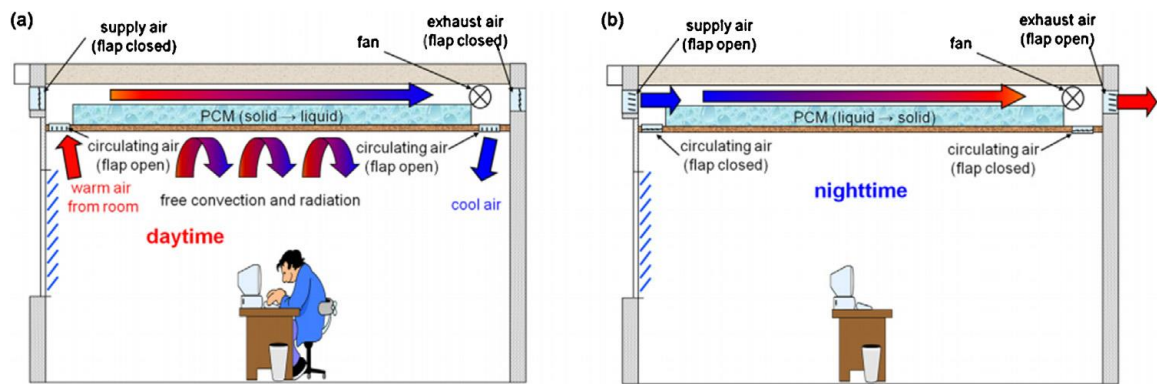


Figure 2.5 Ventilated cooling ceiling employing a PCM [96].

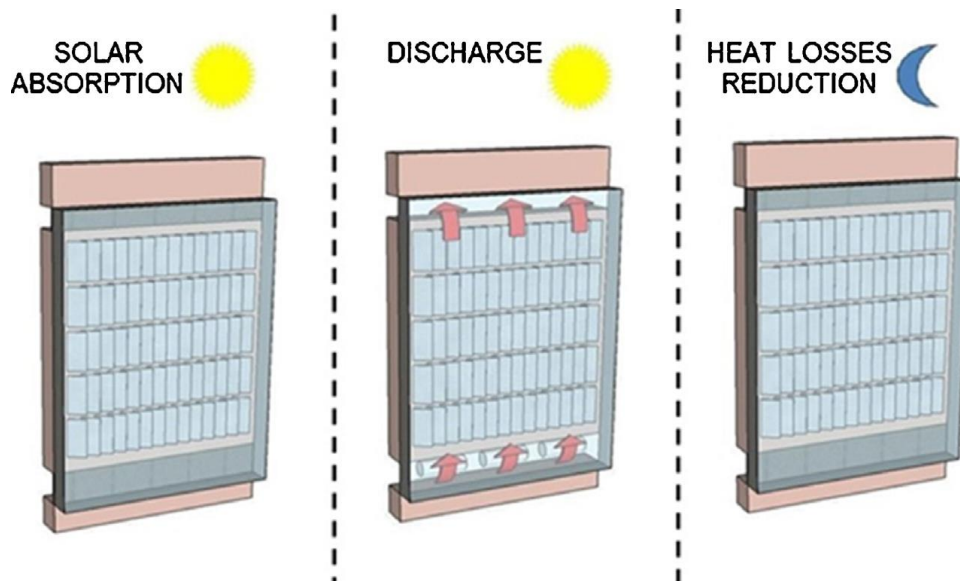


Figure 2.6 Ventilated facade employing a PCM [98].

Water tanks are the most common type of solar thermal storage devices. Their use in building construction has recently been questioned owing to the enormous volume they occupy. Typically, this technology is implemented using on-site tanks elsewhere meeting the storage requirements of the living quarters. For seasonal thermal energy recovery, underground storage can be used [88]. Solar thermal energy collection is now achieved using solar collectors incorporated in construction walls [99] and in ventilated facades [98]. The use of active TES systems in the construction industry is not restricted to renewable resources. They can also be used to enhance the reliability and performance of mature technologies. For example, the use of TES heat pumps is recognized as a technology that is promising to translate electric loads from peak-to-peak cycles and thus function as an effective method of managing the demand [100]. The benefits of this technique rely on low power tariffs for thermal tools to decrease energy costs. The integration of these devices into buildings has been investigated for both space heating and refrigeration. In addition to shifting loads, TES technologies have also been used in the unblocking of exhaust systems

and heat recovery applications with substantial energy savings [101]. Integrating any TES technology with active architecture of buildings requires the use of intelligent control strategies, which can enhance the reliability of these costly systems and make them more attractive for architects and engineers. Attractiveness can be further increased by decreasing costs, increasing device compressibility, increasing the storage capability of materials and systems, increasing the thermal conductivity of materials and developing new materials, particularly those liquids that can work both as a storage fluid and heat transfer fluid.

2.6 Applications of PCMs in buildings

A building is a complex entity, which is subjected to internal and external energy fluxes. The internal energy fluxes are due to internal loads and the ingress of solar radiative flux, while the external energy fluxes are determined by local weather conditions. Heat transfer due to convective, conductive, shortwave radiative, and longwave radiative processes are the known heat transfer processes within a room of a building [102]. Any energy-efficient building ensures the thermal comfort of its occupants with a minimum energy requirement through the deployment of an energy-efficient envelope. Thermal energy storage in the envelope can be considered the key factor in achieving energy efficiency in the building. Temperature inside a building as well as other air conditioning applications can be controlled with the aid of PCMs that will lead to substantial economic and environmental benefits [103]. This process prevents air temperature extrema and decreases the fluctuations in the indoor temperature by storing the energy in the building envelope. The storage capacity depends on the mass, mass-specific heat capacity and the technological solutions, and the composition of the wall envelope, e.g., a concrete wall with external

insulation has a better capacity compared to the same wall with internal insulation [102]. Also, a lightweight building has a lower thermal storage capacity owing to the materials used in construction. In such cases, construction materials containing PCMs are used to enhance the overall storage capacity. The materials containing PCMs absorb heat when the temperature increases by changing the phase of PCMs from solid to liquid, and when the temperature decreases, they release energy by changing their phase from liquid to solid, thus controlling the building air temperature. In general, a high-efficiency building should overcome a couple of limitations, including energy losses through thermal insulation, overheating, and the glazing of windows. The following subsections reviewed related works on the different ways of PCM application for maintaining comfort in buildings.

2.6.1 Effect of PCM on Building Walls

Incorporating a PCM backed with extended graphite nano-sheets to enhance thermal conductivity for improving thermal efficiency and distribution of energy (Fig. 2.7) [104] is a novel approach used for PCM-wallboards. The same outcome has been achieved by using an aluminum honey-comb in a micro-encapsulated PCM wall-board (Fig. 2.8) [105]. Similarly, a PCM may be saturated or assorted with concretes [106] or mortar [106,107]. One of the aims of this approach is to maintain the mechanical properties of concretes, while increasing their specific heat capacity.

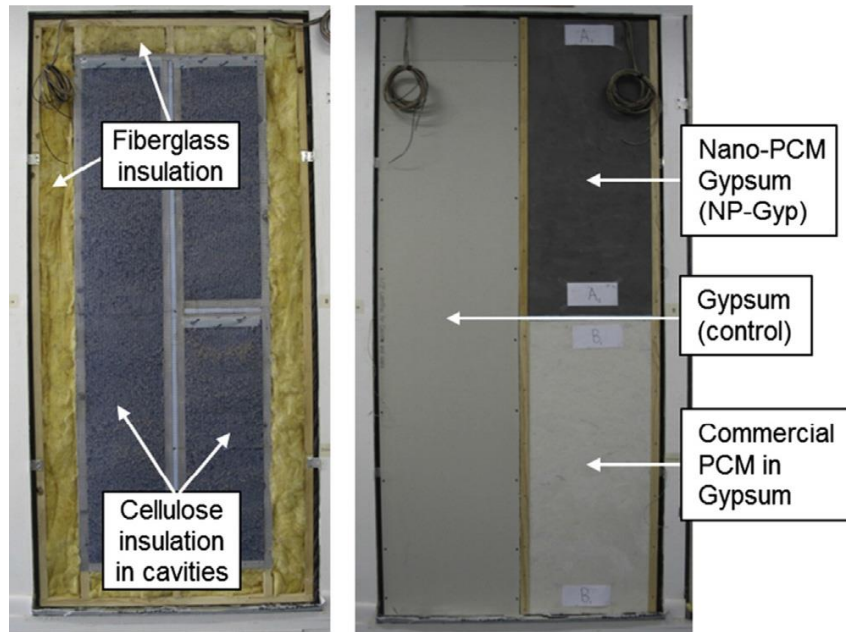


Figure 2.7 Test wall with PCM-enhanced wallboards [104].

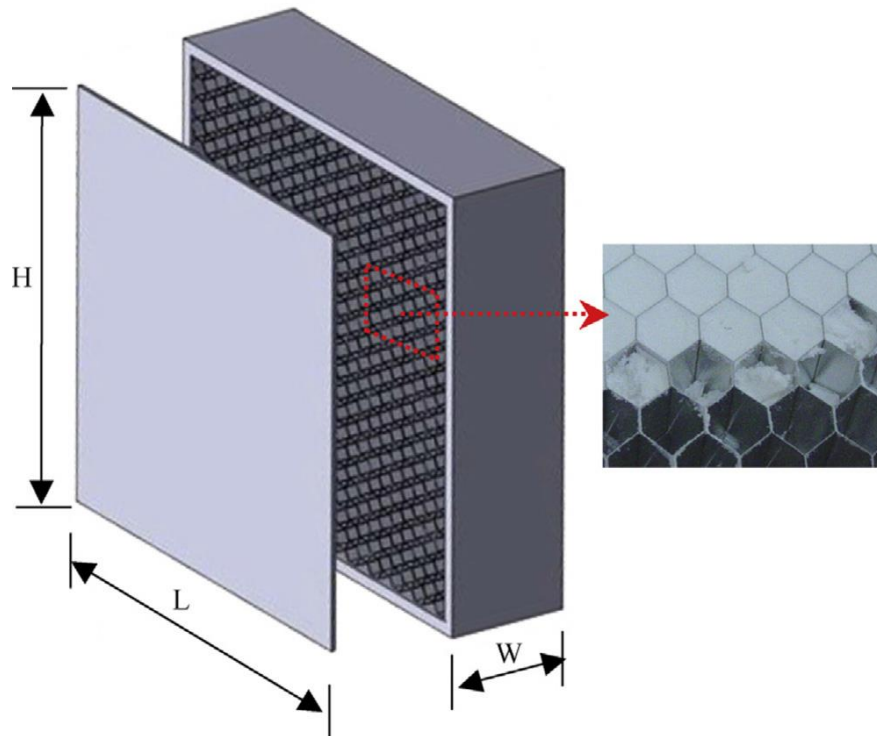


Figure 2.8 Microencapsulated PCM honeycomb wallboard [105].

Another advantage of incorporating a PCM in concrete is that it decreases its density, which has a major impact on the weight of a building structure. Combining a PCM with insulation

materials is another way of incorporating it into concrete walls. According to Yang et al. [108], combined benefits of the storage capabilities of a PCM and the insulation performance of polyurethane foams have a high potential to enhance the energy efficiency of buildings. However, further research is required to enhance this composite.

So far, studies have primarily focused on the synthesis techniques and TES capabilities of PCMs. However, some key parameters, specifically heat transfer resistance, which is the most important property of thermally insulating material, have not received much attention. As a PCM is encapsulated in building components, the location of the PCM inside a building is more important than microencapsulation aspects for optimal system output in larger enclosures. Various positioning points of a PCM within a typical lightweight construction framework [109] are depicted in Fig. 2.9. A PCM can also be incorporated into masonry walls via clay bricks (Figures 2.10 and 2.11) [51].

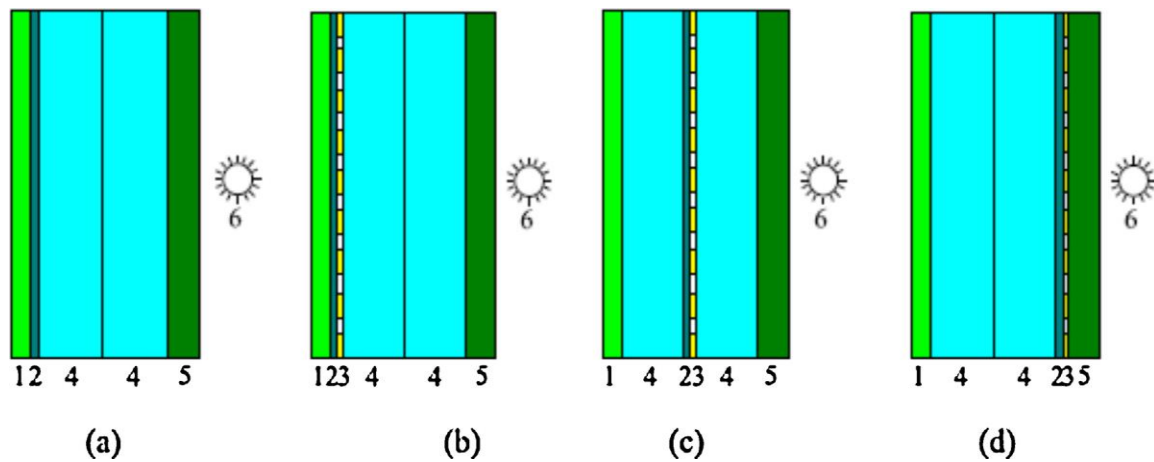


Figure 2.9 Wall with a PCM positioned at different points: (a) control wall; (b) PCM positioned next to the internal face of a gypsum wallboard; (c) PCM positioned between two insulation layers; and (d) PCM positioned next to the internal face of an oriented strand board [109].



Figure 2.10 Clay bricks containing PCM macro-capsules [51].

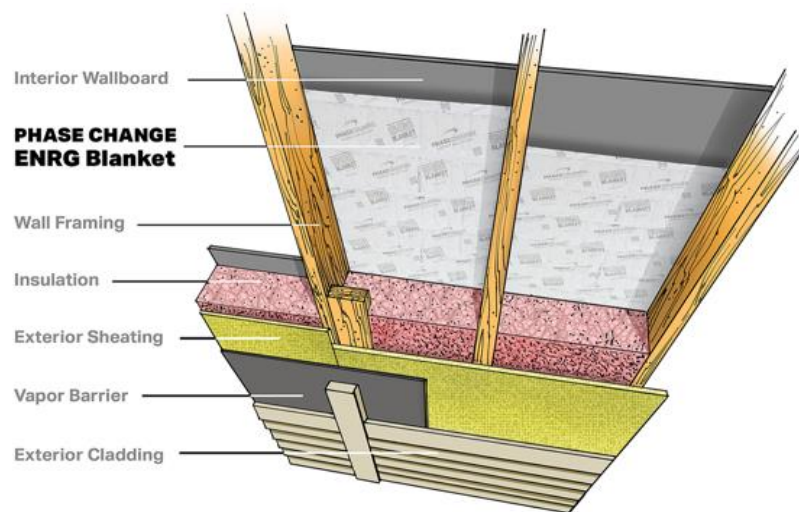


Figure 2.11 A PCM ENRG blanket [110].

One of the simplest ways of incorporating a PCM is to directly impregnate the PCM into concrete, gypsum or other porous materials to create a phase-change material integrated in a building wall (PCMIBW). Different types of enclosures can be used for the integration of phase change materials in building walls. Ahmad et al. have described the use of PVC panels filled with a PCM [111,112]. Carbonari et al. [113] used sandwiched panels that has rigid plastic enclosures that are filled with phase change materials Konuklu and Paksoy [114] evaluated aluminum foil to incorporate phase change materials in a multi-layer panel. Medina et al. [37], Voelker et al. [115], Zhang et al. [116] and Gucer and Faunce [117] have described the filling of tubes with phase-change materials and integrating them in walls. Pasupathy et al. [118] have described the use of a steel container filled with phase-change materials for incorporation in a roof slab.

Average outdoor temperature (T_o) and indoor temperature (T_i) of a building in Al-Khobar in the Eastern province of Saudi Arabia are around 45 °C and 24 °C, respectively [103]. A 20-mm bricks and 2-mm insulation of polyurethane were used to construct the wall of the building in question, and the other properties of the BioPCM used are provided in Table 2.1 [103]. Cooling load of the building was calculated assuming the use of both regular construction materials and construction materials containing a PCM. The load is lowered by 20% for the latter compared to the former (16 tons to 13 tons) [103].

Table 2.1 Properties of BioPCM [103].

Description	BioPCM	GR27	Water
Melting point (°C)	29.0	28.0	0.0
Boiling point (°C)	418.0	-	100.0
Density (kgm ⁻³)	860.0	710.0	1000.0
Thermal conductivity (Wm ⁻¹ °C ⁻¹)	0.20	0.15	0.60
Viscosity @ 30 °C (CP)	7.0	-	0.798
Specific heat (kJkg ⁻¹ °C ⁻¹)	1.97	1.125	4.179
Latent heat (kJkg ⁻¹)	219.0	72.0	334.0

2.6.2 Effect of incorporating PCMs on the roof

Al-Sallal [119] demonstrated, using case studies involving simulations, that the law of diminishing returns is applicable when improving the conservation level of residential buildings. They explored the effect of different climates on selecting the type of insulation and its thickness. The authors demonstrated the importance of using the life-cycle cost model when deciding to add more insulation levels and when to stop. They estimated the annual cooling and heating requirements of a 108 m² house using the RENCON program. Regarding fiberglass, researchers found that R10 provides the most cost-effective thermal resistance in the two areas, while R5 was the most cost-

effective polystyrene. They also found that investing money to enhance the insulation levels of a house in a room with a cold climate provides more profitable returns than improving the insulation levels of a home in a hot environment. Alawadhi and Alqallaf [120] presented thermal analyses for a 3-D model of a roof of a building with cone frustum holes filled with a PCM. The objective was to reduce the heat transfer from outside to the inner space by allowing the PCM to absorb and melt, preventing heat from getting into the internal space. This system is meant to reduce the cooling loads in hot months from May to September. The overall average decrease in heat flux is obtained by subtracting the heat flux of a roof with a PCM from the heat flux of a roof without a PCM, and the results are shown in Fig. 2.12. When the geometry of the PCM changes from that of a cylinder to a cone, the overall decrease in the heat flux considerably increases. According to the bar graph, a PCM holder with a conical shape will reduce the total heat flux in indoor space by 39 percent. Thus, the integration of a PCM with a roof in this manner will decrease the energy required for cooling by this percentage during normal working hours [120]. However, the PCM remains solid during the cooler weather, from November to March.

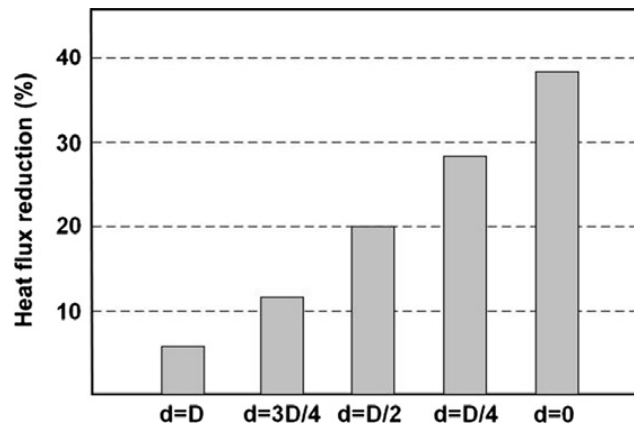


Figure 2.12 Total heat flux reduction during working hours at the interior surface of a roof with PCM holders of different geometries containing n-eicosane [120].

The energy used for cooling of a building is highly dependent on the physical features of the material used in the construction of the roof and walls. Low thermal conductivity of the roof and walls limits the ingress of heat at a steady state level. Among the building materials mostly used as thermal insulation materials are cotton, foams, and fiberglass. Transfer of heat to and from a building can be significant during the day in the summer months, during which the temperature can be as low as 30 °C and as high as 50 °C [121]. In addition to the thermal conductivity, the heat capacity and density of building materials, in particular, often influence the heat gain at these high temperature variations through the absorption and storage of the heat gained in the form of sensible heat. Hence, materials with a high thermal mass are ideal for the construction of roofs and walls. Integration of PCMs into roofs and walls can also be used to increase the thermal mass of the walls and buildings.

2.6.3 Effect of incorporation of PCMs in bricks

Among the various forms of PCMs documented in the literature, the majority of the PCMs investigated are hydrated salts and organic paraffin-containing compounds. The hydrated salts, on the other hand, degrade quickly at high temperatures because of water content loss during heating and cooling cycles. Organic PCM's including paraffin and non-paraffin have attracted the interest of researchers in recent decades due to the capability of these materials to circumvent the intrinsic weaknesses of inorganic PCMs. The organic PCM's are compatible with a variety of building materials, chemically stable without toxicity and recyclable. Most of the published literatures reported the paraffin based PCM for building application. The major problem for the paraffin PCM is their thermal expansion. Among the organic PCMs, Polyethylene glycol (PEG) is an attractive candidate to be used as TES

material in building applications. It is a solid-liquid organic PCM having a wide range of melting temperature (from 3 to 69 °C) corresponding to different molecular weight. Moreover, it has a small volume change in compare with paraffin, low supercooling, chemically and physically stable without gas generation and cost effective.

Alawadhi et al. [48] have investigated the effectiveness of a PCM-brick structure by comparing the heat flux at the interior surface of the structure to one made using bricks without a PCM, with the aim of optimizing the quantity of the PCM in the bricks. The melting temperature of the three PCMs, n-octadecane, P116, and n-eicosane paraffins, lies within the operating temperature of the structure. According to the results, the temperature of the bricks without a PCM ranges between 25.7 °C and 55.6 °C. The melting temperature of n-octadecane is closer to the minimum operating temperature limit, while that of P116 wax is closer to the upper limit. Melting temperature of n-eicosane is midway between the upper and lower temperature limits. The heat flux at the interior surface of a structure made with bricks containing the three PCMs and bricks without a PCM between 7 am and 5 pm is shown in Fig. 2.13. The researchers placed the PCMs in three cylindrical holders located at the center of each brick, with the height of each cylinder, H_c , equal to half the height of each cylinder ($H/2$). The heat flux for bricks without a PCM was initially 26 W/m² at 7 am, which increased to reach its maximum value at 3 pm. According to results in Fig. 2.13, n-octadecane and P116 are not very effective in mitigating the heat flow to the interior space. The heat flux when these PCMs are used is close to the heat flux in the absence of a PCM. The low melting point of n-octadecane kept it in the liquid phase during the experiment time, while the high melting temperature of P116 kept it in the solid phase. Thus, the operating temperature range does not allow their high latent heat of fusion to be used to

minimize the transfer of heat to the interior space. However, the researchers achieved a maximum reduction in the heat flux of 24.2% from 10 am to 5 pm when n-eicosane was used as the PCM. The results also indicate that the differences in the heat flux from 7 am to 10 am is negligible owing to the temperature of the bricks remaining below the melting temperature of the three PCMs.

In order to maintain the strength of the bricks, the quantity of PCM incorporated in them should be kept to a minimum. The researchers used bricks with three, two, and one cylindrical PCM holders, along with bricks without a PCM to study the effect of the quantity of a PCM incorporated in the bricks. The cylinders were located at the center of the bricks, $H_c = H/2$. The heat flux at the interior surface of a structure made with the three types of bricks containing n-eicosane and bricks without a PCM is shown in Fig. 2.14. The reduction in the maximum heat flux is 11.5%, 17.9%, and 24.2% for the bricks with one, two, and three cylindrical PCM holders, respectively. The heat transfer through the interior surface must be counter-balanced by the HVAC system. The total heat flux is obtained by integrating the heat flux values plotted in Fig. 2.14 throughout the working hours.

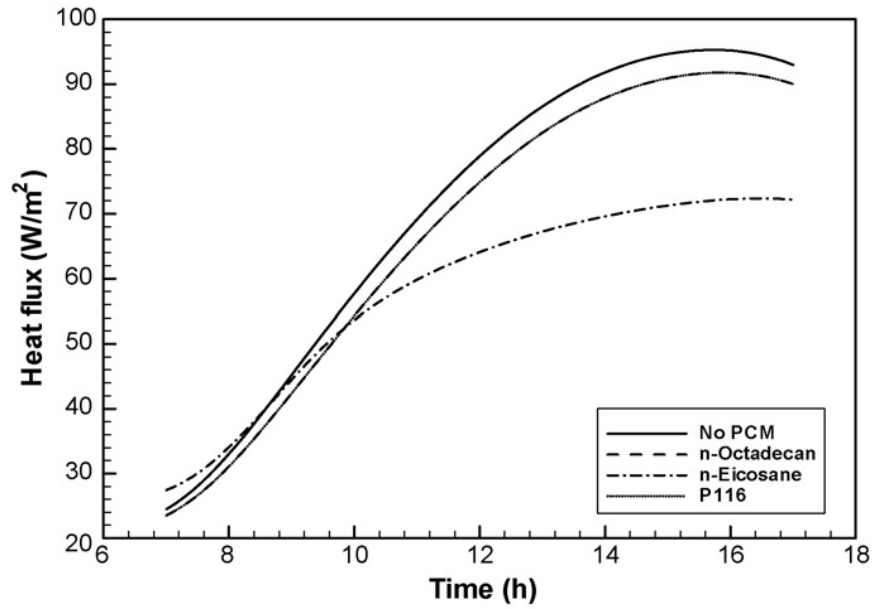


Figure 2.13 Heat flux at the interior surface of bricks containing three different PCMs in comparison with bricks without a PCM [48].

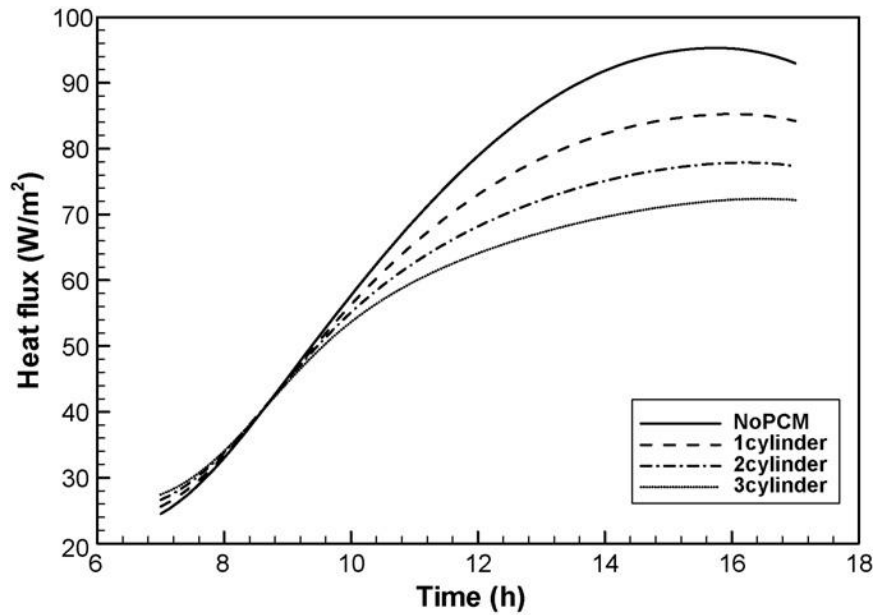


Figure 2.14 Heat flux at the interior surface of bricks with a different number of cylindrical PCM holders in comparison with bricks without a PCM [48].

2.6.4 Effect of incorporation of PCMs in concrete blocks

Hasan et al. [122] studied two concrete blocks containing a PCM (Block B and Block C) and the cooling produced by them was compared with a concrete block without a PCM (Block A). They used two different configurations for Block B and Block C, which were fabricated with the PCM and insulation layers placed at different locations (Fig. 15). The addition of the PCM decreased indoor heat flow by 44% (Block B) and 10.5% (Block C) at an energy balance of 24 h and delayed the occurrence of the maximum indoor temperature by 2.6 h. Block B remained cooler throughout the daytime and most of the night compared to the reference Block A. Block C was cooler throughout daytime compared to the reference Block A, and warmer at night. However, inclusion of a PCM in the concrete blocks prevented 137 Wh/m² and 32 Wh/m² of heat flow when Block B and Block C are used, respectively, on a 24 h basis [122]. Alawadhi et al. [48] also studied the thermal behavior of a brick containing a PCM for use in building construction under hot weather conditions. They conducted a parametric study to evaluate the effect of changes in design parameters, such as location of the PCM in the brick and type and quantity of the PCM. The study showed that the heat gain remarkably decreases when the phase change material is incorporated into the bricks, and increasing the amount of the phase change material has a positive effect. The best performance is achieved when cylindrical holders containing the phase change material are at the centerline of the bricks.

A. Compare thermal performance with and without PCM on concrete blocks

Hasan et al. [122] evaluated insulated concrete blocks containing a PCM at a location with very hot weather conditions in the UAE to assess their performance in cooling interior

space. They placed a protected chamber enclosed with a non-conducting material behind the blocks containing the PCM to mimic a scaled-down indoor space. The authors studied the impact of the presence of the PCM layer on interior heat gain by placing the PCM at two locations: closer to the external surface and closer to the internal surface of the concrete blocks. The incorporation of the PCM decreases the heat transmitted via the concrete blocks, with the placement of the PCM and insulation layers adjacent to the interior surface displaying better cooling compared to placing them adjacent to the exterior surface. The thickness of concrete, PCM, and insulation sheet layers is 2.5 cm, 5 cm, and 1 cm, respectively, as shown in Fig. 2.15. Behind the bricks, a scaled-down test chamber with dimensions of 40 x 40 x 40 cm³ was placed to simulate an indoor environment. The test chambers were made using 20 cm thick polystyrene sheets, glued together with epoxy resin, to make the chambers impermeable and ensure the applicability of adiabatic boundary conditions. As the total mass of polystyrene and epoxy is very small in comparison to the mass of the concrete blocks and PCM, their thermal energy storage potential is neglected. The authors conducted the study outdoors in Al Ain, United Arab Emirates (latitude: 24.21N, longitude: 55.74E) facing the south using the setup with and without a PCM. They calculated the thickness of the PCM layer using solar heat gain on a typical summer day and found that a 5 cm thick paraffin-based PCM layer was adequate to absorb all solar thermal energy entering the concrete blocks [122].

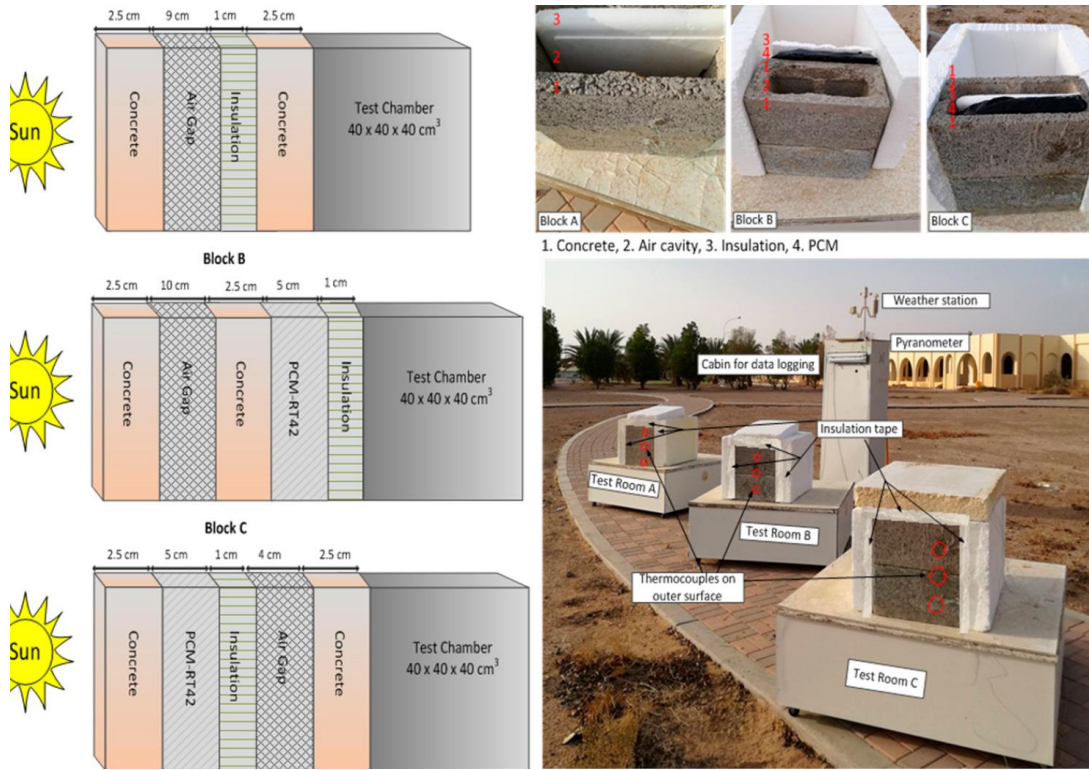


Figure 2.15 Schematic diagram and the experimental set-up of the concrete blocks, with the construction layers and the attached test chamber [122].

B. Selection of the Time

Fig. 2.16 shows daytime and nighttime average ambient temperature for a typical day of each month at the site of the experiment, indicating the peak summer season from May to August, with comparable average temperatures (42 °C during the day and 35 °C at night) over the four months. The temperature at night in August, however, is marginally higher than that of the other months of the summer. Hence, experiment was performed in August to investigate the conversion of the PCM to its solid state during the night, with August considered the worst-case scenario. Hot weather continues throughout the year, with average daytime temperatures above 27 °C, which is the upper limit for thermal comfort. As a result, it was concluded that the results from the intense hot season can be applied to the rest of the year.

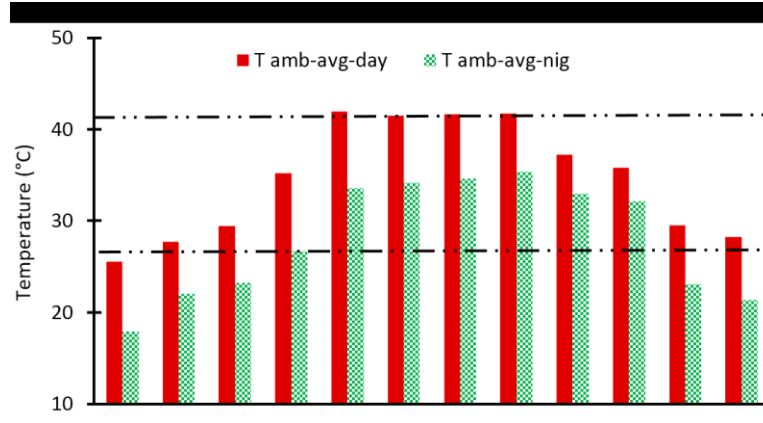


Figure 2.16 Typical ambient temperature of each month by average daytime ($T_{amb-avg-day}$) and average nighttime ($T_{amb-avg-nig}$) temperature at the site of the experiment [122].

Commercially available PCM RT42, which is based on a paraffin, was melted and poured into polymer holders with an air cavity between two concrete layers. Free space is available in the holders to accommodate volume changes during melting and solidification of the PCM as well as the ability to release trapped air during the process. The materials used for the fabrication of the PCM holders and their thermo-physical properties are given in Table 2.2 [122].

Table 2.2 PCM thermal properties [122].

Properties	Melting Point (°C)	Congeeing Point (°C)	Latent Heat (KJ/kg)	Specific Heat Capacity (KJ/kg.K)	Heat Conductivity (W/m.K)	Density (kg/m ³)	Volume Expansion	Flash Point (°C)
PCM-RT42 [35]	38–42	42–37	145% ± 7.5%	2	0.2	880 * 760 ¹	12.5%	186
Polystyrene	240	NA	NA	1.3–1.5	0.032	NA	NA	350
Epoxy Resin	130	NA	NA	1	1.26	2.09	34 × 10 ^{−6} /K	350

Note: * solid; ¹ liquid.

Temperature was measured using several t-type copper-constantan thermocouples calibrated in an ice bath with a measurement error of 0.30 °C. As shown in Fig. 2.17, the thermocouples were connected to the outer and inner surfaces of the blocks (A, B, and C) as well as within the test chamber. The schematic representation in Fig. 2.17 depicts the configuration for Block C, which is the same as the rest of the bricks. The thermocouples

were glued with epoxy glue, shielded from direct irradiation, and checked for proper attachment on a regular basis. A self-powered Apogee pyranometer (model # SP-110 with 0.2 mV per Wm^2 sensitivity and $\pm 5\%$ calibration uncertainty) was used to test global solar radiation intensities. At room temperature, all sensors were attached to an NI compact Rio (NI cRIO-9073) data acquisition device with an error of 0.03 percent [66]. A weather station (Starmeter-WS1041) with a temperature resolution of 0.1 °C, a wind speed measurement range of 0–50 m/s, and a wind speed resolution of 0.1 m/s was installed to determine the ambient temperature (T_{amb}) and wind speed (v_w). Temperatures were determined at the outer surfaces of blocks A (T_{af}), B (T_{bf}), and C (T_{gf}), as well as on the inner surfaces of blocks A (T_{ab}), B (T_{bb}), and C (T_{gb}) and inside the test chamber for blocks A (T_{ai}), B (T_{bi}), and C (T_{gi}) (T_{gi}). Values of both temperatures were measured at three different locations and combined.

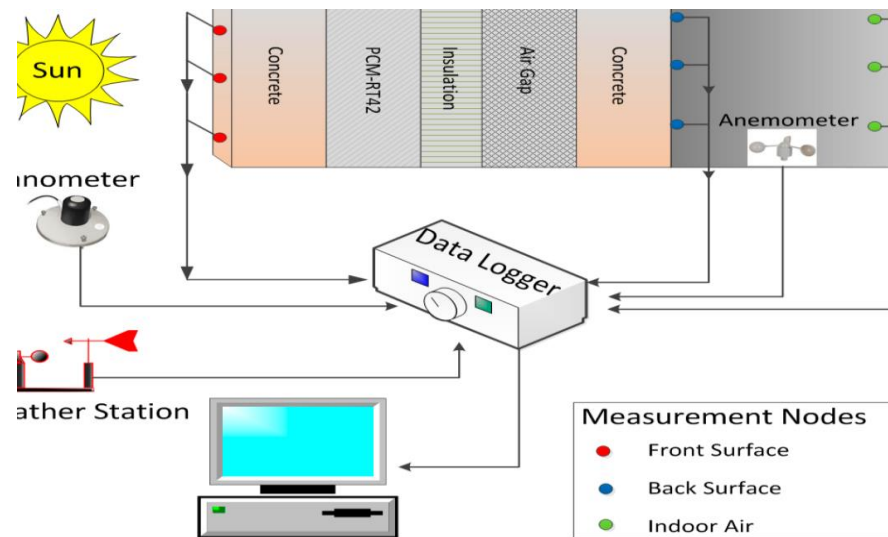


Figure 2.17 Experimental setup with Block C configuration (the same set-up is used for Block A and Block B) [122].

The results of the study reveal that passive heat removal by a PCM through natural ventilation alone is insufficient under hot weather conditions, even when a PCM with a

higher solidification temperature (37 °C) is used, which somewhat limits the efficiency of a PCM. Future research should look into active methods for extracting the heat that has been trapped in PCMs. The air stream must be linked to the air circuitry in the air conditioning system via a cavity wall containing the PCM [122].

Fig. 2.18 depicts how a PCM is used in buildings for heating and cooling. The PCM is used in conjunction with porous materials, such as plasterboard to maximize heat transfer. A PCM releases heat to ambient air during the night in cold conditions. Moreover, PCMs are used in thermoelectric refrigeration to improve the efficiency of a heat sink, such as when a window device is used with a PCM curtain. A PCM curtain may be mounted between the window and the double sheeted opening of the air vent, and when they freeze PCMs prevent the air temperature from dropping, reducing overheating around the window. By changing the state of PCMs (i.e., solid or liquid) in a specified temperature range, PCMs can be used in fabrics, blankets, surgical instruments, antibacterial and hygiene applications, insulation, clothing, and many other applications.

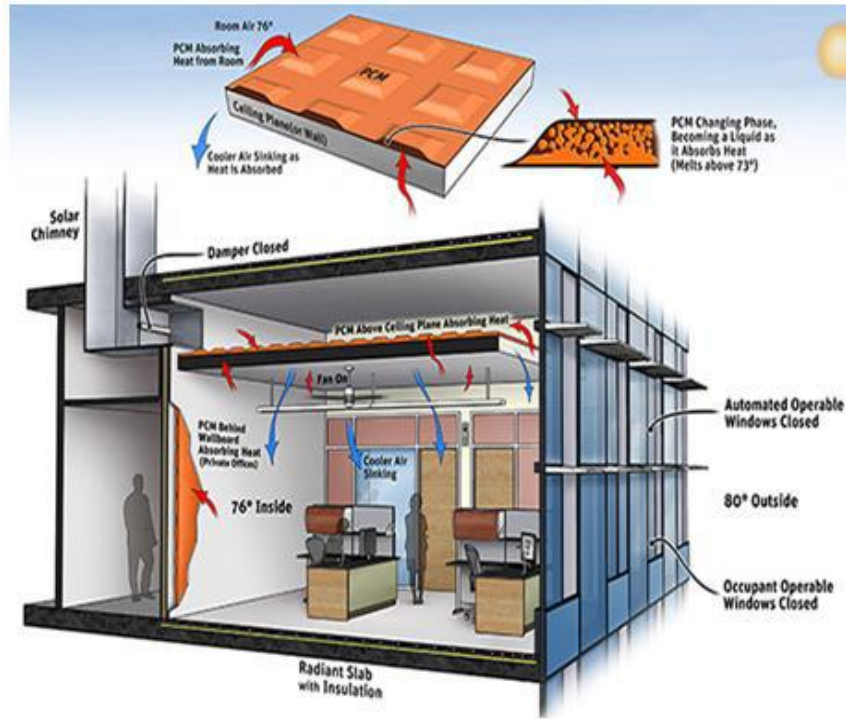


Figure 2.18 Application of a PCM in a building [123].

2.6.5 PCMs in wallboards

Kuznik et al. [103] have studied the heating and cooling performance of a building incorporated with a microencapsulated PCM. The PCM was placed within porous material such as plasterboard (wallboard) and a double-sheeted gap in the window for better thermal management. Wallboards enhanced with PCMs can provide thermal storage and they can be used for the construction of a room or even the entire building. Such wallboards enable a passive solar heating/cooling design and off-peak cooling in traditional frame constructions with a typical low thermal mass. Selection of these wallboards will depend on a variety of factors, including the climatic conditions of the area, building design, and the PCM used, most importantly, its melting temperature and latent heat storage capacity per unit area [73].

Mazzeo et al. [124] have performed an effective energetic study of PCM layers in a steady periodic regime, with boundary conditions typical for the exterior walls of an air-conditioned building. The analysis allowed the evaluation of the effects of phase change on energy transfer and thermal storage within the layers. They determined both the energy leaving the indoor environment, which represents a loss in the winter and a heat gain in the summer, and the energy entering the indoor environment, which represents a heat gain in the winter and a load in the summer, to determine the energy transmitted through the layer. The developed technique allows the selection of the most appropriate PCM for summer air conditioning, winter air conditioning, or even year-round air conditioning [124].

Owing to high air temperatures and intense solar radiation, majority of the energy is absorbed by buildings during the day in regions with hot weather, resulting in different pricing systems for on-peak and off-peak energy usage. Incorporating PCMs in the envelope of residential and commercial buildings will result in potential cost savings by reducing the energy usage and shifting peak load during the day. In the field of applications of PCMs in heating and cooling of buildings, many technologies are currently available. Kuznik et al. [103] has examined the use of a PCM in the walls and ducts of the cooling units of a building to decrease the energy consumption in both heating and cooling. Pasupathy et al. [72] have investigated the use of a PCM in roofs of buildings using both experimental and simulation methods. Chen et al. [125] tested a new form of a PCM and discovered that its heat storing/releasing capacity is significantly higher than that of other PCMs. The author performed simulation and experimental measurements using the efficient heat capacity process to confirm the results. Huang et al. [126] used a validated model to determine the ability of PCMs to save energy by incorporating them into the walls

of buildings. Nagano et al. [127] have conducted an experimental study to investigate the use of a PCM in floor-supply air conditioning systems to increase the thermal mass of the building.

A PCM wall can capture a significant portion of the solar radiation that falls on walls or roof of a building [73]. Owing to their high thermal mass, PCM walls can decrease the impact of significant variations in the ambient temperature in the interior of a building. They can be extremely useful in moving cooling loads to off-peak periods. Arkar and Medved [128] developed and tested a building ventilation system, which they identified as a latent heat storage system (LHTS). They mounted the porous absorbing and storing media encapsulated in spherical polyethylene spheres in a duct of a building ventilation system. The heat produced by the PCM was used to preheat ambient air flowing into the living room of a building. Another use of PCMs for thermal storage is their use in a ‘solar wall’. Solar radiation that enters the wall is absorbed by the PCM that is incorporated in the wall. Stritih and Novak [129] developed an ‘experimental wall’ that uses black paraffin wax as the PCM heat storage agent, which collects the heat and uses it to heat and ventilate a home. According to the authors, the findings of this study are very positive, and as shown in Fig. 2.19, the wall is made of six key components. Transparent insulation material (TIM) (1, 2) allows short-wave solar radiation to pass through glass, preventing heat transfer due to convective action and thermal radiation. PCM (3) placed in a clear plastic casing made of polycarbonate absorbs and retains energy primarily as latent heat. The air required for the ventilation of the house is heated and fed into the room via the air channel. Other standard elements include insulation and plaster.

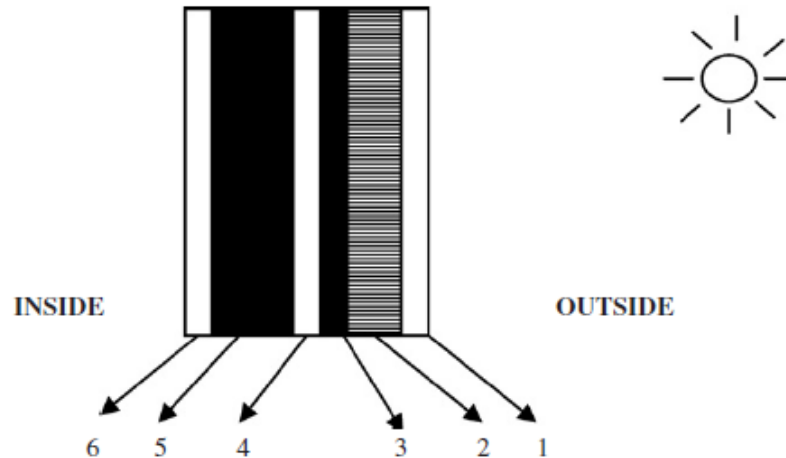


Figure 2.19 Elements of a PCM solar wall [129].

Solar walls have been shown to outperform other structures in a number of ways [72]:

- Absorption of solar radiation directly into paraffin through transparent plastic glass, which is also an insulation medium that avoids convective and radiation losses into the surrounding, is a highly efficient method of conversion of solar energy into latent heat.
- This design also decreases the conductive heat losses from the room through the wall [72].

2.6.6 Incorporation of PCMs in window shutters to reduce solar heat gain

Exterior to interior heat flow in buildings in GCC and other countries with a similar climatic conditions is decreased using thermal insulation materials in the structure of buildings [130]. Exterior to interior heat flow is affected by the thermal conductivity and specific heat of the insulation, especially with fluctuating solar intensity and outdoor weather conditions. Hence, insulating materials with a higher thermal capacity and a lower conductivity are preferred in the construction of buildings. However, windows of buildings

in these countries are the weak link, in terms of heat ingress, that often account for a large proportion of the increase in the interior temperature of buildings due to solar heat during the summer season [72]. Thus, the decrease of solar heat ingress through the windows plays a critical role in making a building energy-efficient by reducing energy usage [73]. One effective method is blocking the heat flow through the windows into buildings using exterior shutters. Figure 2.20 shows a widely adopted window shutter system in residential buildings that are typically made of foam-filled slats [130].



Figure 2.20 A widely used window shutter to block the heat flow into residential buildings [130].

Alawadhi et al. [130] used a technique based on finite element analysis to evaluate window shutters containing a PCM instead of foam to reduce solar heat gain through windows of buildings. During the daytime, the PCM absorbs heat entering a building through the melting process and releases the stored heat at night through the solidification process. The authors were able to reduce the heat gain by the indoor space using the high latent heat associated with the melting process of the PCM and evaluated the effectiveness of the

shutter containing a PCM in reducing the heat gain by the interior space compared to when a foam shutter is used during typical working hours. They also conducted a parametric study to assess the design parameters of the PCM, which revealed that a PCM with a higher melting temperature demonstrates a better performance. Heat gain by the interior space can be reduced by up to 23.39% using P116 PCM with a thickness of 0.03 m in the window shutter.

Researchers have evaluated the performance of thermally efficient windows numerically and experimentally using moving PCM curtains [131], and glass windows fabricated using composites containing a PCM [132]. Szimmat et al. [133] presented a numerical simulation model to show the effects of solidification and convection to account for the processes associated with the PCM using finite element analysis with a moving boundary at the liquid-solid interface. Duan et al. [134] have studied the solidification of PCM n-hexadecane inside a rectangular enclosure using enthalpy formulation. Liu and Ma [135] have presented another numerical study on the melting process in a finite slab using second generation boundary conditions. Regarding the boundary conditions, researchers have evaluated pulsed heating and melting using an oscillatory surface temperature [136].

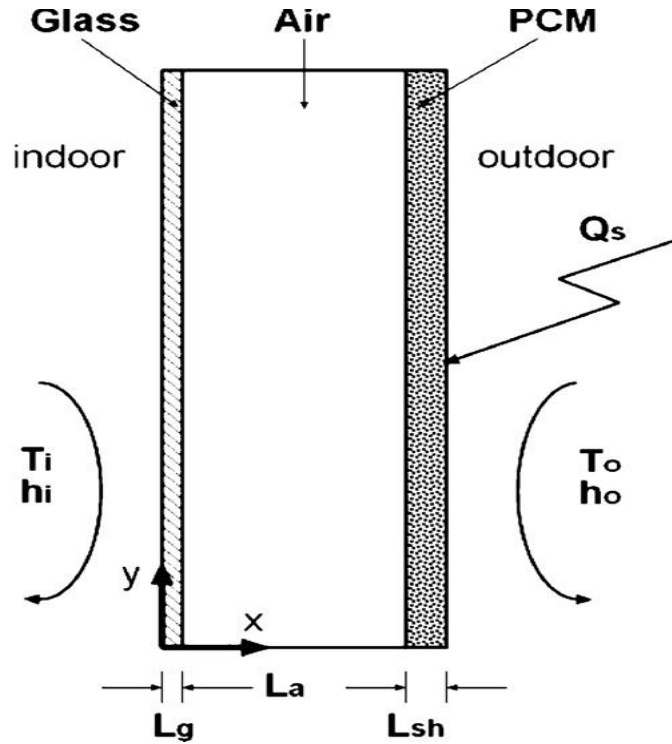


Figure 2.21 A schematic representation of a window shutter containing a PCM and the boundary conditions involved in decrease of indoor heat gain [130].

Figure 2.21 depicts the geometric configuration of a window shutter containing a PCM and the boundary conditions associated with the reduction of indoor heat gain. The outdoor surface of the shutter system, composed of a PCM, air gap, and a glass panel, is subjected to time-dependent solar radiation with forced convection enhanced at the boundary of the frame wall, while the indoor surface is subjected to time-independent free convection boundary conditions. Based on the findings [130], the authors have reported a decrease of the peak energy demand for air conditioning in residential buildings by 10.8% when crystalline paraffin is used as the PCM. They assessed the thermal characteristics of the shutter containing the PCM by varying the shutter thickness (L_{sh}) while keeping the glass thickness (L_g) and air gap thickness (L_a) constant, based on radiation data for June, one of the hottest months in Kuwait City. The researchers evaluated the performance of a shutter containing four different thicknesses of the P116 PCM, i.e., 0.01 m, 0.015 m, 0.02 m, and

0.03 m, in comparison to a foam shutter. Fig. 2.22 shows the average heat flux at the interior glass surface of the investigated scenarios for both PCM and foam shutters. The heat flux of the PCM shutter with a thickness of 0.01 m is less than that of the foam shutter during the first half of the day (7 AM to 11:45 AM). However, as the outdoor temperature increases the PCM completely melts, increasing the heat flux at the interior surface significantly, even higher than that of the foam shutter (by 14.28%). When the thickness of the PCM layer is 0.015 m, the heat flux at the interior surface remains lower than that of the shutter with the foam layer until 3 PM. With a P116 PCM thickness of 0.03 m, interior heat gain is lowered by 23.29%. Thermal efficiency of a shutter with a PCM layer, therefore, depends significantly on the PCM layer thickness. The melting temperature of the PCM should be closer to the upper temperature limit a window reaches daily, and the quantity of the PCM should be adequate to absorb outside heat during the day (working hours) without completely melting.

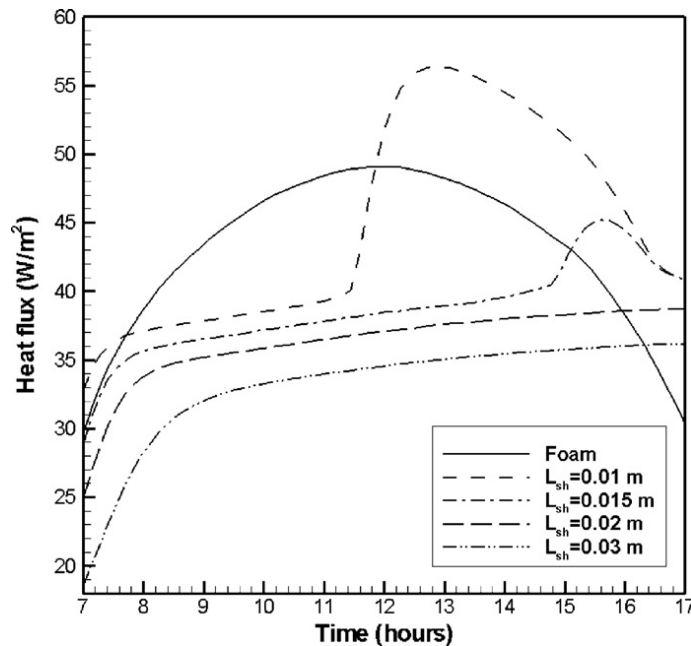


Figure 2.22 Comparison of the heat flux at the interior glass surface of a shutter with a P116 PCM layer of different thicknesses with that of a foam shutter [130].

A. Window shutters without a PCM layer in areas with hot weather

Building envelope isolates the controlled environment of the interior of a building from the outdoor environment [137]. Proper design and thermophysical properties of the envelope play a critical role in enhancing the comfort of occupants and lowering the energy consumption. Typically, an envelope of a building is composed of the walls, doors, windows, and roofs. Thermal insulation materials are commonly used in the walls and roofs of buildings to minimize heat ingress [138]. However, the windows of a building are responsible for a significant increase of the cooling load (amounting to ~32% of the total load) as they are the weak links for heat flow from the outdoor space to the indoor space [139,140]. Hence, the energy consumption of a building can be significantly reduced by controlling the direct solar radiation and convective heat transfer through windows [141], and researchers have explored many techniques for this purpose [142]. Besides, new stricter regulations for energy-efficient buildings along with innovative techniques and development of special materials have promoted the design of energy-efficient windows. Researchers have evaluated a simple glass window model to understand the effects of thermo-physics of glass on the heat gain, taking reflection, transmission, and absorption of glass into account [143]. Researchers have also numerically modeled the conjugate heat transfer mechanism of a window with double panes to determine the optimal air layer thickness between the two panes [144], and have investigated the minimization of the thermal bridging through a window [145]. Cuevas et al. [146] have evaluated a window with blinds to determine the heat transfer coefficient of the window. Dalal et al. [147] theoretically analyzed the performance of double-glazed windows, whereas Naylor and Collins [148] evaluated heat transfer through conjugate conduction, convection, and

radiation in a double-glazed window with a ventilated blind. Researchers have determined the influence of glass reflectance on the total heat gain by evaluating gas-filled and naturally ventilated windows in regions with hot weather [149].

Installation of exterior shading devices, also known as window shutters, is the most effective technique in reducing indoor heat gain [150,151]. Foam-filled rolling aluminum shutter slats are mostly used in window shutters. Hammad and Abu-Hijleh [152] have investigated the impact of a dynamic external shutter in lowering overall energy consumption in an office building. Palmero-Marrero and Oliveira [153] studied the performance of a shutter shading device in Egypt and observed a 55% decrease in overall energy consumption compared to when the shading device is absent. Researchers were able to achieve up to 23.3% reduction of indoor heat gain by incorporating a PCM in a shutter [130]. Yazicioglu et al. [154] has presented a comparative analysis of the energy performance when a window with a traditional wooden shutter and an aluminum roller shutter are used and found that the U-value of the window with a wooden shutter is more than double that of the window with an aluminum shutter. Freewan et al. [155], has shown that the indoor temperature can be decreased to an acceptable level with an adequate level of illumination of the interior space in a study of the effect of shading devices on the indoor air temperature and indoor illumination.

Fig. 2.23 presents the indoor and outdoor views of a window with an incompletely closed shutter, allowing the passage of outdoor light through the opening to illuminate the indoor space [137]. The authors of the study compared the decrease of the heat gain when the shutter of the window is partially and completely closed. They also investigated the effect of the extent of closure of the shutter on the level of illumination of the indoor space. In

some cases the window shutters are kept partially closed to maintain adequate lighting in the indoor space during daytime, which can worsen their effectiveness and increase heat ingress. Researchers found that the indoor illumination was insufficient when a 10-cm opening was left in the window shutter, which also increased the indoor heat gain by 22.10%. Even though sufficient indoor illumination can be achieved by partially closing the shutter with a 30-cm opening, it also increased the heat gain by 73.40%. Hence, the authors recommended keeping the shutter completely closed during working hours and relying on energy-saving lamps [137].



(a)



(b)

Figure 2.23 (a) Outdoor and (b) indoor views of the window with a shutter partially closed [137].

2.6.7 PCM in building-integrated photovoltaic systems

Building-integrated photovoltaics (BIPV) are becoming highly attractive and are providing the momentum for future green and intelligent buildings. An estimated 22% of the electricity in the EU countries is expected to be produced from BIPV by 2030 [156]. However, Hasan et al. [157] reported that the higher frame temperature of BIPV compared to rack-mounted free-back PV systems will considerably lower their efficiency. To deal with the issue, natural and forced ventilation techniques have been explored to overcome the overheating problem of BIPV. However, both methods have pros and cons, including natural ventilation is dependent on the airflow rates and does not overcome the overheating issue completely, while forced ventilation uses an external system that consumes additional energy. In response, the researchers employed PCMs at the rear of PV panels as passive temperature regulators for effective cooling that enhanced the efficiency of the BIPV systems [158–161]. The authors of Ref. [157] constructed a 53 cm × 63 cm × 73 cm test room (Fig. 2.24) to study and determine the usefulness of PCM-based thermal control of a PV module and a space. The authors investigated a PV-PCM system to enhance the energy efficiency and cooling of a building and reduce the ingress of heat into the interior. In their proposed method, the PCM layer was placed behind the PV system, and an insulated chamber was affixed to the rear of the PV-PCM system to mimic a scaled-down indoor space. The presence of the PCM decreases both the temperature of the PV system and the indoor transient temperature and delays the indoor temperature peak. The PV-PCM system reduces the temperature by 12.3 °C and 22.6 °C at the front and rear surfaces of the PV, respectively, compared to the PV system without a PCM. The proposed system boosted the output power of the PV system by 7.2% at peak temperature and 5.0% on average

during daytime. The PV-PCM system can store 47.7% of the incident radiation as thermal energy compared to 0.36% in the case of the PV system without a PCM. Hence, the PV-PCM system reduces ambient heat losses, which enhances indoor cooling by 9.6% (equivalent to a drop of 5 °C) at peak temperature and 7.0% (equivalent to a drop of 3.5 °C) on average during daytime. Besides, the increase of thermal inertia by the PV-PCM system delays the indoor peak temperature by two hours, which further decreases the cooling demand for daytime occupancy. In another study, Kośny et al. [52] set up a PV module on a naturally ventilated roof and used a PCM as another additional heat sink, as shown in Fig. 2.25. For comparison, a conventional PV system was also installed beside the PV-PCM system. They conducted the study for one year, from November 2009 to October 2010, in Oak Ridge, Tennessee, USA. The study revealed that the PV-PCM integrated system reduces the cooling load by 550% in the summer and the heating load by 30% in the winter.

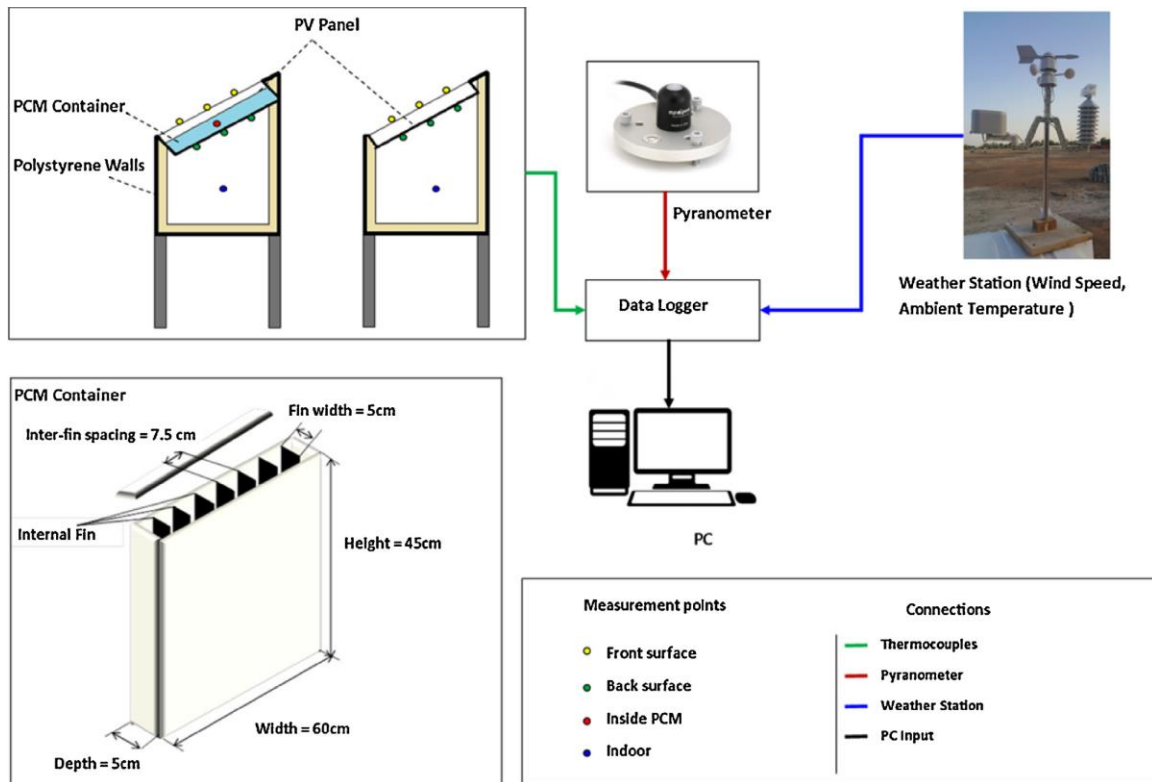


Figure 2.24 Schematic diagram of a PV-PCM system (taken from Ref. [157]).

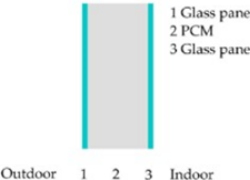
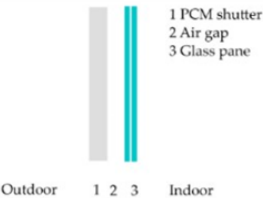
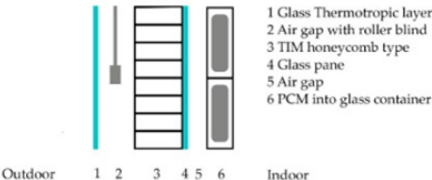


Figure 2.25 PV-PCM system installed on a naturally ventilated roof (taken from Ref. [52]).

2.6.8 Incorporation of PCMs in transparent materials

Transparent materials in building envelopes are increasing in commercial and residential buildings in regions with hot weather. Hence, researchers are interested in incorporating PCMs in transparent building materials [162] to minimize the heating and cooling loads of buildings. For example, as windows with transparent glass contribute a significant proportion of indoor heat gain, studying the performance of PCMs in combination with glazing materials is worthwhile. Fokaides et al. [162] and Vigna et al. [163] published reviews on integrating PCMs with transparent building elements. They made a comprehensive list of applications of PCMs in combination with transparent building materials, which lists nine different layouts incorporating PCMs under three major categories, as shown in Table 2.3.

Table 2.3 Major categories of layouts with a PCM incorporated in the transparent envelope (taken from Ref. [163]).

Sketch	Description	Concept
1_ basic glazing technology: integration of the PCM in DGU glazing		
 1 Glass pane 2 PCM 3 Glass pane Outdoor 1 2 3 Indoor	Integration of the PCM in a double glazing unit (DGU + PCM)	Solar control modulation and thermal inertia improvement
2_ shutter technology: integration of the PCM in a shutter		
 1 PCM shutter 2 Air gap 3 Glass pane Outdoor 1 2 3 Indoor	PCM external shutter	Time shift of incoming peak loads; glare reduction
3_ façade system: integration of the PCM in a façade		
 1 Glass Thermotropic layer 2 Air gap with roller blind 3 TIM honeycomb type 4 Glass pane 5 Air gap 6 PCM into glass container Outdoor 1 2 3 4 5 6 Indoor	TIM + PCM	Selective optical transmittance of solar radiation; improvement in the thermal inertia of the glazing system

A photovoltaic panel integrated with a PCM (PV-PCM) allows less heat ingress than a PCM-glass panel in hot summer conditions [164]. Li et al. [165] also compared the performance of air-filled double-glazed windows and glass panels filled with a PCM. In addition, Biwole et al. [166] conducted a study employing a passive solar wall constructed using glass bricks filled with a PCM containing an additional layer of silica aerogel (Fig. 2.26). Researchers found that the performance of the PCM in reducing heat transfer between external and internal window surfaces depends on the geographic location and orientation of the building.

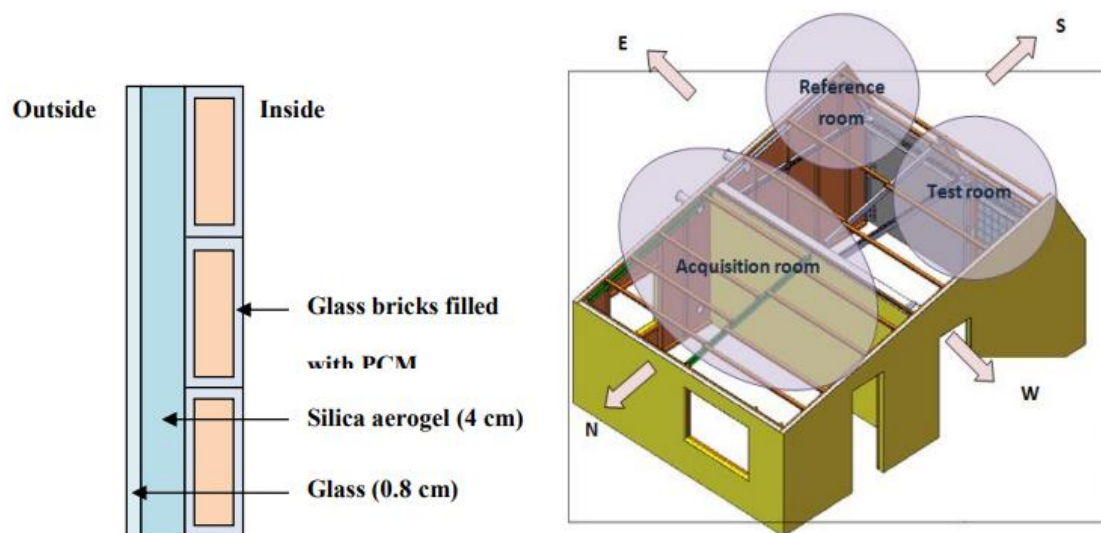


Figure 2.26 The layout of a PCM-aerogel solar wall constructed using a silica-aerogel layer and glass bricks filled with a PCM [166]

Visual appearance and transparency are two of the fundamental factors that are considered in assessing functional and aesthetic qualities in architecture. The inhomogeneity of a PCM is maximum during the melting and freezing stages. Helmut et al. [167] indicated that the inhomogeneous appearance of a PCM, which is not visually pleasant and architecturally undesirable, is a significant drawback when a PCM is used in window glazing. They proposed to conceal the inhomogeneous nature of a PCM with the help of screen-printed or translucent PCM holders. This design can be implemented using the concept of a PCM-

aerogel solar wall [166]. Applying PCM-filled glass bricks with their regular pattern may provide a homogenous appearance and create a translucent effect for those inside the building (Figure 2.27). Incorporating a PCM in glazing windows is recommended when visibility through the window is not an issue [167]. Faircloth et al. [168] conducted a multiscale modeling study to assess visibility through a PCM layer in architectural applications. The authors studied the change in the properties and appearance of a PCM (organic paraffin type) in terms of state, color, and transparency. They showed that the PCM is opaque in the solid state and clear-transparent, and homogenous when it is in the liquid form. Fokaides et al. [162] proposed different orientations to overcome the barriers to incorporating PCMs in glazings, such as inhomogeneity and lack of transparency. They suggested applying a rotary, re-configurable glazing system and nano-encapsulation of the PCMs as significant future improvements to overcome the problem of inhomogeneity and low transparency.



Figure 2.27 External view of the PCM-aerogel passive solar wall [166].

2.7 Environmental impact of using PCM in buildings

The surging growth of energy demand all over the world is the primary reason for greenhouse gas (GHG) emissions and climate change [169–171]. For instance, Global primary energy consumption rose from 95,527 TWh (terawatt-hour) in 1990 to 165,320 TWh in 2021 [172], which resulted in GHG emissions from 32.52 billion tons of carbon dioxide-equivalents (CO₂eq) in 1990 to 49.76 billion tons (CO₂eq) [173]. According to the International Energy Agency reports, the building sector is responsible for around 30% of total final energy consumption and 27% of total energy sector emissions [174]. To reduce the GHG emissions in the sector; eventually mitigate climate change and environmental pollution, net-zero energy building or zero-carbon homes ideas are being implemented globally [175]. Among many strategies, multi-layer insulated and single-layered walls achieve the goal of zero-energy homes by preventing severe heat gain/loss [176–179]. The absorption coefficient of an exterior wall can be modified by choosing the best coating material to induce a time lag in the heat flow and prevent temperature fluctuations [180–182]. The increase in the thermal inertia of the building materials can further increase the induced time lag [183]. Structures built with higher thermal inertia are known to be more energy efficient, particularly when subjected to a higher heat load [184]. Incorporating PCMs in building construction to improve thermal inertia is progressively replacing traditional, expensive, and extensive construction techniques used for this purpose [89,185,186]. PCMs have been incorporated into concrete by directly mixing them with concrete used to make blocks or by incorporating microencapsulated PCMs in concrete aggregates. As the direct introduction of PCMs into concrete leads to problems associated with PCM leakage and moisture transfer, this practice is gradually abandoned [187]. Hasan

et al. [122] reported that direct mixing PCMs with insulating material leads to the evaporation of the PCM (for inorganic PCMs) or deterioration and eventual dematerialization of the PCM (for organic PCMs), leading to failure. Besides, integrating microencapsulated PCMs into concrete aggregate causes unequal distribution of the PCM within the concrete, resulting in structural failure. They also reported that conduction is the dominant heat transfer mode during melting and solidification when a cavity is filled with a microencapsulated PCM, resulting in a decrease in supercooling effect compared to when the PCM is not encapsulated. Eventually, the authors reported various case studies that justified the positive environmental impact of the PCM, including reduction of heat flux, better storage capacity, minimization of load, and energy consumption.

2.8 Drawbacks of Incorporation of PCMs in Buildings

Knowledge of the importance of saving energy and how that can be achieved, such as using high-efficiency HVAC systems, among building owners and tenants are poor. The existing energy tariff structure of KSA does not promote investment in power conservation. All previous research and reviews stressed the importance of implementing a program to save energy consumed by the HVAC systems used in the Kingdom [123,188]. The short-term option of optimizing the energy efficiency of newly built buildings by using energy-efficient HVAC systems alone will not be sufficient to enhance energy usage performance. The recommendation is to reform the program by offering cash incentives to landlords who upgrade to energy-efficient HVAC equipment, restructuring the energy tariff system, and increasing public awareness. Several researchers recently studied using PCMs in houses as energy-conserving materials. The rise in oil costs motivates researchers to look for alternative technologies to reduce oil demand [123]. Considering their thermo-physical

properties, including the melting point scale, fusion heat, thermal conductivity, and density, PCMs offer a good choice for energy-saving applications [123].

Incorporating microencapsulated PCMs into building materials such as concrete is a very effective way to apply PCMs in construction [189]. PCMs used in construction materials are typically encapsulated in metallic or polymeric capsules. Among the disadvantages are that PCM encapsulation is expensive and may affect the mechanical strength of the building materials [189]. Alawadhi et al. [48] undertook theoretical studies on incorporating PCMs in bricks and achieved positive results over the summer in decreasing heat transfer to the interior space. Even though state-of-the-art PCMs that function over a wide range of temperature scales are available, this analysis has been restricted to PCMs with a phase-change temperature within the range suitable for houses [48]. In an exhaustive study, Castell et al. experimentally tested using alveolar bricks containing a macro-encapsulated PCM and traditional bricks [49]. Their work was conducted in Spain, under real-life conditions using five separate cubicles employing two types of testing, i.e., testing with a controlled temperature and testing with a free-floating temperature. The findings indicate that the system functions well, is technologically feasible, and saves energy. However, the system did not function as expected during the nighttime trials due to incomplete solidification of the PCM. The authors suggested that this shortcoming can be overcome by applying a cooling strategy [189]. The analysis and observations listed above have the following limitations:

- a. The tests were performed under peak summer conditions. However, even though the weather in the GCC region is primarily hot and dry, several months are

moderate to cold. Hence, the net heat benefit in the peak summertime is projected to decrease when computed for the entire year.

- b. As the tests were performed during the summer and results were extrapolated to a time scale of one-year, potential leaks of the PCM during repetitive cycling are not considered. Nevertheless, this aspect is essential in real-world applications that should be evaluated.
- c. The tests should not combine heat removal from the air cavity using both normal means and induced convection, which will compromise the results on the effects of re-solidification of the PCM.
- d. The test objects are tiny in scale and would be less representative of a building.
- e. The authors plan to address all the encountered limitations in future research.

Bland et al. [190] also recently evaluated PCM systems for applications in residential buildings. They outlined some drawbacks encountered when this technology is used in building applications, including super refrigeration, low thermal conductivity, phase segregation, fire control, and low quality. Supercooling and phase isolation contribute to the incomplete thermal cycling of the material, hindering their ability in construction applications, which require systems with a long life. Low thermal conductivity will slow the rate at which heat is transmitted or absorbed from the house, thus affecting the comfort of occupants and device performance. The authors proposed two ideas (Pump and Tap System and Wall Panel System) for overcoming the abovementioned problems. Due to their poor flame-retardant properties, PCMs must be overcome for the actual application.

2.9 Recommendations

The emphasis has turned to a new range of products to overcome the shortcomings of inorganic PCMs, including their low stability. Among them are organic anhydrous compounds such as fatty acids, polyethylene glycol, and paraffin. Paraffin is ideal for use in a broad temperature range, allowing them to be used as PCMs in various areas other than building construction. Despite repeated spinning, latent heat is mass-dependent and shows no signs of phase separation by solid-liquid transitions and low vapor pressure [191]. Initially denied these goods since these are costlier than standard hydrates salt and have much less ability to retain heat per unit volume. However, many of the above substances have many advantages, including chemical and physical stability, efficient thermal performance, and a flexible transition region. In building construction applications, PCMs, with their phase transition in the temperature range, are considered suitable for maintaining the thermal comfort of occupants of buildings.

Different energy-saving plastic building components containing PCMs for processing thermal energy are available [192]. BCPCMs are prepared by combining gypsum, mortar, diatomite, perlite, and vermiculite esters of liquid xylitol pentalaurate (XPL) and xylitol pentamyrystate (XPM) as supporting matrices. Pasupathy and Velraj [72] investigated the effect of a double layer of a PCM on the thermal comfort of occupants of a building for one entire year in climatic conditions prevailing in India. In addition, they experimented using roof frames with and without a PCM employing similar rooms. The inorganic PCM used is a eutectic of salt hydrates, and the results show that indoor air temperature fluctuation is significantly reduced by using a roof with a PCM panel.

2.10 Conclusions

The primary purpose of this paper is to review published studies on a range of latent heat energy storage (LHES) and cold thermal energy storage (CTES) systems devoted exclusively to heating, cooling, and air conditioning (A/C) applications. This paper reviews research and development in applications of PCM technology in building construction. Initially, a detailed description of the phase shift of PCMs and their classification and implementation are provided. Furthermore, types of PCMs evaluated for incorporation in walls, roofs, floors, and refrigeration systems of buildings are described. Findings based on data gathered from experiments involving PCMs are also presented. Finally, construction materials with a potential for incorporating PCMs that have not yet been tested for practical use are also described. Given their excellent thermo-physical properties, using PCMs in construction materials, heat transfer and other future applications are promising. The application of PCMs in net zero energy storage strategies for reduced environmental impacts should be further evaluated. Analysis of the published findings indicates a 20 percent decrease in the cooling load when PCMs are incorporated into conventional building materials. Hence, a PCM wall can be used to store energy in the form of latent heat in buildings for air conditioning, portable air conditioning, and many other uses as a possible solution to the high demand for diminishing fuel supplies.

Al-Khobar City in Saudi Arabia is developing fast. As a result, there is an immediate demand for an increased electricity supply to run additional AC devices because air conditioning is essential, and the demand is growing daily. PCM materials and solar hybrid air conditioning systems are the keys to improving thermal insulation and, thus, reducing power consumption. PCMs can be integrated with passive or active structures in building

applications. Passive systems do not need extra electricity and are simple to deploy, with the energy consumption of the integrated devices low. However, they depend entirely on the temperature outside and the changing weather conditions. Therefore, if the night temperature does not drop significantly below the phase-change temperature of the PCM, it will not wholly solidify, hindering its functioning. In addition, the heat transfer between the air and the wall during day-night cycles limits the potential storage capacity, which restricts the use of passive systems.

CHAPTER 3

DEVELOPMENT OF A SHAPE-STABILIZED PHASE CHANGE MATERIAL UTILIZING NATURAL AND INDUSTRIAL BYPRODUCTS FOR THERMAL ENERGY STORAGE IN BUILDINGS

3.1 Introduction

A comprehensive study was conducted to develop and utilize a novel shape-stabilized phase change material utilizing two abundantly available and low-cost natural materials, namely scoria and expanded perlite and an industrial byproduct, heavy oil ash, in combination with polyethylene glycol. The thermal and energy storage characteristics of the composite materials were evaluated with the aim of using them to conserve energy in the domestic facilities. The results of differential scanning calorimetry showed that expanded perlite composite has the highest melting and solidification latent heat values, 150.7 J/g and 134.6 J/g, respectively, compared to scoria and oil ash composite. However, expanded perlite composite has lower thermal conductivity compared to other composites. Consequently, a novel system incorporating carbon nano tubes (0.5 wt.% and 1 wt.%) in the expanded perlite composite was developed to improve its thermal conductivity. The thermal conductivity (0.453 W/m.K) of the new system with 0.5% carbon nano tubes is remarkably more than that of commonly used phase change materials. Further, the developed PCM with 0.5% carbon nano tubes can transform sunlight into thermal energy with a solar-to-thermal energy conversion efficiency of 59.4% and it has a thermal conductivity that is 97% more than that of polyethylene glycol alone. Besides, the newly

developed PCM also shows excellent energy storage and release performance. All these favorable characteristics indicate that the developed phase change material can be beneficially utilized in thermal storage systems.

3.2 Introduction

Phase change materials (PCMs) are thermal storage media that possess a high latent heat capacity and maintain a constant heat/release temperature [193]. The temperature of PCMs increases during the phase conversion, resulting in the absorption of heat. However, PCMs absorb/release heat at nearly a stable temperature. PCMs can store five to 14 times as much heat (energy) compared to other heat storage materials, including rock, sand, gravel, water, masonry, etc. [194]. They possess excellent energy conservation characteristics required for residential solar water heating systems, textile production, energy efficient buildings, food and agro-industry, water desalination, biomedical products, air conditioning, waste heat recovery and other applications [195].

The energy consumption by the building industry has been estimated to be around 40% of the total, which accounts to 30% of the world's greenhouse gas emission [196]. Therefore, there is a strong demand for the use of PCMs to decrease the energy demand in buildings, and consequently greenhouse gas emission. Considerable energy is utilized for heating, lighting, air conditioning, and ventilation in buildings. Consequently, there is a need to develop energy conserving technologies, such as the use of PCMs. However, the accelerated aging of PCMs under harsh weather conditions must also be taken into consideration while designing energy saving infrastructure. In view of this, few studies have been conducted to develop low-cost building materials containing PCMs of the desired characteristics [5,6].

In areas with mild climatic conditions, building elements incorporating PCMs can store thermal energy supplied by direct solar radiation through the windows in the daytime and release it in the night. Such a process of storing and releasing of energy minimizes the power required to preserve buildings thermal comfort during the relatively hot daytimes and cold nights [194]. In Africa, South Asia, and the Middle East, where the daytime temperature is almost 50 °C from mid-May to the end of August, the energy demand for cooling the building has increased dramatically. Consequently, currently, the focus is on decreasing the energy demand for cooling buildings through the incorporation of methods based on renewable energy. Owing to the abundant supply of sunlight in these areas, storage and reuse of thermal energy is considered among the most promising areas of renewable energy. An interesting approach in this respect is the use of PCMs to collect and store solar energy in the latent heat form. Even though using a suitable PCM for maintaining comfort in buildings has received considerable attention, limited information is available on the use of this approach in buildings under hot climatic conditions. Consequently, there is a need for developing PCMs for the hot weather conditions of the world.

Recently, few researchers have claimed that shape stabilized phase change materials (ss-PCMs) can be used to store solar energy [7,8]. A ss-PCM is a composite with an organic PCM confined in an inorganic porous media. The PCM packed in a porous media provides an effective approach to produce an ss-PCM with enhanced and improved mechanical strength, flame resistance, thermal conductivity, and chemical stability [198,199]. Natural materials or industrial waste byproducts that are abundantly available and economic and are porous and possess good thermal conductivity can be used as carriers of PCM. In this

study, three supporting materials namely scoria, expanded perlite and heavy oil fuel ash were evaluated to develop efficient and economic ss-PCM.

Oil ash (OA), a fine black powder, is formed as a result of burning of heavy oil in power plants. It contains more than 90% carbon and has an average particle size of (20 – 100) μm [200,201]. Al-Mehthel et al. [22] developed high quality concrete utilizing up to 10% OA (0, 5, 7, and 10%) used as a replacement of Portland cement. They reported that incorporation of OA improved the compressive strength of concrete. Maslehuddin et al. [202] used OA to produce a thermal-insulating lightweight concrete with a strength ranging from 21 to 25 MPa and thermal conductivity of about 0.65 K/W.m [202].

Scoria (SC) is a natural lightweight aggregate with gray to black color, which can be used in many applications, (e.g., production of lightweight concrete, filler in low-cost paint and filtering media) [18]. Bogas and Cunha [203] studied the behavior of lightweight concrete containing SC with improved tensile strength and enhanced thermal resistance compared with other traditional non-structural solutions [203]. Considering that OA and SC have a porous structure, they can be utilized in the preparation of ss-PCM as a carrier.

Expanded perlite (ExP), which is a well-known thermal and acoustic insulator and can expand 4– 20 times on heating between 760 oC and 1100 oC, can also be considered for the development of ss-PCM [204]. In fact, the lightweight and low-density of ExP make it one of the best energy storage materials [204–206]. The other advantage of ExP is that it is a relatively low-cost material with high thermal stability [206,207].

The use of several PCMs in the preparation of ss-PCMs has been reported in the literature [208]. Organic PCMs have received more attention in recent years owing to their ability to

overcome the inherent shortcomings of inorganic PCMs. Organic PCMs do not suffer from problems associated with super cooling, flammability and phase segregation. Moreover, they are consistent with different building materials and are ideal for heat absorption. However, recent studies have shown that they suffer from high flammability, high volume change, low thermal conductivity, leakage problems, and recalescence [209]. Nevertheless, due to their proper thermal reliability and self-nucleate ability, organic solid-to-liquid PCMs, including paraffin wax, polyethylene glycol, and fatty acids, represent the most widely used materials for heat storage [210–212]. However, low thermal conductivity and leakage are the main drawbacks of organic PCMs. Material loss because of leakage could result in the failure of the system, posing major contamination concerns for the environment. However, shape-stabilization of organic PCMs can be used to solve leakage issues.

Non-paraffin organic PCMs include a broad range of compounds, like fatty acids, glycols, esters, and alcohols [14], which have excellent enthalpies. However, they are nearly three times costlier than paraffins [26]. Hence, building materials containing non-paraffin organics cannot be readily commercialized. Ramakrishnan et al. [213] have reported that an ss-PCM with paraffin and ExP can be incorporated in cement composites without a protective surface layer. Moreover, they reported that the thermal storage capacity of paraffin/ExP with graphene composites and its thermal properties are significantly enhanced compared with the paraffin/ExP composites [213]. It was also reported that paraffin can be impregnated in the pores of ExP very well and they are compatible with each other [214]. Paraffin-based PCMs are used in buildings due to their broad working temperature range and high latent heat [215]. Even though differential scanning

calorimetry (DSC) of paraffin reveals that technical grade paraffin waxes do not show any sign of degradation of their performance even after 100 thermal cycles [216]. Furthermore, the melting latent heat of commercial grade paraffin-wax-53 PCM decreases from 184 to 165 J/g after only 300 cycles [215]. In addition, a large volume change during phase conversion besides low conductivity are the major disadvantages of using paraffin as a PCM [204,217].

Polyethylene glycol (PEG) is a more suitable PCM for use in buildings located in the hot weather conditions. It is a very promising organic solid-liquid PCM due to its chemical stability and wide melting temperature of about 3 to 69 °C, that can be adjusted by its molecular weight. In addition, PEG has a low degree of super cooling and a high chemical/physical stability without phase segregation and is non-toxic, erosion-resistant, and cost-effective. Also, PEG has a smaller volumetric change and lower vapor pressure compared with paraffin [218]. Hence, PEG is a promising compound to be used as a PCM in conjunction porous materials, such as OA, SC, and ExP, to produce ss-PCMs for use under hot weather conditions. Further, due to its suitable melting and freezing temperature, PEG-based PCM could be used as an efficient thermal energy storage (TES) material in buildings.

Zhang et al. [5] prepared an ss-PCM using PEG/ExP with a layer of carbon to enhance its conductivity and prevent leakage. However, a high quantity of sucrose was used to form a layer of carbon at elevated temperature, which is risky since the sucrose solution can explode accidentally during the drying process. More importantly, the conductivity of the carbon layer is not comparable with that of carbon nano tubes (CNTs). Consequently, CNTs have been embedded in PCMs to enhance their thermal conductivity, absorption

capacity, compatibility, and thermal stability [14]. CNTs can also act support the PCM to overcome the drawbacks of low thermal conductivity, minimize leakage, and can greatly enhance the heat transfer efficiency [10]. Other researchers have reported that it is not appropriate to use paraffin RT-27 for real world applications, due to its very low latent heat and conductivity of 51.6 J/g and 0.112 W/m.K, respectively [219]. Zhang et al. [220] have shown that employing PEG containing Ag-graphene might enhance the solar-thermal energy conversion rate of the PCM. The developed composite has a relatively high latent heat and conductivity values of 0.414 W/m.k and 166.1 J/g, respectively. However, their system possesses higher supercooling values. In real applications, the prepared Ag-graphene PCM is unviable as graphene *is very expensive* (\$100 – 200 per gram) compared to CNTs (\$100 – 200 per kg).

Though some research, as discussed earlier, has been conducted to develop PCMs for building applications, they are either costly or thermally unstable. Consequently, a comprehensive study was conducted to develop PCMs that satisfy the thermal, phase change and cost requirements. Three cheap and easily available materials, namely OA, SC, and ExP were investigated as carriers in an ss-PCM along with PEG. To the best of our knowledge, this study is the first one that explored the preparation, characterization and thermal evaluation of OA-PEG (OAP), SC-PEG (SCP) and ExP-PEG (ExPP). It is expected that the developed ss-PCMs will contribute to significant energy savings in buildings under both moderate and hot weather conditions.

3.3 Experimental Work

3.3.1 Materials

Polyethylene glycol (Molecular Weight = 6000, ultrapure > 99% purity) used as the PCM was purchased from Sigma-Aldrich Co. St. Louis, MO, USA. CH₃CH₂OH (ethyl alcohol, purity ≥ 99.8%) was procured from BDH Chemicals Co. OA was obtained from a power plant (Saudi Electricity Company) in Shaybah, Saudi Arabia (> 90% wt. carbon) and SC was collected from a quarry in the Western Province of Saudi Arabia (Average rod density: 866 kg/m³ and porosity: 43%). ExP was purchased from Saudi Perlite Industries Company in Riyadh (Average bulk density: 85 kg/m³). Multi walled carbon nanotubes (CNTs) were purchased from Cheap Tubes USA (Purity 90 wt.%, length 10 – 30 microns, density 0.06 g/cm³, and surface area > 200 m²/g).

3.3.2 Preparation of PCMs

The composite PCMs comprising PEG-6000 with the three carriers, namely OAP, SCP, and ExPP were fabricated by dissolving 0.5 g of PEG-6000 in 50 mL of ethanol and then adding 0.2 g of each matrix to the solution. The slurry was then stirred for 30 minutes followed by another 30 min of sonication. Finally, the slurry was let to settle for 24 h at 80 °C to evaporate ethanol and provide the OAP, SCP, and ExPP composite PCMs. In comparison with other preparation methods, the method of direct incorporation is considered the cheapest, fastest, and easiest, as additional equipment is not required. Moreover, the direct incorporation process is the most effective method for producing composite PCMs, in particular for industrial applications, where PCM composites are specifically incorporated in porous materials [221].

3.3.3 Preparation of ExP/PEG/CNT composite PCMs

A two-step method was used to prepare ExP/PEG/CNT composites. In the first step, the ExPP composite was prepared using the vacuum impregnation method. During this step, a specific quantity of ExP was incorporated in a vial with a vacuum system and a vacuum of 65 KPa was applied for a duration of 90 min. Then, PEG was gradually added to the ExP sample using a funnel. Subsequently, air was permitted to enter the vial for 30 min to increase the pressure inside the vial, which allowed PEG to enter the porous structure of ExP. Finally, the prepared composite was allowed to cool for 24 hours to allow it to completely solidify in the pores of ExP. The optimum ratio of PEG to ExP was evaluated for each composite by applying the leakage test. The prepared composite, which can be considered as an ss-PCM, did not show any seepage. Secondly, ExP/PEG/CNT composite was prepared. In this preparation, a certain quantity of CNT was dispersed in acetone under ultrasonic treatment. The CNT/acetone suspension was then added to shape stabilized ExPP composite prepared in the first step. A magnetic stirrer was used to stir the suspension continuously for 3 h to ensure uniform distribution of CNTs inside the prepared ExPP composite. The suspension was then kept at 60 °C in an oven for 6 h to remove acetone. Two shape-stabilized composite PCMs with ExPP-CNT containing 0.5 wt.% CNT (ExPP/CNT(0.5%)) and 1 wt.% CNT (ExPP/CNT(1.0%)) were prepared using appropriate quantities of CNT.

3.4 Characterization

The elemental composition of OA, SC and ExP was determined using ARL ADVANT XP + XRF. A Rigaku X-ray diffractometer (XRD) that operated at 15 mA and 30 kV at a 2°/min scanning rate and utilized Cu-K α radiation was used to determine the mineralogical

composition. Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer (16F PC) spectrometer. JEOL JSM-6400F FE-SEM was used with an acceleration voltage of 10 kV to examine the morphology. In addition, an X-mass detector was used to detect the energy dispersive X-ray spectra (EDS). The structure and chemical composition of the mesoporous carriers was determined using an X-ray photoelectron spectrometer (ESCALAB-250, Thermo-VG Scientific, 1486.6 eV, USA), with Al-K α radiation and 0.5 eV instrument resolution. A thermal conductivity analyzer (C-Therm Technologies - TCi) was used to determine the thermal conductivity of the composite PCMs. A JEOL model JEM 2011 Transmission Electron Microscope with a camera operated at 200 kV with 94 k CCD was used to obtain the TEM images. Thermogravimetric analysis was performed using 10 mg samples using a Shimadzu TA-50 thermal analyzer. The heating rate was maintained at 5°C/min from room temperature to 600°C under dry nitrogen. The DSC data were obtained by heating sealed samples of 10 mg in an aluminum pan with the temperature increased at a rate of 5°C/min under a fixed stream of argon at a 20 mL/min flow rate. Hitachi U-4100 spectrophotometer was used to obtain the UV–Vis absorption spectra. For light irradiation, disk samples with 5 cm dia. were subjected to heat insulation according to [15]. A solar power meter (PIS-SXE300, Beijing, Chang Tuo, China; TES-1333R, TES Electronic Corp, Taipei, Taiwan) was used to determine the solar simulator intensity. The temperature-time curves were captured using an instrument consist of a Pt-thermocouples, a thermocouple to analogue connection and a data logger (RS-232-RS-485, Instrument Co., Ltd., Jiangsu Suke, Suzhou, China).

3.5 Results and Discussion

3.5.1 Chemical compositions of OA, SC and ExP

Table 3.1 shows the chemical composition of ExP, OA and SC. The ExP consists of mainly Al_2O_3 and SiO_2 , with minor quantities of other oxides, without including any radioactive elements. Hence, the composite PCMs containing ExP do not have any harmful effects on human health, and as such they can be utilized as possible candidates for applications involving TES in a building envelope.

Table 3.1: Chemical composition of OA, SC and ExP determined by XRF.

Material	Constituent, %						
	MgO	Al_2O_3	SiO_2	SO_3	CaO	FeO	Others
OA	19.25	5.93	8.41	54.37	4.28	1.08	6.68
SC	7.23	9.64	30.14	-	18.07	30.69	4.23
ExP	-	10.43	81.72	-	1.06	0.4	6.39

3.5.2 Mineralogical Composition of Porous Matrices

Figure 3.1 (a) describes the X-Ray diffraction patterns of OA sample. X-ray peaks in the range of 10° to 15° 2θ and 28° 2θ , which can be assigned to tremolite ($\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$), and at 26° 2θ is due to quartz (SiO_2). An XRD peak is also present at 30° 2θ , which is due to the formation of calcite (CaCO_3) [222,223]. The XRD patterns of SC are shown in Figure 3.1 (b), and the peaks located at 18° , 31° , and 46° 2θ can be ascribed to aluminum silicate ($\text{Al}_{1.9}\text{Si}_{0.05}\text{O}_{2.95}$) and those at 30° , 42.5° , and 62° 2θ indicate the presence of magnetite ($\text{Fe}(\text{Fe}_{1.04}\text{Ti}_{0.67})$). In addition, the peaks due to anorthite ($\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$) and hematite (Fe_2O_3) appear in the range of 20° to 30° 2θ and 40° to 50° 2θ , respectively [224–227]. Figure 3.1 (c) shows the XRD patterns of ExP,

which clearly indicates that it has an amorphous structure [228,229]. Also, SiO_2 and Al_2O_3 constitute more than 92% of ExP, as shown in Table 3.1 [230–235].

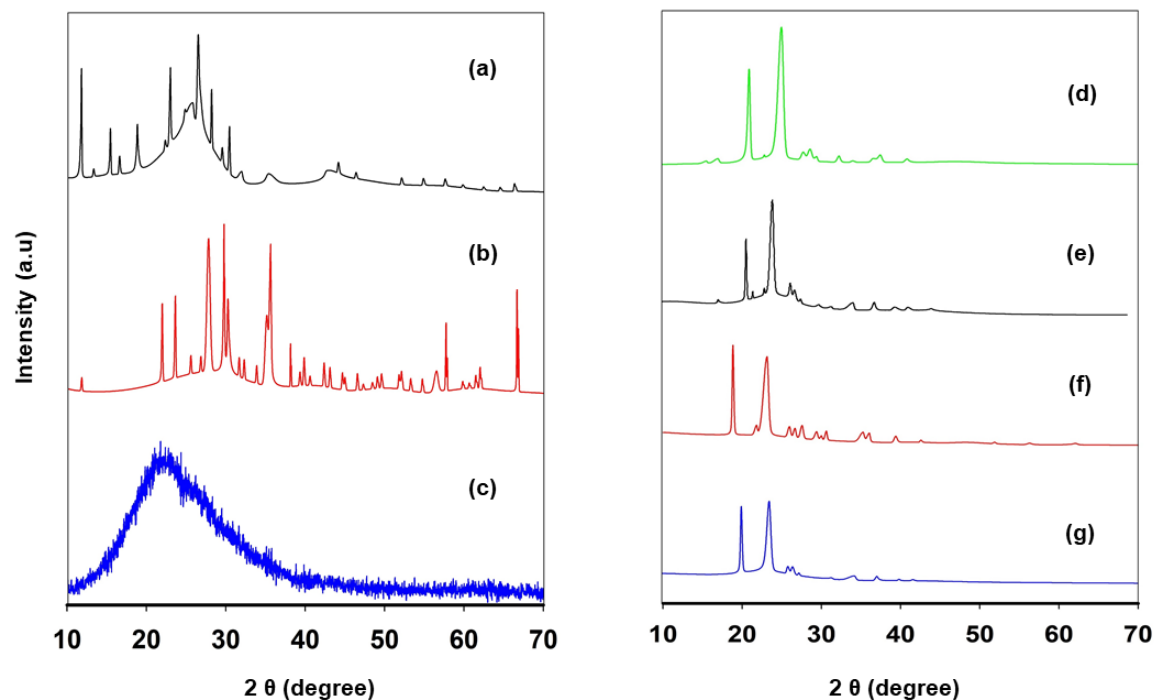


Figure 3.1 XRD patterns of: (a) OA, (b) SC, (c) ExP, (d) PEG, (e) OAP, (f) SCP and (g) ExPP.

The XRD patterns of PEG, OAP, SCP and ExPP are shown in Figure 3.1 (d) to (g). The as-synthesized composites have very intense diffraction peaks in the range of 20° to 30° 2θ . The peaks observed for the composite material match with those obtained for PEG, as shown in Figure 3.1 (d). OAP, SCP, and ExPP composites have lower X-ray intensities compared to those for pure PEG. The weakest intensities were observed for the ExPP composite, which indicates that the pores of ExP are filled with liquid PEG [193]. Moreover, only peaks for PEG are present in the OAP, SCP, and ExPP composites, indicating that the prepared composites are completely mixed without any chemical transformations.

Figure 3.2 displays the FTIR spectra of: (a) OA, (b) SC, (c) ExP, (d) PEG, (e) OAP, (f) SCP and (g) ExPP recorded between 500 cm^{-1} to 4000 cm^{-1} wavenumber range. The FTIR spectrum of OA has a broad band in the range of 500 cm^{-1} to 1000 cm^{-1} , which is most likely caused by the C–O stretching [200,223]. The FTIR spectrum of SC, shown in Figure 3.2 (b), has a broad band in the range of 970 cm^{-1} to 1100 cm^{-1} , which is attributed to Si–O–Si stretching, confirming that SC is mostly composed of silica. Two additional peaks located around 850 cm^{-1} and 2950 cm^{-1} are attributed to OH and Si–O stretching [225–227]. The FTIR spectrum of ExP, shown in Figure 3.2 (c), has a peak at 995 cm^{-1} due to the stretching vibration of Si–O–Si. The 844 cm^{-1} and 995 cm^{-1} peaks are attributed to the Si–O–Al and SiO–H stretching vibration, respectively [206,233–236].

The FTIR spectroscopy was also used to characterize the interaction between the matrices and the PEG. The FTIR spectra for PEG are shown in Figure 3.2 (d), which has a broad absorption band at 2882 cm^{-1} that reflects the stretching of C–H. Also, two peaks due to C–H bending vibrations were noted at 1465 and 1339 cm^{-1} . The peak of PEG at 1278 cm^{-1} is most likely because of the stretching of C–O–C. The spectra for OAP, SCP, and ExPP, shown in Figure 3.2 (e) – (g), are very similar to the FTIR spectra for PEG, depicted in Figure 2 (d). On comparing the composite spectra in Figure 3.2 (e – g) with the spectra for PEG in Figure 3.2 (d), there are no noticeable new peaks, indicating that the matrices and PEG are combined through only physical interaction and the incorporation of PEG into the matrices takes place without any accompanied chemical reactions.

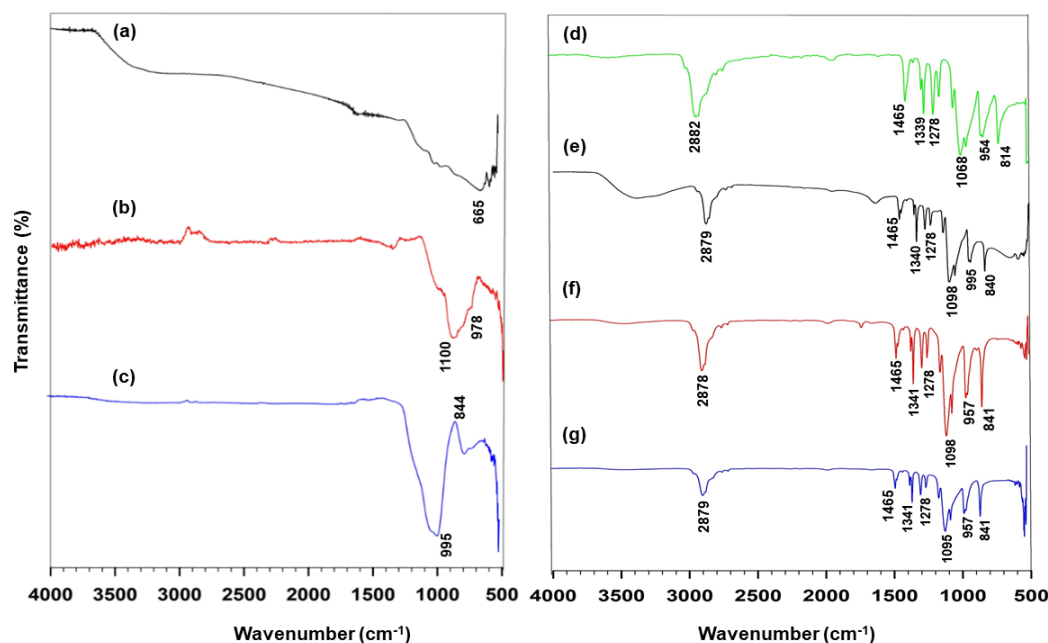


Figure 3.2 FTIR spectra for: (a) OA, (b) SC, (c) ExP, (d) PEG, (e) OAP, (f) SCP and (g) ExPP.

3.5.3 Morphology

Figure 3.3 shows the FE-SEM images of OA, SC, and ExP at lower magnification (Figure 3(a), (b) and (c)) and higher magnification (Figure 3.3(d), (e) and (f)) magnifications. OA has a spherical shape with a highly porous structure and a variable diameter ranging from ~ 30 to ~ 100 μm , as shown in Figure 3 (a). The high magnification image of OA, shown in Figure 3(d), indicates that the diameter of OA particles is about 40 μm and the size of the pores is less than 10 μm . Also, SC has a highly porous structure, as shown in Figure 3.3(b), and its particles are circular, with an urchin-type morphology. The ExP has a sheet type structure, very similar to the morphology of graphene. However, the external surface of ExP is very smooth. The elemental maps of ExP, shown in Figure 3.4(a), indicate that the particles are well distributed. Figure 3.4 (b) shows the energy dispersive spectroscopic data for ExP and the elemental data are similar to XPS data at different locations of ExP. The

surface morphology of the three composites was also examined using TEM for the first time. The morphology as observed under the TEM is unique (Figure 3.5) with OA morphology resembling a long hollow tube, similar to a silkworm. Further, the SC sample contains wires similar to carbon tubes with agglomerated particles and the ExP particles are arranged in a layer by layer structure with a smooth surface, which is consistent with that reported earlier [206,232,233,236].

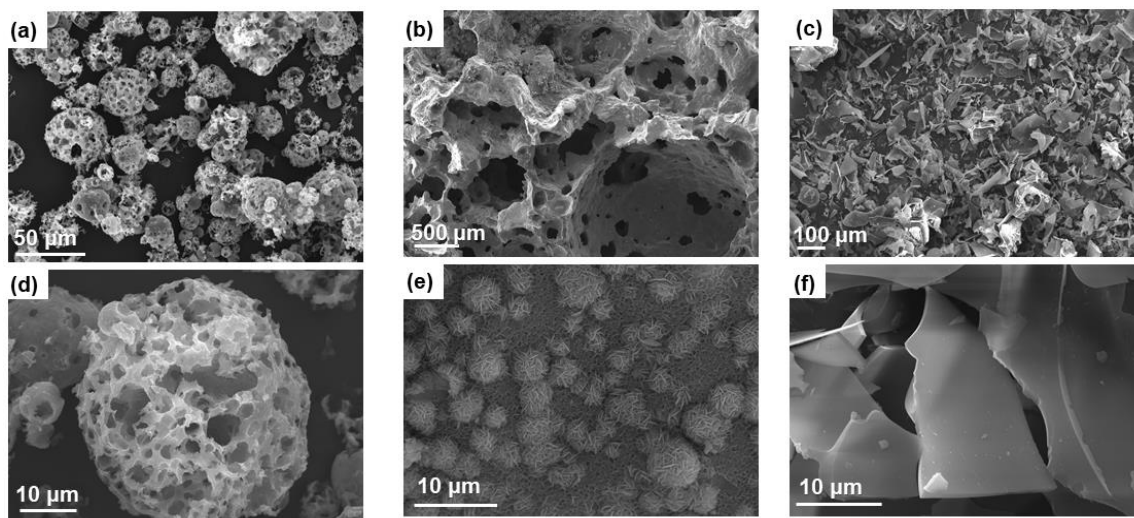


Figure 3.3 FE-SEM images of: (a) OA, (b) SC and (c) ExP at low magnification and (d, e and f) at high magnification.

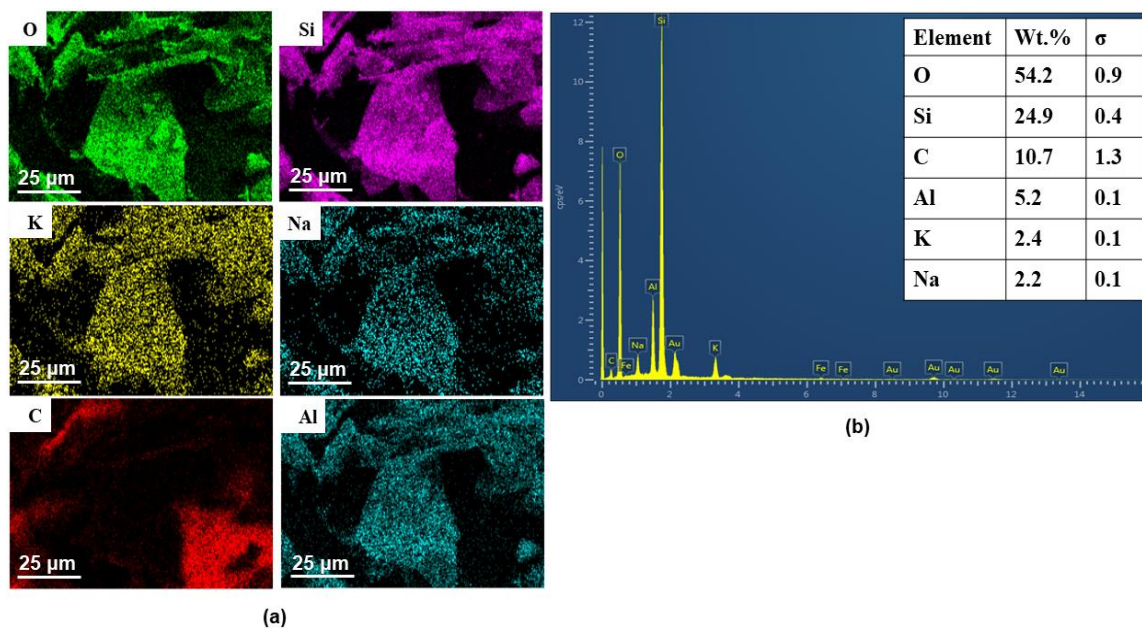


Figure 3.4 (a) Mapping and (b) Energy dispersive spectra (EDS) of ExP.

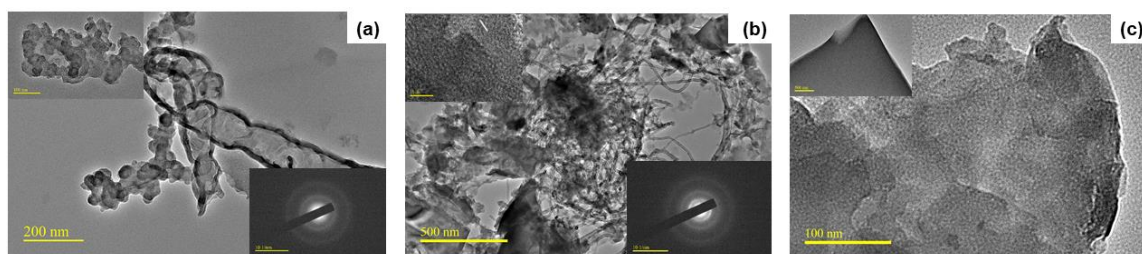


Figure 3.5 TEM images of (a) OA, (b) SC, and (c) ExP.

3.5.4 Differential Scanning Calorimetry

The melting and freezing curves of: (a) PEG, (b) OAP, (c) SCP, and (d) ExPP are shown in Figure 3.6. The region beneath the DSC curves of melting/freezing cycles was used to determine the latent heat of PEG. The melting latent heat of PEG is 189.6 J/g, while its freezing latent heat is 170.1 J/g. Although most of the reported values of PEG enthalpy ranged from 176 J/g to 190 J/g [5,220]. Further, the developed systems show a partial loss of both the latent heat at freezing and melting due to the presence of the matrix.

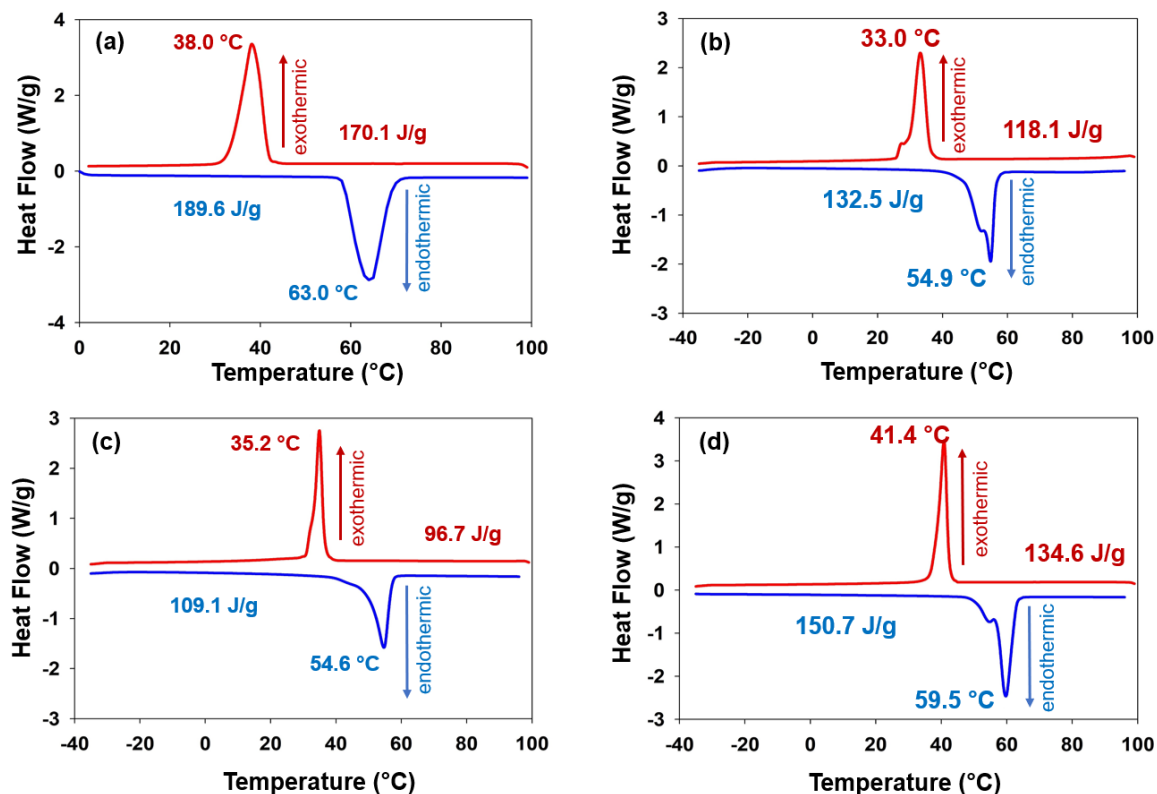


Figure 3.6 Melting-freezing DSC curves of: (a) PEG, (b) OAP (c) SCP and (d) ExPP composites.

The PCMs based on the composite system of OAP, SCP, and ExPP exhibit an obvious melting latent heat (computed with the matrix mass taken into consideration) and impregnation ratio (R) of 69.9%, 57.5%, and 79.5%, respectively (Table 3.2). This behavior can be explained in terms of the heterogeneous nature of the composites, in which PEG is less than optimal for mixing and/or penetration. This conclusion is supported by the weaker melting and freezing peaks of the composites shown in Figure 3.6 [b, c and d]. For comparison, the thermal activity data for ss-PCM consisting of PEG/paraffin are included in Table 3.2 along with the relevant information available in the literature.

Table 3.2: Thermal activity of PEG and PEG Composites.

Sample	T_m (°C)	ΔH_m (J/g)	T_f (°C)	ΔH_f (J/g)	ΔT_s (°C)	R (%)	E (%)	Φ (%)	E_{eff} (J/g)	Reference
PEG	63.0	189.6	38.0	170.1	25.0	-	-	-	189.6	This study
OAP	54.9	132.5	33.0	118.1	21.9	69.9	69.7	99.7	185.5	This study
SCP	54.6	109.1	35.2	96.7	19.5	57.5	57.2	99.4	152.7	This study
ExPP	59.5	150.7	41.4	134.6	18.1	79.5	79.3	99.8	211.0	This study
ExPP/CNT(0.5%)	61.6	132.1	41.2	118.5	20.3	69.7	69.7	100.0	184.9	This study
ExPP/CNT(1%)	61.8	121.9	39.2	109.2	22.6	64.3	64.2	99.9	170.7	This study
PEG	56.9	190.1	42.0	176.4	14.9	-	-	-	-	[5]
PEP (PEG/ExP)	58.4	145.1	46.3	137.3	12.1	76.4	77.1	100.9	-	[5]
PEPC (PEG/ExP/Carbon)	55.2	134.9	46.7	129.3	8.5	71.0	72.1	101.6	-	[5]
Eicosane (C20)	36.2	275.9	32.9	268.1	3.2	-	-	-	-	[237]
ExP/C20	36.1	161.2	34.3	155.3	1.8	58.4	58.2	99.6	-	[237]
ExP/C20/CNT0.3%	36.2	160.4	34.3	155.3	1.9	58.1	58.0	99.8	-	[237]
ExP/C20/CNT0.5%	36.3	159.0	35.6	145.9	0.8	57.6	56.1	97.3	-	[237]
ExP/C20/CNT1%	36.5	157.4	35.5	141.2	0.9	57.1	54.9	96.2	-	[237]
Paraffin	26.8	136.2	23.0	135.8	3.8	-	-	-	-	[221]

ExP/Paraffin 20%	27.5	10.4	22.6	11.3	4.9	7.6	8.0	104.5	-	[221]
ExP/Paraffin 40%	27.3	53.5	22.4	51.6	5.0	39.3	38.6	98.4	-	[221]
ExP/Paraffin 60%	27.6	80.9	22.5	80.8	5.0	59.4	59.5	100.1	-	[221]
ExP/Paraffin 80%	27.4	118.2	22.4	118	5.0	86.8	86.8	100.1	-	[221]
Paraffin (RT27)	25.1	154	25	-	0.1	-	-	-	-	[219]
RT27/ExP	26.3	84	25.5	-	0.8	54.6	-	-	-	[219]
RT27/ExP/SL	26.3	51.6	25.8	-	0.5	33.5	-	-	-	[219]
RT27/ExP/SL/AL	26.1	50	25.3	-	0.8	32.5	-	-	-	[219]
PEG6000	61.8	185.3	36.2	187.1	25.6	-	-	-	-	[220]
GNS/PEG	60.5	176.9	37.3	178.8	23.2	95.5	95.5	100.1	-	[220]
Ag-GNS/PEG-1	60.2	177.2	35.9	179.4	24.3	95.6	95.8	100.1	-	[220]
Ag-GNS/PEG-2	60.3	173.3	35.6	175.8	24.7	93.5	93.7	100.2	-	[220]
Ag-GNS/PEG-3	60.2	169.6	36	171.9	24.2	91.5	91.7	100.2	-	[220]
Ag-GNS/PEG-4	60.3	166.1	36.1	167.8	24.2	89.6	89.7	100.0	-	[220]

(-) Data are not available. Uncertainties calculated using the average of three measurements, 1.2 °C and $\pm 8\%$, respectively, for the of phase change temperature and latent heat.

Table 3.2 also lists all the parameters calculated using the formulation listed below [212]. Where: T_m = melting temperature, ΔH_m = melting latent heat, T_f = freezing temperature, ΔH_f = freezing latent heat, ΔT_s = supercooling, R = impregnation ratio, E = impregnation efficiency and φ = energy storage capacity [212]. E_{eff} = efficient energy per unit mass of PEG as shown in Equation 3.4 were calculated according to ref [238], where: X_{PEG} = PEG weight fraction in PCM. The results for few reported PCMs of the type similar to those investigated in the reported study are also included for comparison purposes.

$$R = \frac{\Delta H_{m, com}}{\Delta H_{m, PCM}} \times 100\% \quad (3.1)$$

$$E = \frac{\Delta H_{m, com} + \Delta H_{f, com}}{\Delta H_{m, PCM} + \Delta H_{f, PCM}} \times 100\% \quad (3.2)$$

$$\varphi = \frac{\frac{\Delta H_{m, com} + \Delta H_{f, com}}{R}}{\Delta H_{m, PCM} + \Delta H_{f, PCM}} \times 100\% \quad (3.3)$$

$$E_{eff} = \frac{\Delta H_{m, PCM}}{x_{PEG}} \quad (3.4)$$

In Equations 3.1, 3.2, 3.3 and 3.4, com = OA, SC or ExP matrix and PCM = matrix + PEG.

It is to be noted that ExPP performs marginally better than other composites. ExPP has an impregnation efficiency of 79.3% compared to 69.7% and 57.2% for OAP and SCP, respectively. Moreover, the efficient energy per unit mass of PEG, energy storage capacity and impregnation ratio of ExPP are also better compared to OAP and SCP, as shown in Table 3.2. The energy storage capacity is more than 99% for all the investigated composites, with ExPP/CNT(0.5%) possessing the highest energy storage capacity among all composites.

The findings of the reported study are also comparable with those reported for other ss-PCMs (Table 3.2). Despite the fact that many PCMs have a high latent heat, in the reported study paraffin-based and PEG-based PCMs were studied since their working temperature is ideal for construction application. The difference between the melting and solidification temperatures was used to determine the super cooling values. The ΔT s of PEG, OAP, SCP, ExPP and ExPP with (0.5%) CNT and (1%) CNTs is 25.0 °C, 21.9 °C, 19.5 °C, 18.1 °C, 20.3 °C, and 22.6 °C, respectively. The highest super cooling reduction of 25.5% was exhibited by ExPP.

As compared to PEG, ExPP (Figure 3.1) exhibited the highest decrease in peak height in the XRD pattern among other PCM composites. This indicates that greater mass of PEG penetrates ExPP compared to OAP and SCP. Further, the higher enthalpy of ExPP with an impregnation ratio of 79.5% support this conclusion. Furthermore, the lack of any vapor/gas formation during the melting cycle is noteworthy. In addition, voids were not generated during the solidification.

3.5.5 XPS

The XPS spectra shown in Figure 3.7 demonstrate the composition and chemical state of ExP. The XPS spectra of ExP, shown in Figure 3.7 (a), indicate the presence of characteristic peaks attributed to the presence of C, Si, Al, Na, K, and O. Figure 3.7 (b – g) show the enlarged regions of spectra corresponding to C1s, Si2p, Al2p, Na1s, K2p3, and O1s, respectively. The spectrum for C1s may be attributed to the three overlapping peaks, as shown in Figure 3.7 (b). The peaks at 284.8 and 288.1 eV are most likely due to C-C and C-O bond of hydroxyl C-OH, respectively. The existence of OH group on the PCM surface can potentially mitigate super cooling [239]. The precursor hydrocarbon and

residual carbon also contribute to the C1s peak in the XPS spectra. The spectra in Figure 3.7 (c) show that the binding energies of Si2p are 102.73 eV and 103.26 eV, respectively. A single XPS peak at 531.97 eV due to O1s, shown in Figure 3.7 (g), is observed for the as-prepared sample, which is most likely due to the bonding of hydroxyl groups with Al₂O₃O and KOH. The XPS spectra of the ExP also show peaks due to K2p₃, Na1s, and Al2p. The XPS spectra also show that chlorine or nitrogen are not present in the ExP sample, implying that the starting reagents possess the desired purity.

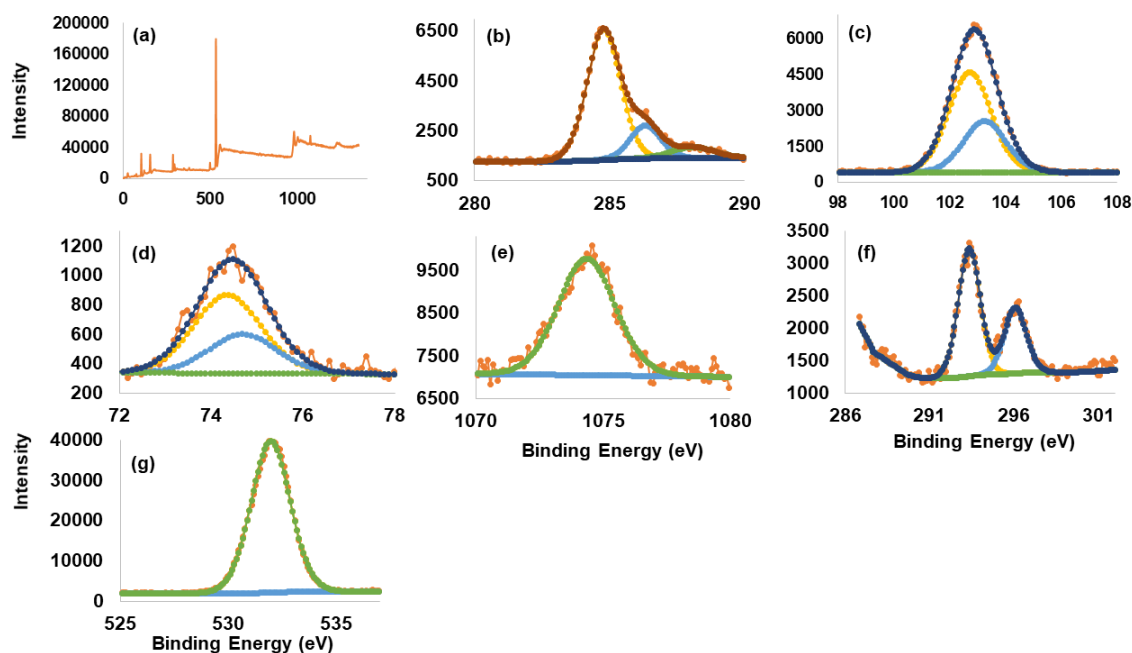


Figure 3.7 XPS spectra of ExP: (a) survey spectrum, (b, c, d, e, f and g) C1s, Si 2p and Al 2p, Na1s, K2p₃ and O1s regions, respectively.

3.5.6 Compatibility of PCM

As the synthesized PCM has to be kept in an appropriate container for later use, its compatibility with several materials used to fabricate containers was evaluated. For this purpose, sheets of copper, galvanized iron, stainless steel, aluminum, and tin, shown in

Figure 3.8 (a – e), were exposed to atmospheric conditions while they were in contact with the PCM. Figure 3.8 shows the ExPP specimens prior to (a' – e') and after five months of exposure (a'' – e'') to atmospheric conditions (May to September, the highest temperature 50 °C and the lowest of about 15 °C). The PCM specimens were placed on the upper surface of the metal sheets and their surface properties were characterized after exposure under atmospheric conditions of high solar radiation and humidity for five months. There was no change in color of any of the sheet samples that were in direct contact with PCMs, implying that the metal substrate was not affected by the PCM. Also, there was no change in the weight of the specimen due to the atmospheric exposure. The results indicate that OAP, SCP and ExPP are compatible with Cu, galvanized iron, stainless steel, Al and Sn and as such these metals can be used to fabricate containers for long-term storage of the prepared PCM.

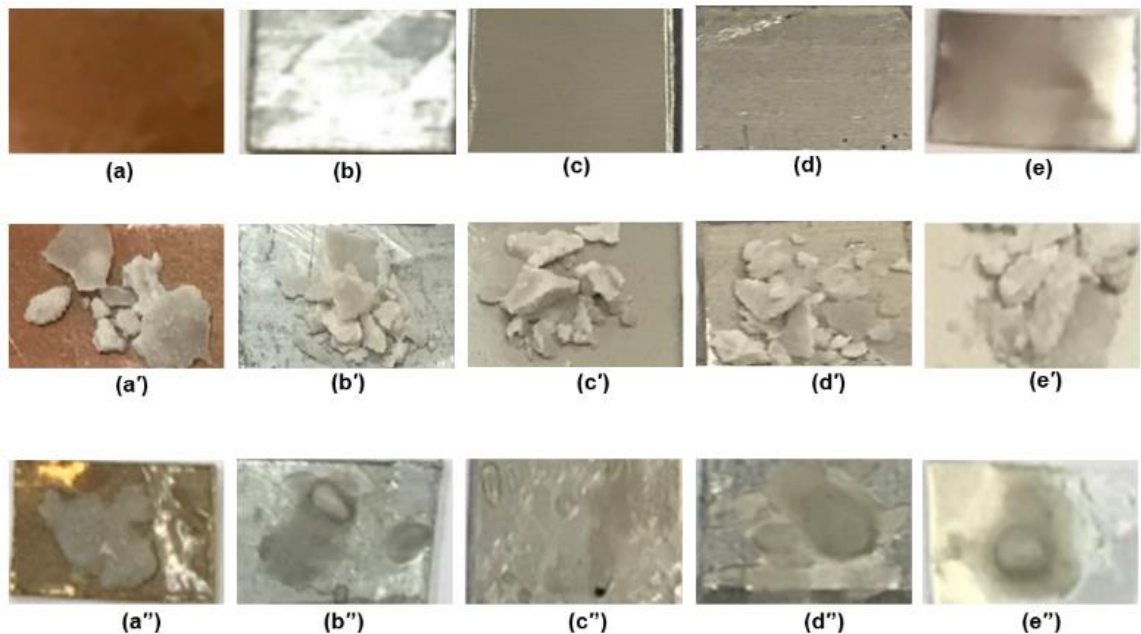


Figure 3.8 Photographs of (a) Copper, (b) Galvanized steel, (c) Stainless steel (d) Aluminum, and (e) Tin metal sheets embedded in ExPP samples before (a', b', c', d' and e') and after (a'', b'', c'', d'' and e'') five months of exposure at atmospheric conditions (highest temperature May to September, 50 °C; lowest temperature, 10 °C).

3.5.7 Thermal-resistance of the prepared ss-PCMs

The thermal resistance of a PCM is one of the important factors to be considered in the selection of a PCM. The PCM composite should possess sufficient thermal resistance even at elevated temperature. TGA technique was used to evaluate the thermal resistance of the developed ss-PCMs. Figure 3.9 shows the weight loss recorded during TGA of PEG, OAP, SCP, and ExPP. ExPP is thermally stable above 800 °C, as seen from TGA curve, making it an outstanding matrix for the encapsulation of organic PCMs. The PEG decomposes in a single stage within a temperature range of 380 – 800 °C. Under the heating process, if the melted phase of the ss-PCM is decomposed in more than one stage (2nd and 3rd stages), the alkaline oxide components can be identified. The first thermal decomposition of OAP is between a temperature range of 130 and 230 °C due to the evaporation of PEG in the composite, and the ss-PCM weight loss is approximately 62% at this point. The loss is consistent with the PEG fraction encapsulated (60 wt.%) in the composite.

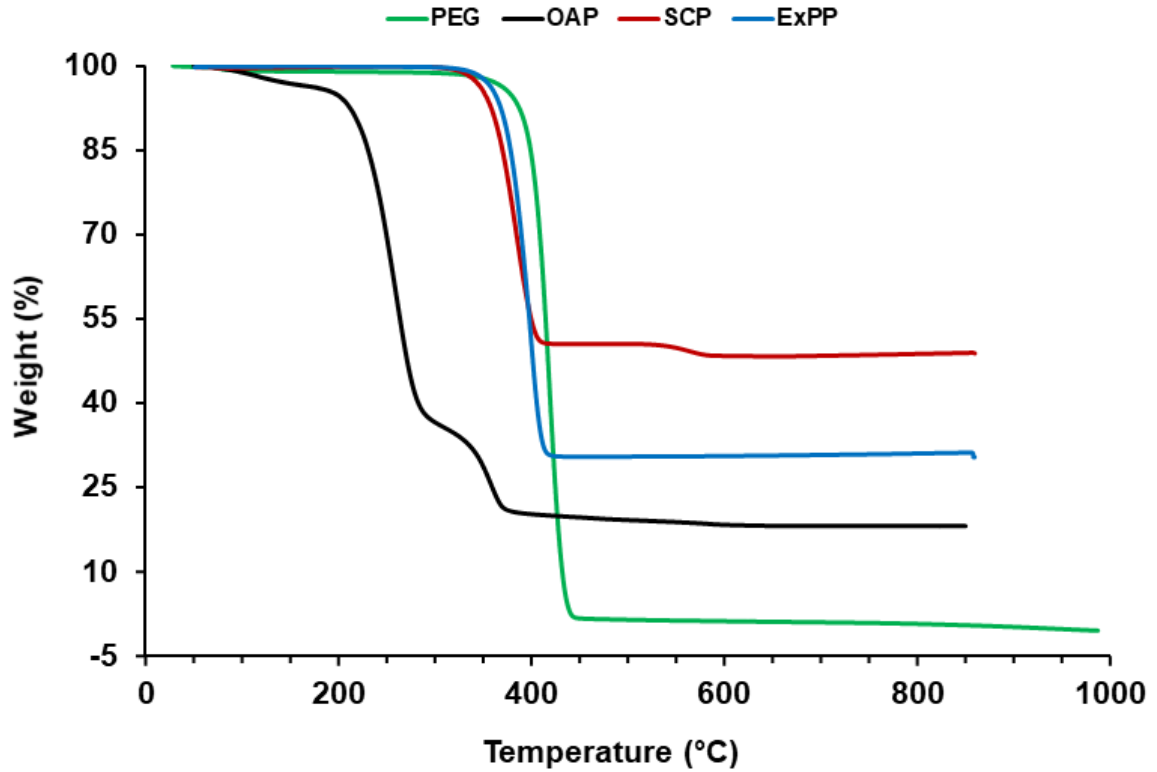


Figure 3.9 TGA curves for PEG, OAP, SCP and ExPP composites

3.5.8 Thermal Conductivity

A high thermal conductivity is a prerequisite for TES applications and thermal regulation of a PCM. A material with low thermal conductivity has two disadvantages: (i) delays the thermal storage response and (ii) releases latent heat. Hence, the conductivity of PCMs must be increased for their efficient application. For practical use, a low thermal conductivity of PEG is not desirable [240]. However, the conductivity of PEG can be improved by mixing it with inorganic porous materials, such as carbon nanotubes, or graphene [241]. As listed in Table 3.3, the thermal conductivity measurements of PEG, OAP, SCP, ExPP, ExPP/CNT(0.5%), and ExPP/CNT(1%) is 0.230, 0.791, 0.547, 0.153, 0.453, and 0.485 W/m.K, respectively. The OAP exhibited the highest increase in the

conductivity of 224% than that of PEG; this may be attributed to the high carbon content of OA compared with other materials. Secondly, SCP has a conductivity of 0.547 W/m.K, however, it has the lowest latent heat among the developed ss-PCMs. The best sample in terms of enthalpy (ExPP) has a lower conductivity than PEG, this trend may be attributed to the poor conductivity of ExP (0.04 – 0.065 W/m.K) [3]. Consequently, CNTs were added to enhance the conductivity of ExPP. However, the addition of 0.5% CNT improved the thermal conductivity of ExPP by more than 97% compared to PEG, while only additional 7% improvement in the conductivity was noted in the composite due to the addition of 1% CNT compared with the addition of 0.5% CNT. The PEG:ExP ratio in ExPP/CNT(0.5%) composite is 0.5:0.2 with 0.5% by weight of CNT. This PEG:ExP ratio offers the best PEG impregnation. Consequently, CNT has a significant impact in improving the conductivity of the composite material. However, an interesting feature of the conductivity enhancement of ExPP/CNT(0.5%) is that it is more than that of ExP/paraffin/CNT(0.5%) reported in Ref. [237]. The density of ExP/paraffin/CNT(0.5%) [237] and ExPP/CNT(0.5%) is 1.025 g/cm³ and 1.497 g/cm³, respectively. As the heat transfer is faster at higher density, the increased thermal conductivity of ExPP/CNT(0.5%) is most likely due to its higher density. Thus, it is noticeable that the incorporation of CNTs significantly improved the conductivity of the PCM composites without affecting its TES properties, compatibility or thermal stability.

Table 3.3: Thermal conductivity of PEG, OAP, SCP, ExPP, ExPP/CNT(0.5%) and ExPP/CNT(1%)

Material	Thermal conductivity (W/m.K)	Reference
PEG	0.230 ± 0.03	This study
OAP	0.791 ± 0.03	This study
SCP	0.547 ± 0.03	This study
ExPP	0.153 ± 0.03	This study
ExPP/CNT(0.5%)	0.453 ± 0.03	This study
ExPP/CNT(1%)	0.485 ± 0.03	This study
PEG	0.263	[5]
PEG	0.058	[5]
PEP (PEG/ExP)	0.161	[5]
PEPC (PEG/ExP/Carbon)	0.479	[5]
ExP	0.05	[237]
Eicosane (C20)	0.22	[237]
ExP/C20	0.15	[237]
ExP/C20/CNT0.3%	0.19	[237]
ExP/C20/CNT0.5%	0.24	[237]

ExP/C20/CNT1%	0.32	[237]
Paraffin (RT27)	0.166	[219]
RT27/ExP	0.167	[219]
RT27/ExP/SL	0.149	[219]
RT27/ExP/SL/AL	0.247	[219]
PEG6000	0.212	[220]
GNS/PEG	0.257	[220]
Ag-GNS/PEG-1	0.317	[220]
Ag-GNS/PEG-2	0.337	[220]
Ag-GNS/PEG-3	0.367	[220]
Ag-GNS/PEG-4	0.414	[220]

As the working temperature of PEG and paraffin based PCMs are quite similar and have been utilized for building applications, their performance was compared. Tables 2 and 3 compare the findings of this study to those of other PCMs that have been reported in the literature. Porous inorganic materials, such as SiO₂ [242] and MgO [240] have been evaluated to confine PCMs to ensure the prevention of leakage. However, their results are not conclusive and the authors have not provided some important performance parameters [240,242]. Zhang et al. [5] developed a PEPC with a layer of carbon that has thermal

conductivity of about 0.479 W/mK. This indicates that the conductivity in the presence of a carbon layer is not as high as that with CNTs.

Several studies have reported that incorporating CNTs within PCMs improved their absorption capacity, thermal stability, compatibility, and thermal conductivity [219,242]. Karaipekli et al. [237] used CNT to improve the conductivity of ExP/paraffine composite. For instance, the best performing PCM with ExP/C20/CNT1% has an enthalpy and conductivity of 157.4 J/g and 0.32 W/m.K, respectively. Furthermore, the eicosane (C20) cost is higher than that of PEG. Another available paraffin (RT-27) is not appropriate for building applications, as its conductivity and latent heat are very low, 0.247 W/m.K and 50 J/g, respectively [219]. In another study on paraffin/ExP composite [221] it has been reported that its enthalpy is low (Table 2). In addition, outstanding data published by Zhang et al. [5] discussed the use of Ag-graphene nanosheets along with PEG for TES applications. The best thermal conductivity of 0.414 W/m.K was obtained for Ag-GNS/PEG-4, with a latent heat of 166.1 J/g. However, the produced composite has high super cooling values (Table 3.2), and it is not practical for real applications as graphene is very expensive than the CNTs. Compared to the reported values discussed earlier, the high enthalpy and thermal conductivity of ExPP developed in this study indicate that this material is highly useful for building applications.

3.5.9 Leakage

The PEG and PCM composites were compressed into disk of 20 mm diameter and placed on a filter paper on a laboratory heating platform. As shown in Figure 3.10, ExPP and ExPP/CNT(0.5%) composites did not melt even after heating them at a temperature of 80 °C for 10 min, indicating no leakage of PEG. However, little leakage was observed in the

OAP and SCP samples after 10 min of heating at 80 °C. PEG, on the other hand, begins to decompose even before reaching 80 °C. This indicates that large pores in OA and SC are not appropriate to retain the PEG. Consequently, PCMs based on OAP and SCP are not able to store the liquid PEG efficiently, resulting in its leakage. Moreover, the lower latent heat of OAP and SCP compared to that of ExPP and ExPP/CNT(0.5%) (Table 3.2) also support these results. Consequently, a comprehensive study on the characterization and properties of ExPP/CNT(0.5%) will be discussed.

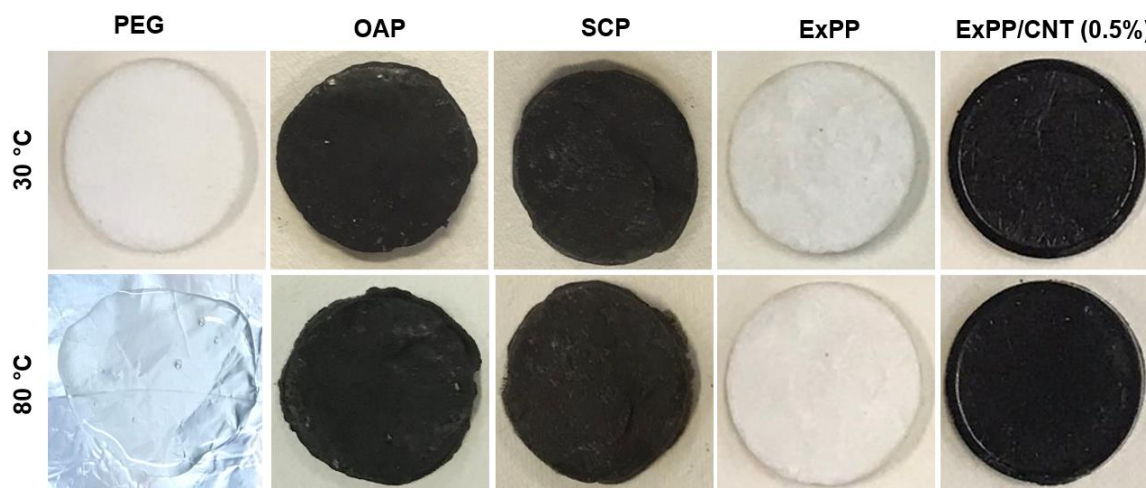


Figure 3.10 Digital photos of PEG, OAP, SCP, ExPP, and ExPP/CNT(0.5%) composites at different temperatures

Figure 3.11 shows the DSC results for ExPP with (0.5%) and (1%) CNTs. The latent heat of ExPP/CNT(0.5%) is 132.1 J/g, which is better than that of ExPP/CNT(1%) at 121.9 J/g. The DSC data for ExPP/CNT(0.5%) exposed to thermal cycles is depicted in Figure 3.12. Thermal cycling had no effect on the exothermic and endothermic peaks, showing that the PCM composite is thermally stable and has a long-life cycle, as illustrated in Figure 3.12. This demonstrates that PEG can maintain nearly a steady phase shift of enthalpies and

temperature over multi-DSC scan cycles. As a result, the developed system can be utilized to store and release enthalpy in applications that are subjected to repeated heat/cool cycles. The images in Figure 3.13 also clearly show the presence of CNT, ExP, and PEG. The liquid PEG appears to have penetrated the carrier because of the surface tension and capillary force. However, few PEG chains cannot penetrate the ExP due to its micro- and nano-sized pores. The existence of meso/macropores could facilitate the PEG adsorption.

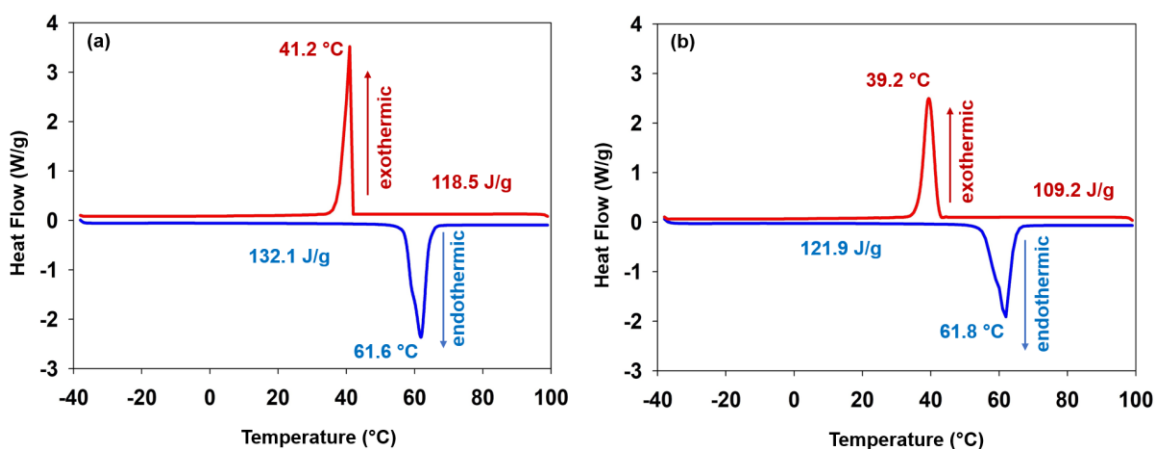


Figure 3.11 DSC curves of: (a) ExPP/CNT(0.5%) and (b) ExPP/CNT(1%) composites

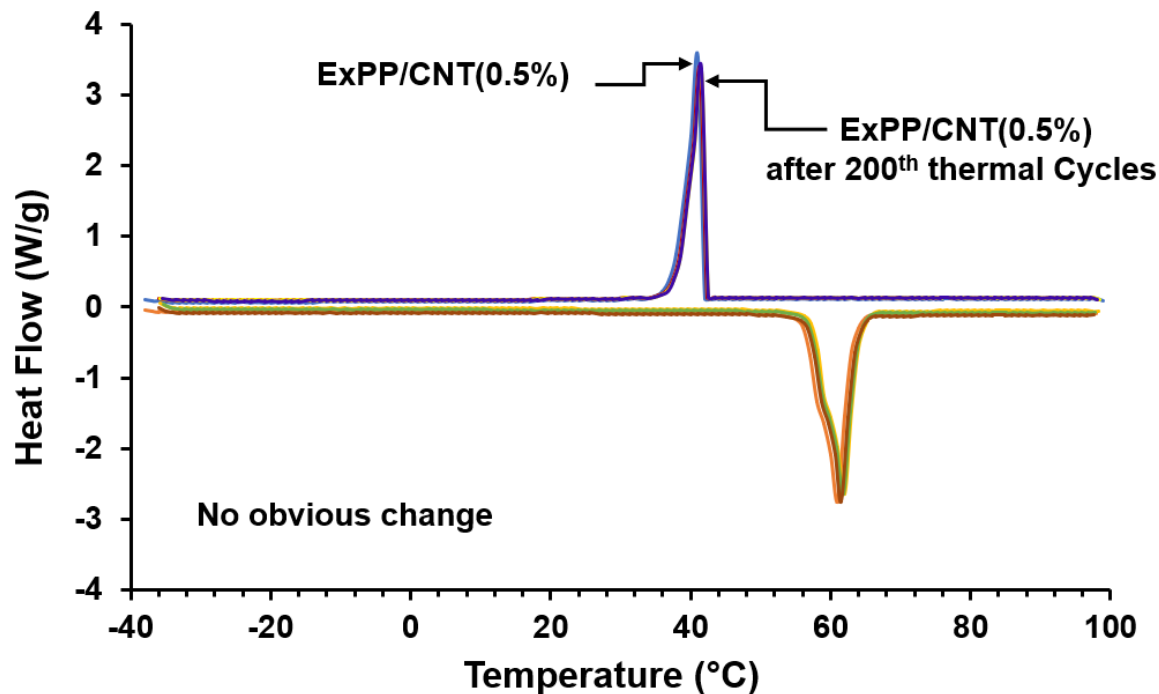


Figure 3.12 DSC cycling curves of ExPP/CNT(0.5%) PCM samples, cycled 200 times

The results of DSC shown in Figure 3.12 and the FE-SEM images depicted in Figure 3.13 indicate that ExPP/CNT(0.5%) PCM can maintain its structure even after vigorous thermal cycling. Even after 200 cycles, extra peaks are not observed in the DSC curves. A careful examination of the FE-SEM image indicates that the particles of CNT, ExP, and PEG are well mixed. The ExP and PEG are agglomerated and/or clay type powders probably formed in a single crystal, in which few CNTs are visible (marked with a red circle in Figure 3.13). The FTIR and DSC results also suggest that the synthesized PCM has exceptional thermal stability. This finding is important considering that the most significant property of a PCM for practical applications is its thermal stability.

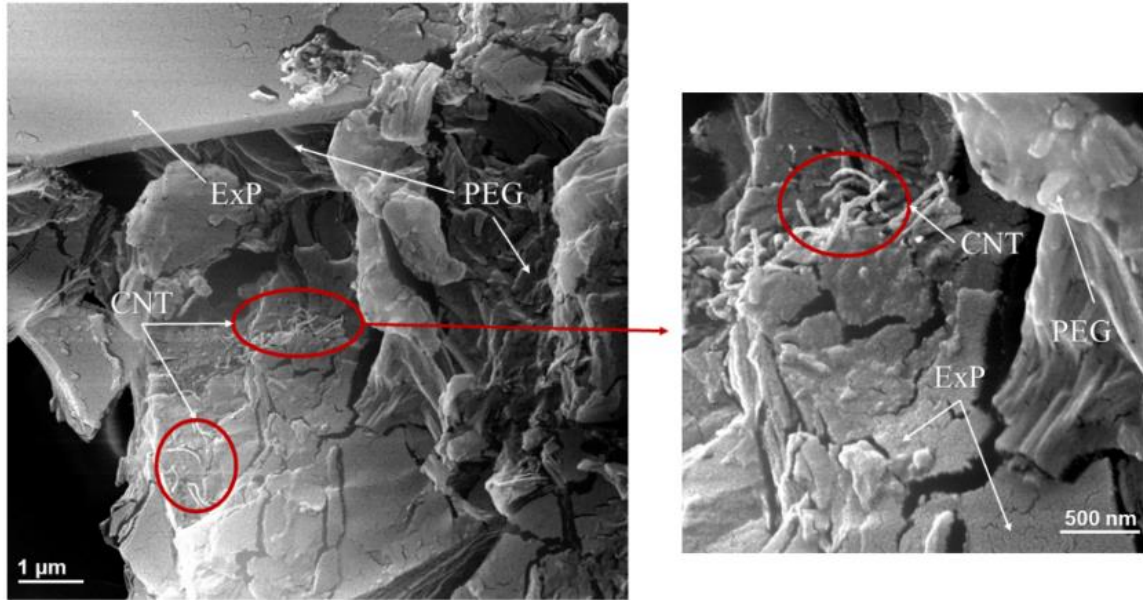


Figure 3.13 Morphology of ExPP/CNT(0.5%)

3.5.10 Solar to thermal energy storage efficiency (TES)

The ExPP/CNT(0.5%) PCM can also be employed for TES and solar to thermal energy conversion due to its good optical properties. ExPP/CNT (0.5%) nanoparticles and/or the porous structure of ExP boost PEG light absorption throughout the bandwidth, increasing it to around 300 nm. The ExPP/CNT (0.5%) composite has excellent photo thermal conversion efficiency caused by the selective and improved full band absorption. The UV-VIS absorption spectra of ExPP/CNT (0.5%) was more than that of pure PEG. The new approach can calculate the solar energy conversion into thermal energy and the energy storage capacity of PCMs at the same time due to the high enthalpy and good optical features of the developed PCM [220]. Furthermore, ExPP/CNT (0.5%) absorbs light across the full visible spectrum, which is significantly higher than pure PEG. The solar to thermal energy conversion was assessed using temperature recorders placed under solar simulators. Figure 3.14 (b) depicts a temperature rise that could be linked to the high activity of

ExPP/CNT (0.5%) and/or PEG due to photon emission and molecular stove creation. The temperature of PEG increased as a result of infrared light from the sun. An optimum value was discovered after long-term radiation exposure. This was an indication of TES because of the composite phase change. As a result of the energy release, a cooling stage appeared in the cooling process.

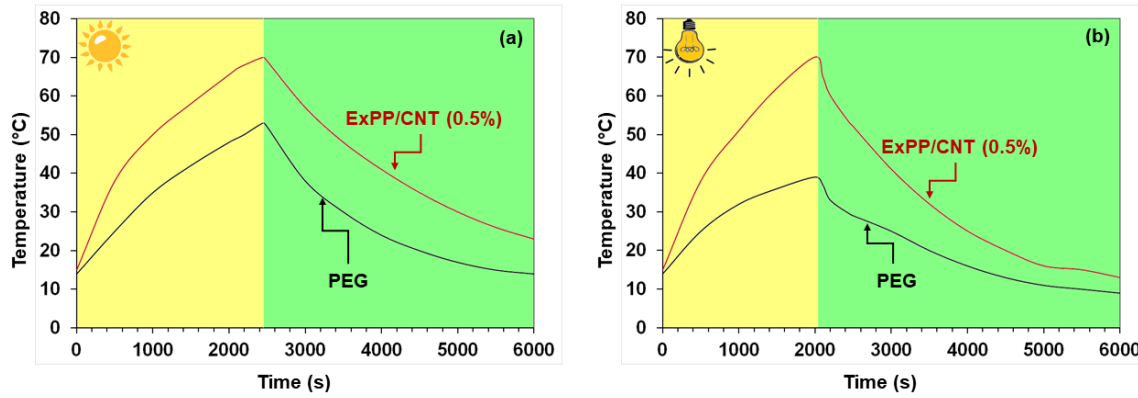


Figure 3.14 (a) Solar to thermal energy conversion curves of PEG and ExPP/CNT(0.5%) composites under sunlight radiation ($I = 120 \text{ mWcm}^{-2}$) and (b) Light to thermal energy conversion curves of PEG and ExPP/CNT(0.5%) composites. ($I = 98 \text{ mWcm}^{-2}$).

Thermal energy can be used to heat composites, and then the stored energy can be maintained by the composites through phase transitions in the PCMs. Equation 3.5 can be used to compute the solar to thermal energy storage efficiency (η) of TES:

$$\eta = \frac{m\Delta H}{IS(T_t - T_f)} \quad (3.5)$$

Where: ($T_t - T_f$) is the difference between the transition time of start and end phases, I is the optical power density, S is the radiated field, m is the sample weight, and ΔH is the melting enthalpy. ExPP/CNT(0.5%) has a solar to thermal efficiency of 75.5%. These findings suggest that photo thermal energy can be stored well when compared to results reported for carbon-based PCMs of approximately 40%-60% [243]. The ExPP/CNT(0.5%)

composite was exposed to sunlight to simulate the real application and to evaluate its performance. The temperature of the PCM increases after a long exposure under solar light. An optimum value was obtained for increasing and decreasing temperature, as shown in Figure 3.14 (a). During a phase conversion, this technology turns solar energy into heat energy. ExPP/CNT(0.5%) has a high latent heat value, indicating that the fabricated PCM has a high thermal storage capacity that can be used in real applications. Furthermore, the melting and freezing temperatures in the energy conversion curves are congruent with the heating and cooling temperatures on the plateau (Figure 3.15 (a) and (b)). The heating time, Fig. 3.15 (a,) required to achieve a temperature of 60 °C for ExPP/CNT(0.5%) composite and PEG were 1326 s and 2017 s, respectively. Consequently, the heating time decreased by 34.3%. Similarly, solidification time for a temperature of 35 °C(Fig. 3.15 (b)) decreased by 16.3%. Further, the time to solidification for PEG and ExPP/CNT(0.5%) decreased from 1780 s to 1490 s, respectively. This shows that the improvement in the thermal conductivity of ExPP/CNT(0.5%) was reflected in the heating and solidification process. This increase of transfer rates due to the addition of CNTs can improve the efficiency and decrease the time of storing (charging) and releasing (discharging) process.

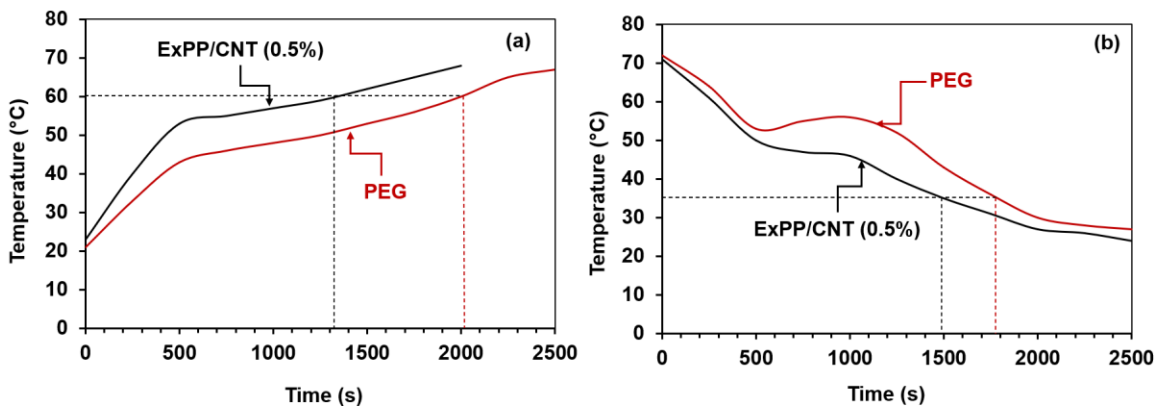


Figure 3.15 ((a) Heating and (b) freezing temperature curves of ExPP/CNT(0.5%) and PEG.

3.6 Conclusions

A comprehensive study was conducted to evaluate the possibility of using three materials, namely oil ash (OA), scoria (SC), and expanded perlite (ExP) in conjunction with polyethylene glycol as phase change materials buildings. The thermal and physico-chemical properties of the selected materials was evaluated utilizing a wide array of analytical techniques. Among the materials investigated, ExPP/CNT(0.5%) exhibited the best performance, showing that it is a viable material for thermal energy storage system. Further, the developed ExPP composite is a promising PCM for TES in energy-efficient buildings due to its remarkable ability of rapid energy storage/release combined with good chemical stability and thermal reliability. Further, ExPP does not have leakage problems, super cooling is minimized, conductivity is high and all other properties that play a crucial role in maintaining building comfort are superior. However, it has low thermal conductivity which limits its application as an energy storage system. OAP and SCP possess a good thermal conductivity, however, they have lower ability to encapsulate and maintain PEG due to a large porous structure, which leads to leakage problems.

Compared to other PCM composites, the developed ExPP/CNT(0.5%) PCM offers greater enthalpy, superior storage capacity, and minimum super cooling. The structural properties and the pore network of ExPP/CNT (0.5%) composite prevents the leakage of liquid PEG during service. Even after 200 cycles of heating and cooling, the ExPP/CNT (0.5%) system displays repeatable performance and has the ability for energy storage/release without any observable change. Also, due to its low-cost, easy availability of raw materials, the developed ExPP/CNT (0.5%) is less expensive than standard inorganic/organic microencapsulation materials, such as PEG, ExP and CNT. The conversion, storage, and

usage of solar energy are some of the key challenges in establishing a renewable energy network. Based on the findings of this study, the developed novel sunlight-driven composite can be utilized to harness solar energy cleanly and efficiently and bridge the gap in the deployment of a renewable energy system.

3.7 Recommendations

The recommended applications of the developed PCMs are summarized below:

ss-PCM	Recommended application
OAP	Non-structural interior and exterior walls in buildings in moderate climatic conditions
SCP	Non-structural interior walls in buildings in moderate climatic conditions
ExPP	Non-structural elements in buildings in hot climatic conditions
ExPP/CNT(0.5%)	Non-structural elements in buildings in hot or moderate climatic conditions
ExPP/CNT(1%)	Non-structural elements in buildings in hot or moderate climatic conditions

CHAPTER 4

SHAPE-STABILIZED PHASE CHANGE MATERIAL FOR THERMAL ENERGY STORAGE: Sr^{+2} DOPED BaCO_3 MATRIX INCORPORATING POLYETHYLENE GLYCOL

4.1 Abstract

An Sr^{2+} -doped BaCO_3 matrix incorporating polyethylene glycol (PEG-6000) was developed using a simple impregnation process to build a shape-stabilized functional phase transition composite for application in thermal energy storage systems. A direct hydrothermal process was used to prepare a unique anhydrous rhombohedral BaCO_3 . The developed rhombohedral material, characterized following a hydrothermal reaction in the presence of 5 mol% Sr^{2+} , was used to prepare extremely tiny porous particles (5% SrBaCO_3). The 5% SrBaCO_3 powder was hydrothermally produced and utilized to encapsulate PEG to create a phase change material (PCM) that prevents leakage of PEG during phase change. The shape-stabilized composite PCM (ss-PCM) that was prepared with nano- and micro-sized porous SrO powder and containing pure BaCO_3 exhibited consistent and superior performance throughout a significant number of heat cycles. DSC results indicated that the melting temperature of the PEG/5 BaCO_3 is 60.17 °C, and the latent heat is 148.8 J/g. The R% (Impregnation ratio) and $E_{\text{eff}}\%$ (Efficient energy per unit mass of PEG) values of 5% SrBaCO_3 were more than those of 10% SrBaCO_3 and 15% SrBaCO_3 , probably due to the presence of micro- and macro-pores and high pore volume. Additionally, it was clear from the XRF, EDX, and XPS data that Ba^{2+} segregation in 5%

SrBaCO₃ was considerably less than that in 10% SrBaCO₃ and 15% SrBaCO₃. Compared to the long-established ss-PCMs, the developed composites exhibited much greater thermal enthalpy, higher thermal conductivity, and lesser super cooling. The presence of OH⁻¹ on the surface of the PCM contributed to a reduction in the super cooling. Furthermore, the supporting materials improved the thermal conductivity of the PEG, overcoming the organic PCM's poor thermal conductivity. As pure PEG is infused in 5% SrBaCO₃, its super cooling effect is diminished by 15.5%. Overall, the PCM with 5% SrBaCO₃/PEG preserves its capacity to store and release energy without a substantial modification its properties after multiple thermal heating and cooling cycles.

4.2 Introduction

The extensive rise in greenhouse gas emission and increasing fuel prices are the key driving causes behind attempts to utilize diverse renewable energy sources more efficiently. Direct solar radiation is regarded as one of the most promising sources of energy in many places of the world [194]. Among various methods for thermal energy storage (TES) systems, latent heat storage (LHS) system is considered the best compared with other systems due to its high energy storage density [244]. Consequently, the use of LHS system has increased in the last decades, due to high energy consumption, which may increase up to 48% in 2040 [245]. TES can control the storage and release of energy in the form of heat. This action controls the high variation in the temperature that leads to high conservation of energy.

The organic PCMs have low super cooling and volume change and phase segregation problems compared to inorganic PCMs. Furthermore, they are compatible with a variety of building materials, chemically stable without toxicity and recyclable. Recent research has indicated that they exhibit significant flammability, rapid volume fluctuations, low

thermal conductivity, and leakage issues [102,246]. Expanded graphite (EG), polymers, and metal foams are being investigated as suitable support matrices for creating shape-stabilized composite PCM (ss-PCMs) [197,198,247,248]. However, the small surface area of these materials, inhomogeneous pore distribution, and time-consuming preparation processes render them uncommon for use. Porous materials, such as CaCO_3 , SiO_2 and MgO have also been explored due to their ability to retain the molten PCMs and prevent leakage [249] [241] [240].

Polyethylene glycol (PEG) is an attractive candidate, among the organic PCMs, to be used as TES material in building applications. It is a solid-liquid organic PCM possessing a wide range of melting temperature (from 3 to 69 °C) corresponding to different molecular weight. Moreover, it has a small volume change, low super cooling, chemically and physically stability without gas generation and cost effective [218,250]. ss-PCMs that can overcome the disadvantages of organic PCMs can be developed by incorporating a supporting material to provide a more efficient media that can be used in a wide range of applications, such as electric regulation, battery management, clothing, building comfort and food industry [251,252]. Several studies used different types of supporting materials along with PEG to prepare an ss-PCM.

Since CaCO_3 has a porous nature, it is an excellent supporting matrix for PCMs. According to Mesalhy et al. [253], the melting/freezing rate of PCMs has been positively influenced by the porous matrix. Metal foams and expanded graphite were used by Wu and Zhao [254]; representing the porous support, as well as NaNO_3 ; representing the PCM, to exhibit higher heat storage/transfer capability of an ss-PCM. In addition, an ss-PCM was developed by Qian et al. [212] using PEG and mesoporous calcium silicate. This material

was able to decrease the solidifying-melting duration and super cooling range of pure PEG [212]. On the other hand, the melting latent heat obtained is low (110.2 J/g).

It has been reported that BaCO_3 can improve the sulfate-resistance of cement paste [255]. Xiong et al. [256] concluded that the addition of BaCO_3 increases the compressive strength of cement paste at early ages and also improves its sulfate-resistance. Similarly, Carmona-Quiroga et al. [257] explored the effect of reactivity and degree of dispersion of the addition of different fineness particles of BaCO_3 in the manufacture of sulfate-resistant cement with different mixing procedures. They concluded that cement containing 15 wt% of BaCO_3 exhibited the highest sulfate-resistance [257]. Moreover, other researchers have reported that higher BaCO_3 content increased the porosity of cement mortar thereby improving the sulfate-resistance [258]. Jamaluddin et al. [259] reported that Barium Strontium Titanate ($\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, BST) with 1%, 2%, 3%, 4%, and 5%, strontium modified the lattice parameter and tetragonality of crystal BST. The grain size and dielectric constant of BST were also altered. Furthermore, the impact of Sr doping on the structure and dielectric characteristics of BaTiO_3 ceramics has been investigated and verified by Arshed et al. [260]. It was reported that barium carbonate is highly stable thermally [261,262].

From the limited literature cited earlier, it is evident that ss-PCM incorporating porous BaCO_3 is expected to produce desirable results. Consequently, hydrothermal synthesis was used to prepare the ss-PCM. BaCO_3 was used as it produces nano-crystalline porous low-temperature materials at a reasonable cost [263]. Furthermore, the hydrothermal process provides a cheaper option that can replace the sol-gel technique, which requires expensive starting ingredients. As a result, Sr-doped BaCO_3 will be an ideal matrix for ss-PCM applications. Consequently, porous powders containing Sr^{2+} doped with BaCO_3 were

produced under hydrothermal conditions by adjusting the molar ratio of Ba and Sr nitrates. A PCM with PEG supported on freshly synthesized Sr^{2+} -doped BaCO_3 exhibits chemical stability with a high latent heat.

4.3 Materials and Methods

4.3.1 Chemicals

Polyethylene glycol (MW 6000) used as the PCM and solvent grade ethanol were purchased from Sigma-Aldrich Co., St. Louis, MO, USA. $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and BaO were procured from BDH Chemical Co. and $(\text{NH}_4)_2\text{CO}_3$ were purchased from Merck (Darmstadt, Germany). The cost of PEG is about \$1.85 per kg.

4.3.2 Hydrothermal Method

Three $\text{Sr}(\text{NO}_3)_2$ -doped BaO support matrices were synthesized with a $\text{Sr}(\text{NO}_3)_2$ concentration of 5 mol %, 10 mol %, and 15 mol %, with the Sr:Ba molar ratios of 5:95, 10:90, and 15:85, respectively. All the materials were dissolved in a suitable volume of deionized water. The sought quantity of the $(\text{NH}_4)_2\text{CO}_3$ solution (4.1 mol cm^{-3}) was supplied for co-precipitating the ions. Gentle stirring of the solution was continued for 12 hours while keeping the pH constant at 13. The precursor suspension was fed into a 500 cm^3 plastic container of the hydrothermal reactor, positioned inside a steel vessel. After no leakage from the system was confirmed, the implementation of the hydrothermal reaction took place within 24 hrs in the vessel at 200 °C. At the end of the reaction, the reactor was left to cool down to room temperature in 2 hrs. Afterwards, ethanol and deionized water were used to wash the resulting product 3-5 times and then exposed to a temperature of 120 °C to dry during night. Three compositions of $\text{Sr}(\text{NO}_3)_2$ doped with BaO were

synthesized, and the as-synthesized samples were labelled as 5SrBaCO₃ (5% Sr), 10SrBaCO₃ (10% Sr), and 15SrBaCO₃ (15% Sr).

4.3.3 Preparation of Composite PCM

The SrBaCO₃/PEG PCM composite was prepared by dissolving 0.5 g PEG-6000 and 0.2 g SrBaCO₃ in 50 mL ethanol, stirring for 30 minutes to thoroughly mix the organic polymer and inorganic support, and then sonicating it for another 30 minutes. Subsequently, the ethanol was allowed to evaporate at 80 °C for 24 hours while stirring the PCM. The composition of 5SrBaCO₃/PEG, 10SrBaCO₃/PEG, and 15SrBaCO₃/PEG composite PCMs was synthesized and studied.

4.3.4 Characterization

A high sensitivity JSX-3400RI model X-Ray Fluorescence Spectrometer (XRF) was used to determine the elemental composition. A Bruker D8 advance diffractometer system (Berlin, Germany) was utilized to determine the mineralogical composition of the developed PCM. The operating voltage and the current of the diffractometer were maintained at 40 kV and 40 mA, respectively. The XRD patterns were noted at $\lambda = 1.5405$ Å for Cu K α emission with monochromator graphite. The data were collected over 10 – 70° 2 θ at a scan rate of 3 2 θ /min⁻¹. The Fourier transform infrared (FT-IR) spectra were recorded with the use of KBr pellet technique with a Bruker FT-IR spectroscope (Bruker AXS Analytical X-ray Systems GmbH, Berlin, Germany). The morphology was recorded using field emission scanning electron microscope (FESEM: TESCAN LYRA3, Brno, Czech Republic). The images were collected at an acceleration voltage of 10 kV. The energy dispersive X-ray spectra (EDS) were determined using an Oxford Instruments X-mass detector fitted with a Lyra3 TESCAN FESEM (JEOL USA Inc., Peabody, MA,

USA). The samples were scanned to obtain TEM images by making use of a transmission electron microscope (JEOL Inc., JEM 2011, Peabody, MA, USA) with a $4k \times 4k$ CCD camera (Ultra Scan 400SP, Gatan) working at 200 kV. A Surface Enhanced Raman Scattering (SERS) spectroscopy (LabRAM HR Evolution from Horiba France SAS) was used to collect the Raman spectra. A laser source of 532 nm with a power of 25 mW was adopted. Raman spectra shift ranges were collected in the range from 500 to 4000 cm^{-1} . A NOVA-1200 device (JEOL USA Inc., Peabody, MA, USA) was utilized to determine the specific surface area, pore diameter, and pore volume of the samples. The BET surface area was calculated using a Tristar II-3020 machine.

The pore size distribution was determined using the Barrett–Joyner–Halenda isotherm. The thermogravimetric analysis (TGA) of the samples was performed using a Shimadzu thermal analyzer (Tokyo, Japan, TA-50). The weight loss data were collected using approximately 10 mg sample and at a heating rate of 5 $^{\circ}\text{C}/\text{min}$ from room temperature to 600 $^{\circ}\text{C}$ under a dry nitrogen flow. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical composition of the samples. In this regard, an ESCALAB-250 (Thermo-VG Scientific, Waltham, Peabody, MA, USA) with Al-K radiation (1486.6 eV) was employed. The XPS spectra were recorded at ambient temperature with a pressure of 5×10^{-10} mbar maintained in the specimen chamber. DSC-Q2000 was used for the determination of the melting point, freezing point, and latent heat. The related data were extracted by heating 8.5 mg of sealed samples in an aluminum pan under an Ar gas flow rate of 20 mL/min at a heating rate of 5 $^{\circ}\text{C}/\text{min}$. The thermal conductivity of the powders was determined with circular disk samples using a TCi Conductivity Analyzer, Canada.

This equipment uses a modified transient plane source (MTPS) and the measurement method of C-Therm Technologies.

4.4 Results and Discussion

4.4.1 Elemental Composition (XRF)

Table 4.1 shows the chemical composition (wt. %) of 5SrBaCO₃, 10SrBaCO₃ and 15SrBaCO₃ determined by XRF. The Ba loss of 10SrBaCO₃ and 15SrBaCO₃ was higher than the 5SrBaCO₃ sample.

Table 4.1: Chemical composition (wt. %) of 5SrBaCO₃, 10SrBaCO₃ and 15SrBaCO₃ determined by XRF.

Component	Weight, %		
	Ba	O	Sr
5SrBaCO ₃	86.17	10.60	3.23
10SrBaCO ₃	83.18	10.79	6.03
15SrBaCO ₃	80.45	10.94	8.61

4.4.2 X-Ray Diffraction (XRD)

Fig. 4.1 displays the XRD patterns of the support matrices, (a) 5SrBaCO₃, (b) 10SrBaCO₃, and (c) 15SrBaCO₃. The diffraction peaks at 19.8, 20, 24, 24.3, 27.9, 30, 34, 34.8, 39.8, 42.2, 43.7, 45.5, 47.2 and 49.4 2θ can be correlated to the miller indices (hkl) of (110), (020), (111), (021), (002), (012), (112), (200), (220), (221), (041), (132), (113), and (222), respectively, of BaCO₃ with a card number (00-005-0378) in JCPDS standards [264,265]. Further, the data in Fig.1 (a – c) indicate that the strongest peak in all the crystals is of BaCO₃ (111). This reflects that the crystals of BaCO₃ are well oriented and grew along (111) face [265]. Several other high diffraction peaks in the XRD pattern, including (111),

indicate that the crystallinity of the BaCO₃ nano-crystallites formed is outstanding, and can be matched with TEM micrographs [265]. The XRD patterns for BaCO₃ are similar to those reported in the literature [264–268]. The XRD patterns for PCM composites (5SrBaCO₃/PEG, 10SrBaCO₃/PEG, and 15SrBaCO₃/PEG) are shown in Fig. 4.1 (e – g) while those for pure PEG6000 are shown in Fig. 1d for comparison purposes. The XRD patterns of the composites in Fig.1 (e – g) are similar to those observed for PEG6000 (Fig. 1d). The highest peaks located between (20–25°) 2θ in PEG were noted in all PCM composites. New peaks were not noted which indicate that the PEG and BaCO₃ were obtained without any chemical reaction (physical mixing only). Moreover, the intensity of peaks for pure PEG is more than those for the PCM composites. This implies that PEG occupies the pores in PCM resulting in a reduction in the crystallite size of PEG [79]. However, among the three PCM composites studied, the peak of 5SrBaCO₃/PEG is the lowest (Fig. 4.1e). This implies that a large part of the PEG has been incorporated into the pores of 5SrBaCO₃/PEG composite.

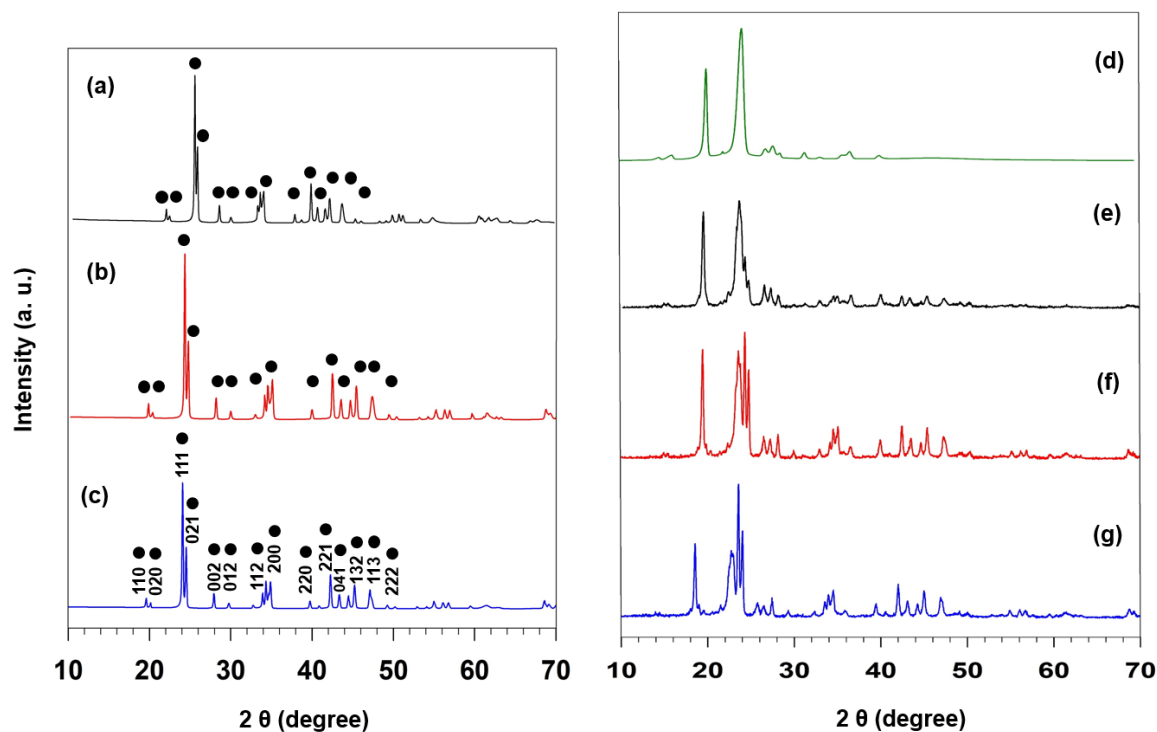


Figure 4.1 XRD patterns of: (a) 5SrBaCO₃, (b) 10SrBaCO₃, (c) 15SrBaCO₃, (d) PEG6000, (e) 5SrBaCO₃/PEG, (f) 10SrBaCO₃/PEG and (g) 15SrBaCO₃/PEG.

4.4.3 Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectra

Fig. 4.2 shows the FTIR patterns related to: (a) 5SrBaCO₃, (b) 10SrBaCO₃, (c) 15SrBaCO₃, (d) PEG, (e) 5SrBaCO₃/PEG, (f) 10SrBaCO₃/PEG and (g) 15SrBaCO₃/PEG samples captured in the range of 500 – 4000 cm⁻¹. Fig. 4.2 (a – c) illustrates the characteristic vibration peaks of CO₃⁻² within 500–3000 cm⁻¹. Sharp peaks noted at 695 and 862 cm⁻¹ are allocated to the out-of-plane and in-plane bending vibrations of the O–C–O and CO₃⁻², respectively [264]. The absorption band located at 1067 cm⁻¹ is attributed to C–O symmetric stretching vibration, whereas the IR band at 1418 cm⁻¹ is credited to an asymmetric stretching vibration of C–O bond [264–266].

Fig. 4.2 (e–g) shows composite spectra with peaks that are identical to the peaks for PEG alone (Fig. 4.2d). Similar peaks appear in Figure 4.2 (a–c) at wave numbers of 795 and 862 cm^{-1} as well as in the spectra related to the composites presented in Fig. 4.2 (e–g). This shows that the support matrix does not undergo any significant change. The FTIR spectra of the composites prove the presence of BaCO_3 and PEG peaks. Since no other peaks are evidenced, it may be presumed that only physical mixing takes place, leading to a properly mixed BaCO_3 and PEG composites.

Figure 4.3 shows the Raman spectra of: (a) 5SrBaCO_3 , (b) 10SrBaCO_3 and (c) 15SrBaCO_3 in the range of 500 – 4000 cm^{-1} . The peaks appearing at 695 cm^{-1} are attributed to the bending in plane vibrations and those at 1069 cm^{-1} are attributed to the symmetric stretching vibrations. The results are in conformance with that reported in the literature [79,269].

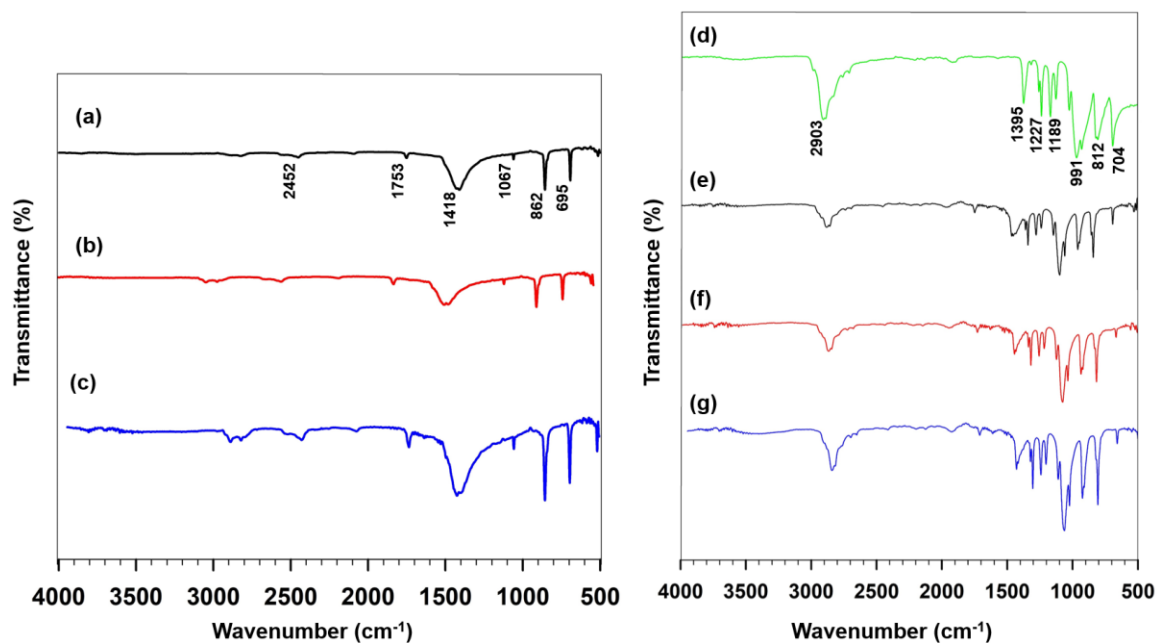


Figure 4.2 FTIR spectra of: (a) 5SrBaCO_3 , (b) 10SrBaCO_3 , (c) 15SrBaCO_3 , (d) PEG6000, (e) $5\text{SrBaCO}_3/\text{PEG}$, (f) $10\text{SrBaCO}_3/\text{PEG}$ and (g) $15\text{SrBaCO}_3/\text{PEG}$.

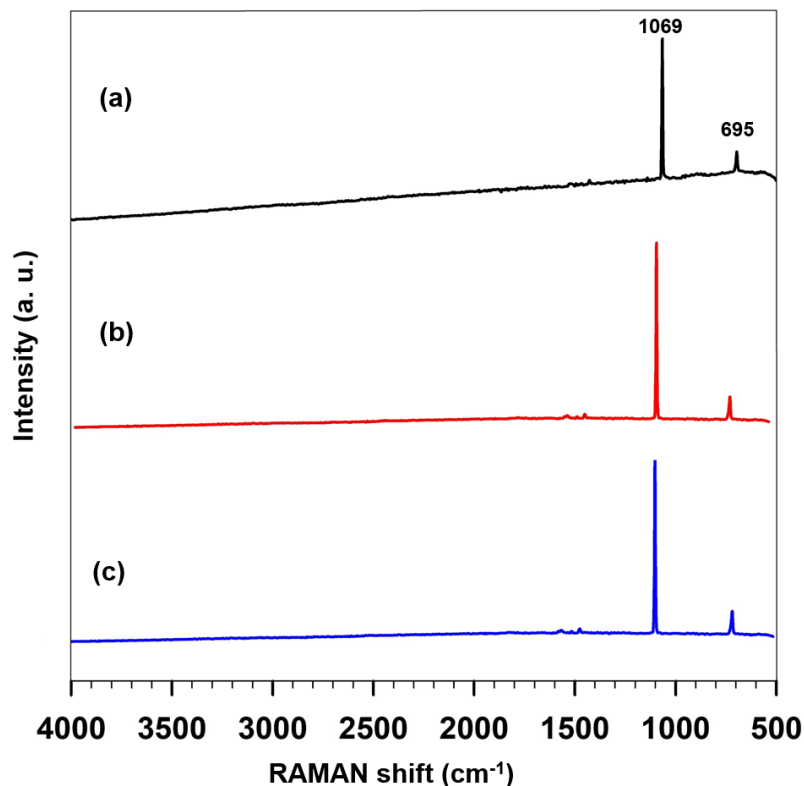


Figure 4.3 Raman spectra of: (a) 5SrBaCO₃, (b) 10SrBaCO₃, and (c) 15SrBaCO₃.

4.4.4 Field Emission Scanning Electron Microscopy (FE-SEM)

Fig. 4.4 shows the FE-SEM images of: (a) 5SrBaCO₃, (b) 10SrBaCO₃, (c) 15SrBaCO₃, and the corresponding EDS spectra (d, e, and f). The image of the as-synthesized BaCO₃ indicates that the material is made from different-sized angular particles ranging from approximately 0.1 μm to 5 μm in size.

A porous nature can be observed in the surface of the as-synthesized single-crystal BaCO₃, presumably formed due to the hydrothermal synthesis. Several layers of smaller BaCO₃ particles with a porous structure result on doping BaCO₃ with 5 mol% Sr (Fig. 4.4a). As seen in Fig. 4.4 (b), increasing the quantity of doping Sr²⁺ to 10 mol% results in bigger

agglomerated particles. The PCM with 5SrBaCO₃ contains the smallest particles among the three Sr²⁺-doped BaCO₃ matrices. On a similar trend, Fig. 4.4 (c) shows that a further increase in the quantity of Sr²⁺ leads to an increase particle size in 15SrBaCO₃ matrix.

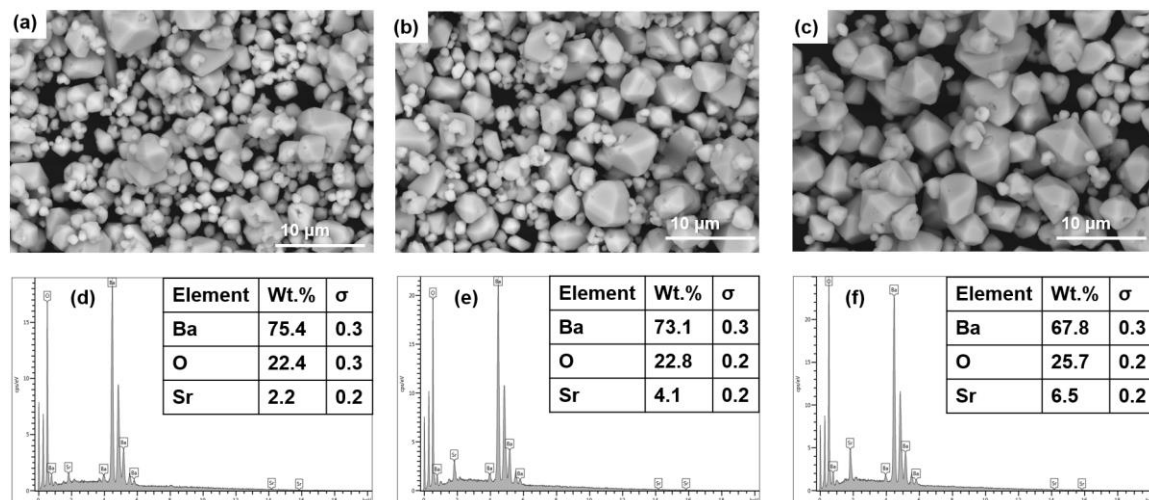


Figure 4.4 FE-SEM images of: (a) 5SrBaCO₃, (b) 10SrBaCO₃, (c) 15SrBaCO₃, and the corresponding EDS spectra (d, e, and f).

The EDS of 5SrBaCO₃, depicted in Fig. 4.4 (d), indicates the existence of Ba (75.4%), O (22.4%), and Sr (2.2%). These values are quite close to the predicted quantities of Ba and Sr, which are 95 mol% and 5 mol%, respectively. The non-uniform distribution of Ba atoms might explain the variation from the predicted values.

The findings of XRD, FTIR, and SEM of the three as-synthesized samples suggest that the 5SrBaCO₃ sample has unique characteristics. The 5SrBaCO₃ sample was then further analyzed using TEM and BET to determine the pore size distribution and surface area. All of the particles in the 5SrBaCO₃ TEM images in Fig. 4.5 are organized layer by layer. The white-circled layered region yielded the chosen area electron diffraction (SAED) pattern (Fig. 4.5b). The separating distance between the lattice fringes is 0.210 ± 0.004 nm (Fig.

4.5b). In addition, the SAED pattern exhibits non-continuous rings, implying crystalline nature of the 5SrBaCO₃ matrix.

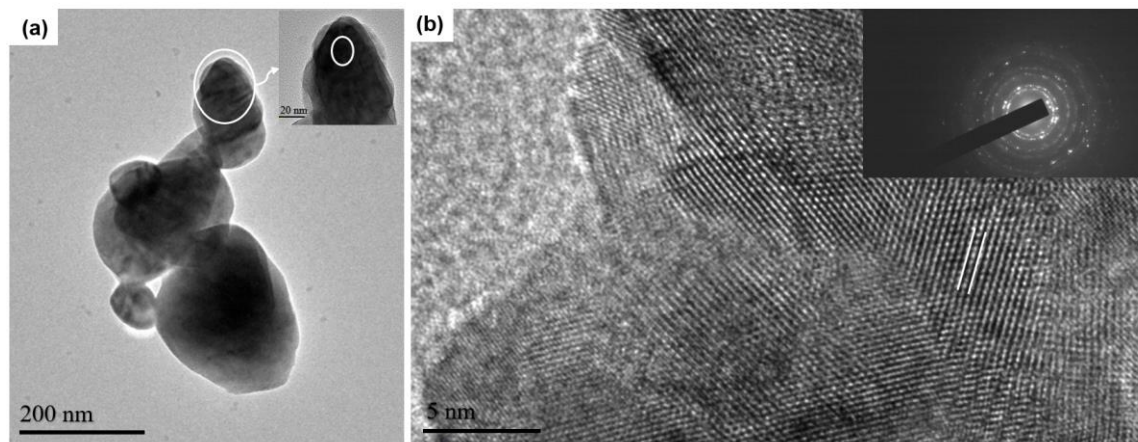


Figure 4.5 TEM image of: (a) as synthesized 5SrBaCO₃, and (b) corresponding HRTEM image with SAED image in the top right.

4.4.5 Pore Size and Pore Volume

The Type IV adsorption and desorption of N₂ in the 5SrBaCO₃ sample is followed by tiny loops for H3 hysteresis, as shown in Fig. 4.6. The existence of both mesopores and macropores in the matrix are indicated by the prominent N₂ adsorption desorption peak in the high P/P₀ range. The estimated BET surface area is 22 m²/g, with a pore volume of 0.365 cm³/g. Based on the pore size distribution curves illustrated in Figure 4.6b, two types of porosity can be observed in 5SrBaCO₃, one existing at almost 14 nm and the other comes within 20-110 nm (inset). A combined mesoporous/macroporous structural support system with a greater latent heat value was recently addressed [44-46]. However, there are still a lot of questions about how PCMs behave when they are encased in a supporting material. Despite the large surface area of some silica [241], ZSM-5 [271], and metal-organic frameworks (MOFs) [272] support materials, the latent heat of PCMs prepared by

combining them with PEG or paraffin is not very high. Materials having a limited surface area, such as calcium carbonate, calcium silicate, graphene, and magnesium oxide, generally show a typical latent heat value. As such, further investigation should be conducted to determine the effect of pore size, pore volume, etc., on the latent heat.

The existence of two types of pores in 5SrBaCO₃ PCM (mesoporous/macroporous) allows for the retention of a significant number of PEGs, increasing the PCM's latent heat. The crystalline structure of a matrix is altered by the formation of very small holes to avoid material relaxation to its lowest energy state. Bigger pores are likewise unsuitable since it is difficult to maintain melted PCM inside the matrix. PEG can be quickly absorbed by mesoporous matrices via capillary action, thereby improving the thermal stability of 5SrBaCO₃/PEG PCM at frequent melting and freezing processes, as will be discussed later.

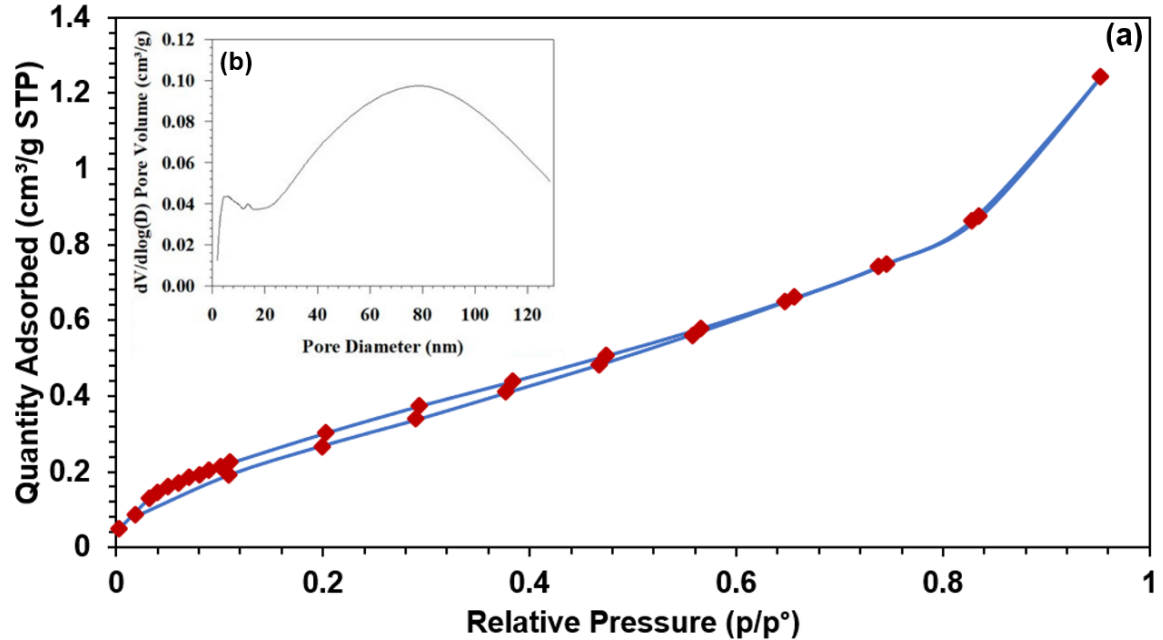


Figure 4.6 (a) Nitrogen adsorption-desorption isotherms of the as-synthesized 5SrBaCO₃ and (b) diameter of the pores.

4.4.6 X-ray Photoelectron Spectroscopy (XPS)

XPS determines the chemical state and composition of a substance. The spectra related to the 5SrBaCO_3 sample shown in Fig.4.7a exhibit distinct peaks of C, Ba, O₂, and Sr on the surface. Spin-orbit splitting leads to the formation of two Ba 3d XPS peaks at high resolution. XPS data reveal that the surface concentration of Ba is 1.44%. Peaks at 282, 289.5, and 526 are probable for the COH and/or OH groups, as well as PEG. It has been proposed that the presence of an OH group shows a major influence on reducing the super cooling effect [273]. Because of C-C, the C1s range contains 2 peaks, as illustrated in Fig. 4.7b at 284.2 and 289.3 eV, respectively. The as-prepared sample has one O1s XPS peak at 530.7, which might be attributable to the bonding of hydroxyl group with BaO.

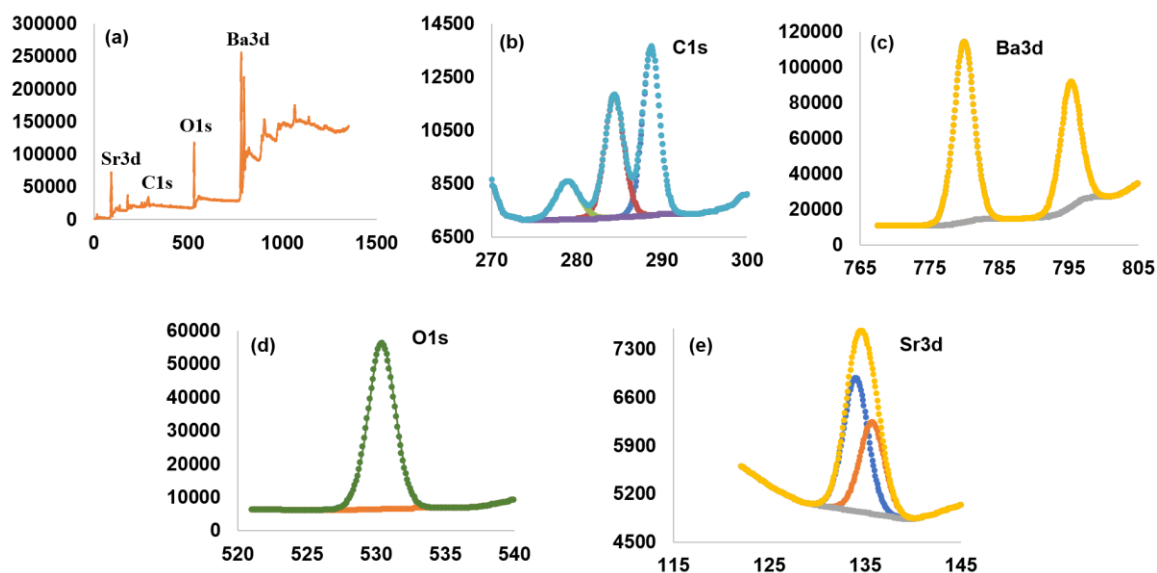


Figure 4.7 XPS spectra of 5SrBaCO_3 : (a) survey spectrum, (b, c, d, e and f) C1s, Ba3d, O1s, N1s and Sr3d regions, respectively.

4.4.7 Thermal Stability

Fig. 4.8 depicts the TGA profiles of PEG, 5SrBaCO_3 and the three developed composites $5\text{SrBaCO}_3/\text{PEG}$, $10\text{SrBaCO}_3/\text{PEG}$, $15\text{SrBaCO}_3/\text{PEG}$. The TGA analysis was conducted in an argon environment with temperature increasing at a rate of $5\text{ }^\circ\text{C}/\text{min}$. Fig. 4.8 shows that at a temperature of over $800\text{ }^\circ\text{C}$, the matrices begin to breakdown into BaO and CO_2 . The disintegration of 5SrBaCO_3 matrices at $800\text{ }^\circ\text{C}$ results in a weight loss of around 2%. Pure PEG begins to breakdown at around $370\text{ }^\circ\text{C}$. Temperature of around $440\text{ }^\circ\text{C}$ marks the completion of PEG decomposition which means 100 % weight loss. The weight loss in the composites that occurs between 370 and $640\text{ }^\circ\text{C}$ most probably results from the elimination of the organic molecules included in the composite. Approximately, the composites consist of 28.6% matrix and 71.4% PEG, based on the weight of the ingredients. The residual weight at $500\text{ }^\circ\text{C}$ for $5\text{SrBaCO}_3/\text{PEG}$, $10\text{SrBaCO}_3/\text{PEG}$, and $15\text{SrBaCO}_3/\text{PEG}$, was 37%, 31%, and 7%, respectively. Apparently, the thermal stability of PEG is enhanced by the $5\text{SrBaCO}_3/\text{PEG}$ inorganic porous support matrix by providing a protection barrier. Among the three composites, the lowest weight loss of 63% belongs to $5\text{SrBaCO}_3/\text{PEG}$ PCM composite. The lower degradation temperature of the $10\text{SrBaCO}_3/\text{PEG}$ and $15\text{SrBaCO}_3/\text{PEG}$ maybe attributed to the larger particle sizes of their matrix (Fig. 4.4). Accordingly, they have lower ability of PEG encapsulation compared with $5\text{SrBaCO}_3/\text{PEG}$. The manufactured composites have high thermal stability, making them suitable for use in energy storage systems. The TGA curve for $5\text{SrBaCO}_3/\text{PEG}$ exhibits a slope that is somewhat small compared to pure PEG as the magnified part of Fig. 4.8 (right side) shows, which displays the TGA curves ranging between $350\text{ }^\circ\text{C}$ to $450\text{ }^\circ\text{C}$.

As a result, PEG heat absorption rate is reduced in 5SrBaCO₃/PEG, indicating that the 5SrBaCO₃/PEG composite prevents encapsulated PEG from decomposition.

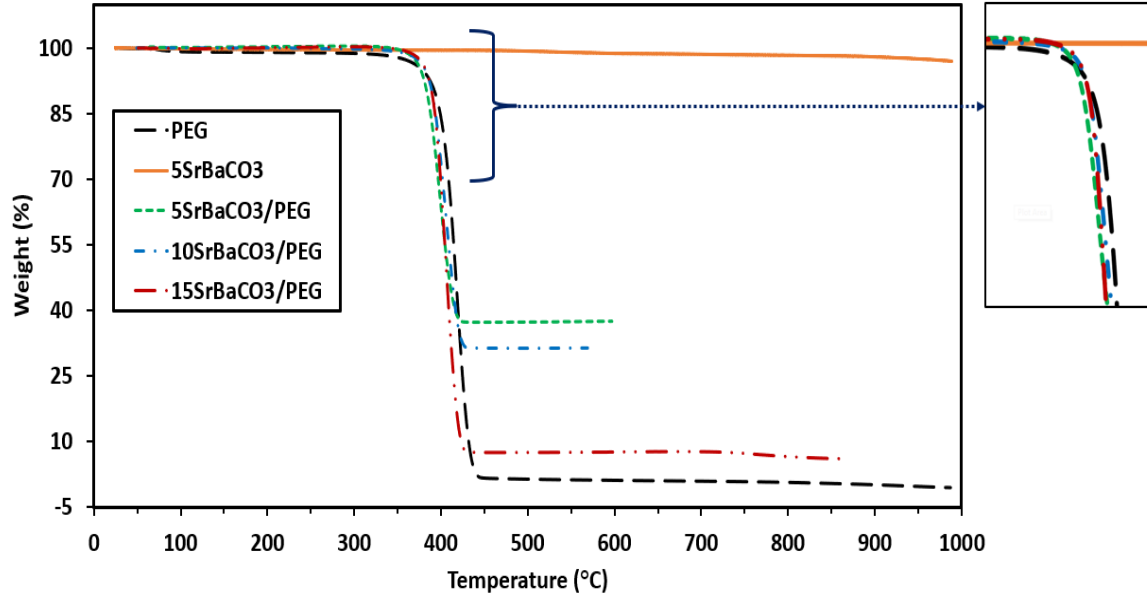


Figure 4.8 TGA curves of PEG, 5SrBaCO₃, 10SrBaCO₃ and 15SrBaCO₃ PCM composites.

4.4.8 Differential Scanning Calorimetry (DSC)

The melting-freezing DSC curves for: (a) pure PEG, (b) 5SrBaCO₃/PEG, (c) 10SrBaCO₃/PEG and (d) 15SrBaCO₃/PEG are shown in Fig. 4.9. Table 2 lists the DSC results of each sample. Enthalpies related to pure PEG and composites were calculated based on the area under the DSC curves for freezing and melting cycles. The melting and freezing enthalpies of pure PEG are 189.6 J/g, and 170.1 J/g, respectively. Comparable latent heat values of PEG have been reported by Liu et al. [274] and Zahir et al. [193].

The highest latent heat value of the composites was noted in 5SrBaCO₃/PEG with a melting and freezing latent heat of 148.8 J/g and 145 J/g, respectively.

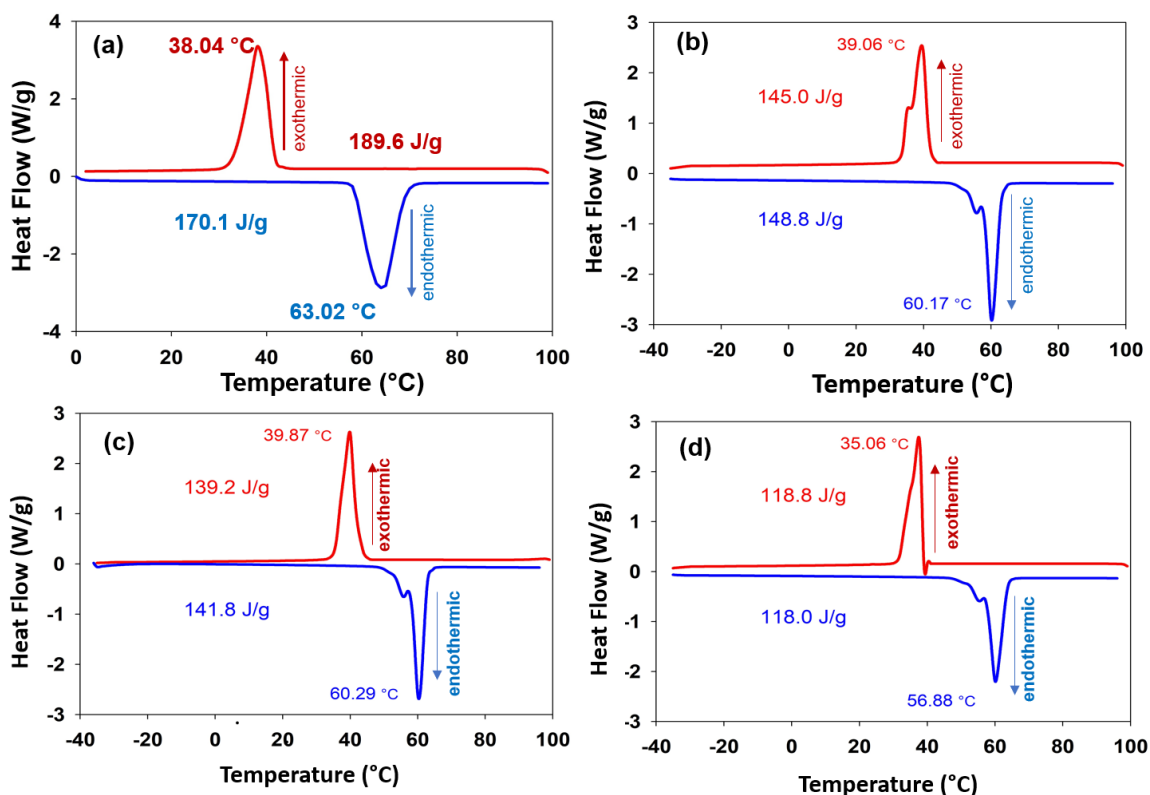


Figure 4.9 Melting-freezing DSC curves for: (a) pure PEG, (b) 5SrBaCO₃, (c) 10SrBaCO₃, and (d) 15SrBaCO₃ PCM composites.

The composite samples 5SrBaCO₃/PEG, 10SrBaCO₃/PEG and 15SrBaCO₃/PEG exhibited an impregnation ratio (R) [212] of 78.48%, 74.79%, and 68.28%, respectively. The heterogeneity of the composites explains these findings where PEG mixing and/or penetration are less than ideal. The modest peaks of melting and solidification indicate the correctness of the hypothesis (Fig. 4.8b).

The Ba segregation in 5SrBaCO₃ was significantly smaller than that in 10SrBaCO₃ and 15SrBaCO₃, which is probably why this compound produced the best results. A Ba containing mixed oxides is a good cathode material for solid fuel cells, according to Duan et al. [50], but it can be challenging to prevent barium loss during processing or the addition

of additional elements to the mixed oxide system. The authors are conducting research to overcome this problem.

Table 4.2: Thermal activities of PEG and SrBaCO₃ composites.

Samples	T_m (°C)	T_f (°C)	ΔT (°C)	H_f (J/g)	H_m (J/g)	E %	R %
PEG	63.02	38.04	24.98	170.1	189.6	-	-
5SrBaCO ₃ /PEG	60.17	39.06	21.11	145	148.8	81.68	78.48
10SrBaCO ₃ /PEG	60.29	39.87	20.42	139.2	141.8	78.12	74.79
15SrBaCO ₃ /PEG	60.1	37.43	22.67	121.5	124.1	68.28	65.45

The values of E (%) and R (%) were calculated using the equations listed below [212]:

$$R = \frac{\Delta H_{m, com}}{\Delta H_{m, PCM}} \times 100\% \quad (1)$$

$$E = \frac{\Delta H_{m, com} + \Delta H_{f, com}}{\Delta H_{m, PCM} + \Delta H_{f, PCM}} \times 100\% \quad (2)$$

Where: T_f = freezing temperature, T_m = melting temperature, ΔH_f = latent heat in the cooling process, ΔH_m = latent heat in the heating process, ΔT = super cooling, R = impregnation ratio, E_{eff} = Efficient energy per unit mass of PEG, E = energy storage efficiency.

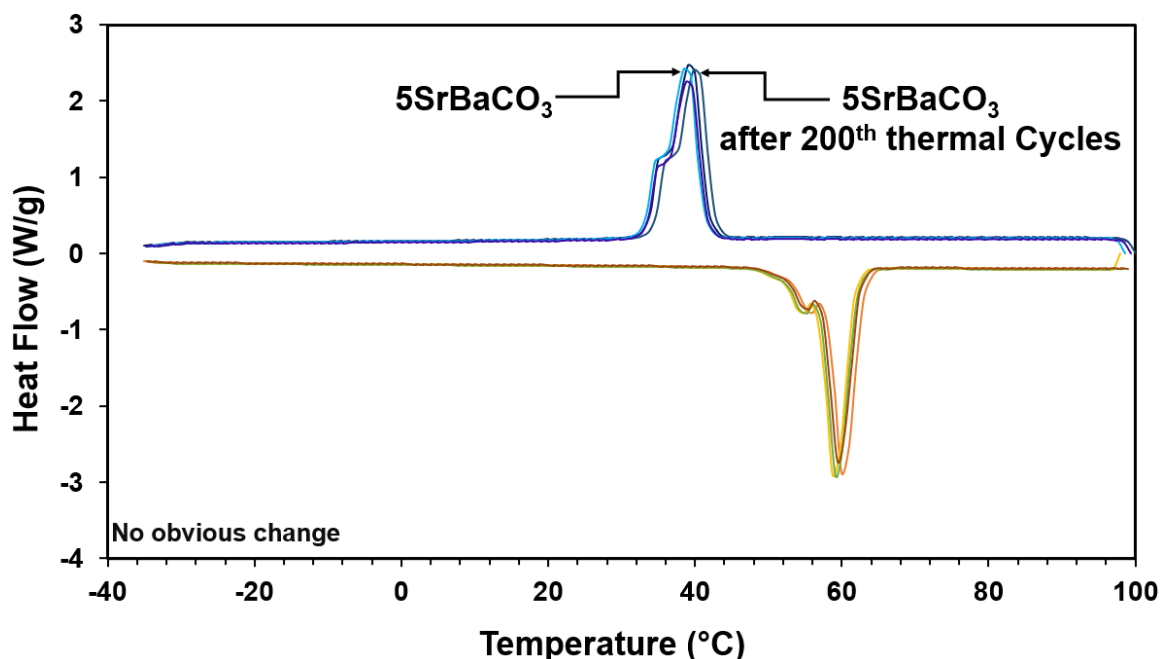


Figure 4.10 DSC curves of 5SrBaCO₃ PCM composite exposed to 200 thermal cycles.

The thermal cycling behavior of the composite 5SrBaCO₃ PCM was also assessed, which is significant for commercial viability. Despite undergoing 200 thermal cycles the 5SrBaCO₃ PCM remained thermally stable. Fig. 10 shows the DSC for 5SrBaCO₃ PCM after 0 and 200 thermal cycles. Both the exothermal and endothermal curves show insignificant change in the heat flow with cycling, which implies long-life cycle and high thermal reliability of the composite. This research demonstrates the ability of the developed PEG to maintain almost fixed temperature and enthalpy phase shifts throughout repeated thermal cycles. Further, it can also store and release latent heat at a fixed temperature under repeated cycles. The sample retains its original structure even after 200 thermal cycles, as the FE-SEM image illustrates (Fig. 4.11). The thermal stability of PCM suggests that liquid PEG has infiltrated the matrix via capillary action and surface tension. Although the micro- or nano-sized holes can prevent PEG chains from penetrating, however, the mesoporous-/macro-porous structures allow the infiltration of PEG chains.

The doping of 5 mol% Ba^{2+} into BaCO_3 results in numerous layers of smaller BaCO_3 particles, as seen in Fig. 4.3a. The 5SrBaCO_3 matrix contains the smallest particles among the three Ba^{2+} doped BaCO_3 matrices. Figure 4.3a shows that increasing the quantity of Ba^{2+} doping has the reverse effect, resulting in bigger particles. The occurrence of two types of pore architecture, as discussed earlier, in $5\text{SrBaCO}_3/\text{PEG}$ (Fig. 4.11), significantly leads to an increase in the latent heat PCM by holding a significant quantity of PEG. The crystalline quality of a matrix is altered by very tiny holes. As a result, the material may face difficulty in relaxing to its lowest energy level.

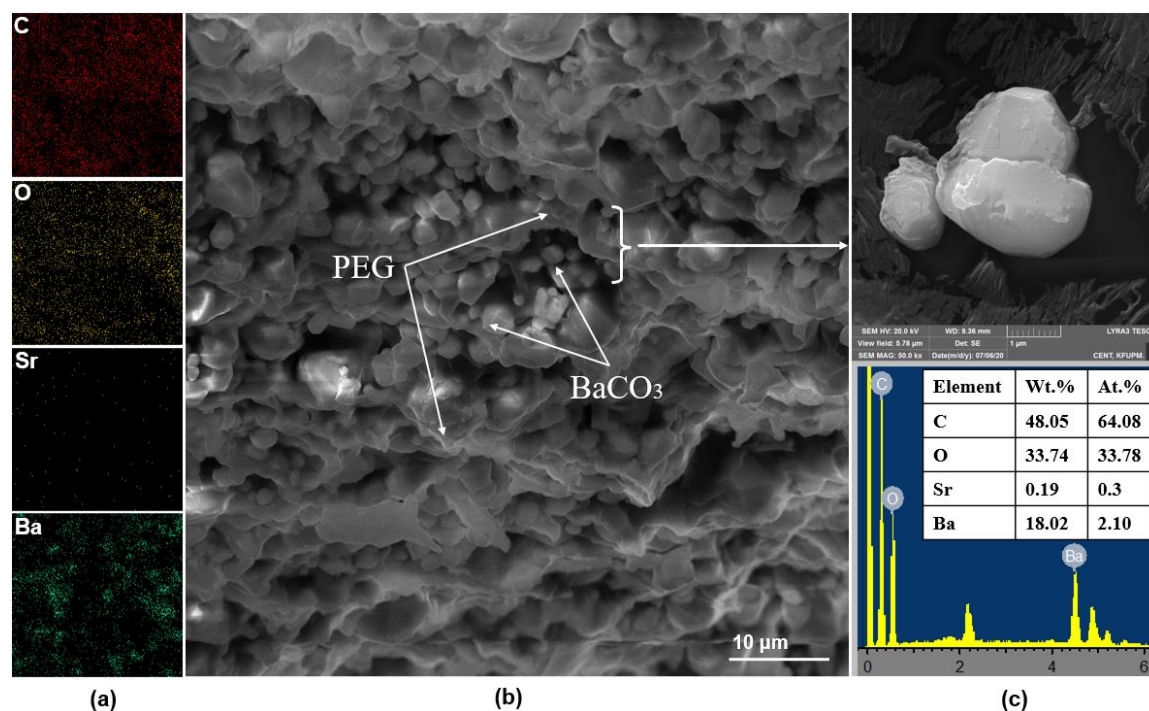


Figure 4.11 (a) Mapping (b) FE-SEM images and (c) Energy dispersive spectra (EDS) of $5\text{SrBaCO}_3/\text{PEG}$.

4.4.9 Compatibility of the PCM with Metals Used for Containers

The synthesized 5SrBaCO_3 PCM must be kept in appropriate containers for future use. As a result, analysis was conducted for several types of container materials, such as Sn (Tin), Al (Aluminum), GI (Galvanized iron), and Cu (copper). The top surfaces of the specimens were coated with $5\text{SrBaCO}_3/\text{PEG}$, and their surface characteristics were measured. The coated metal sheet coupons were exposed to intense sun radiation or humid conditions common in Saudi Arabia (highest at roughly 48°C , lowest at around 23°C). As is evident in Fig. 4.12, the appearance of Sn, Al, and GI coated with $5\text{SrBaCO}_3/\text{PEG}$ were not affected, including color, indicating the corrosion-resistance of these materials and their compatibility with $5\text{SrBaCO}_3/\text{PEG}$. After being exposed to similar hot and humid conditions, Cu specimens coated with $5\text{SrBaCO}_3/\text{PEG}$ displayed significant corrosion (Fig. 4.12). Consequently, Cu containers are not suitable for storing $5\text{SrBaCO}_3/\text{PEG}$ due to the change in color to bright green corrosion product observed on the Cu sheet covered with $5\text{SrBaCO}_3/\text{PEG}$. Further, there was no change in the weight of the specimens, except Cu. As a result, all tested materials, except Cu, are appropriate for storing the developed $5\text{SrBaCO}_3/\text{PEG}$.

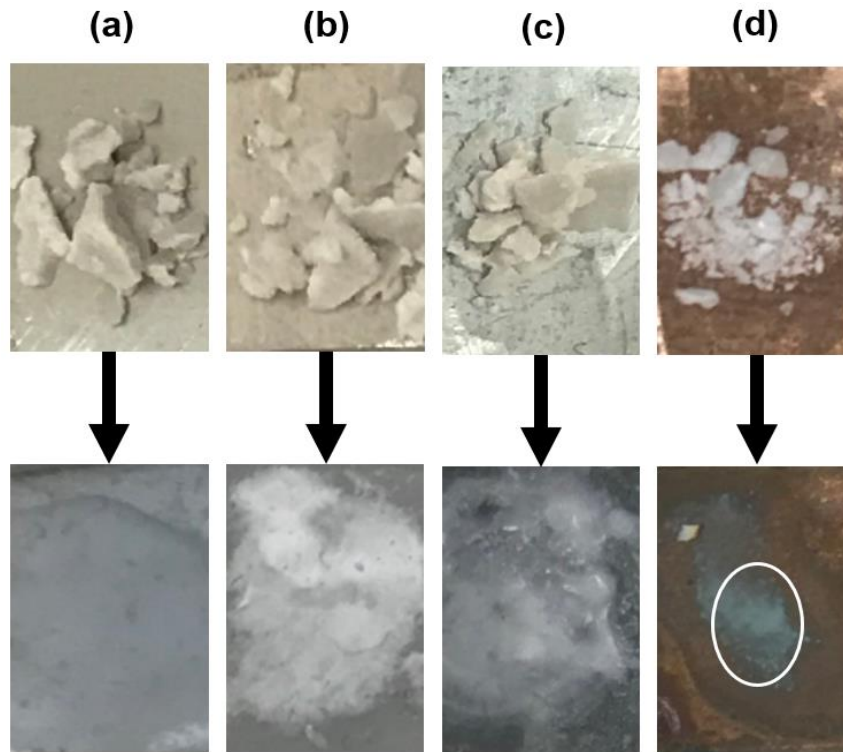


Figure 4.12 Photographs of metallic specimens coated with 5SrBaCO₃ PCM: (a) Al, (b) Sn, (c) GI, and (d) Cu.

4.4.10 Seepage

Two disk specimens of pure PEG and 5SrBaCO₃/PEG measuring 20 mm in diameter were prepared to check their leakage properties. The disks were heated using a heating plate at a temperature of 80 °C for 10 minutes. As is evident in Fig. 4.13, there was no change in the appearance of specimens of 5SrBaCO₃/PEG, indicating that there was no leakage in the specimen. However, melting initiated immediately in pure PEG upon increasing the temperature to more than 80 °C (Fig. 4.13b).

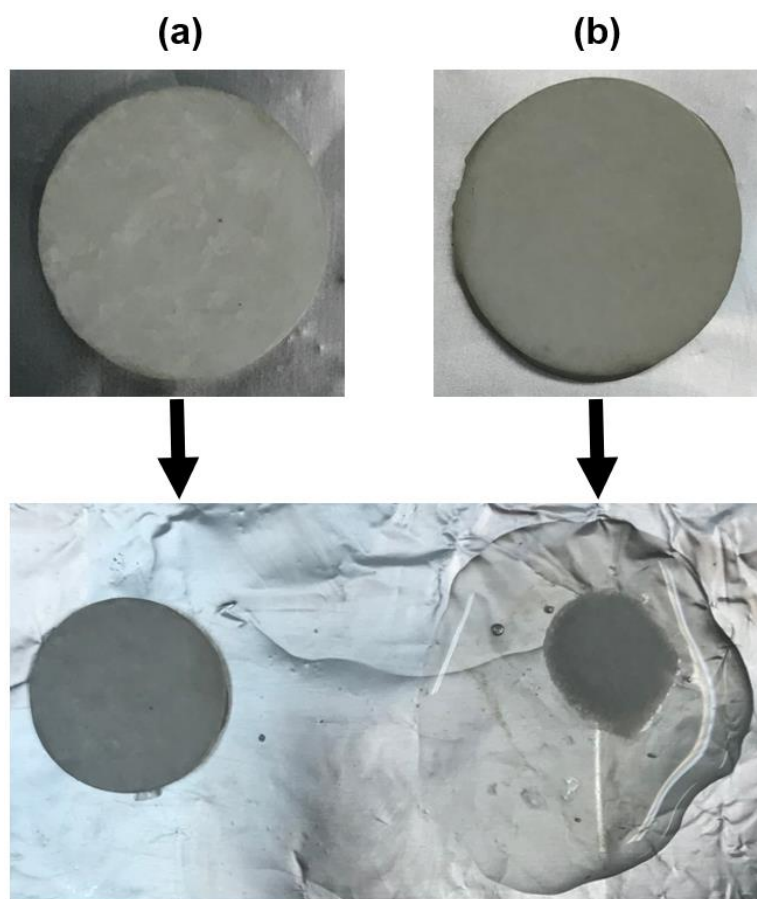


Figure 4.13 Photographs of disks prepared with (a) 5SrBaCO₃/PEG and (b) Pure PEG before and after heating at 80° C on a heating plate.

4.4.11 Thermal Conductivity

The thermal conductivity of pure PEG and the composite PCMs is summarized in Table 4.3. The thermal conductivity of composite PCMs is more than that of pure PEG. Further, the thermal conductivity increased with an increase in the quantity of Sr.

Table 4.3: Thermal conductivity of PEG, and 5SrBaCO₃, 10SrBaCO₃, and 15SrBaCO₃ PCM composites.

Material	Thermal conductivity (W/m.K)
PEG	0.212 ± 0.03
5SrBaCO ₃ /PEG	0.298 ± 0.03
10SrBaCO ₃ /PEG	0.304 ± 0.03
15SrBaCO ₃ /PEG	0.308 ± 0.03

4.4.12 Comparison of Results of the Present Study with earlier studies

Table 4.4 shows a comparison of the data developed in the current work with related studies. Qian et al. [212] studied ssPCM incorporating PEG with calcuim silicate, their best samples (ss-CPCM4) shows a max latent heat value of 122.10 J/g which less than that of the prepared composite 5SrBaCO₃/PEG. Similarly, low latent heat values have been reported in references [5], [275] and [276]. Zahir et al. [79] have reported high latent heat values in their work. However, the impregnation ratio and energy storage efficiency is lower than that of 5SrBaCO₃/PEG. Similarly, the authors [277] have reported lower values of R and E compared to 5SrBaCO₃/PEG.

Table 4.4: Comparison of results of current work with the published work on PEG-based composite PCMs.

PEG based PCM	ΔT (°C)	H_m (J/g)	E %	R %	Thermal conductivity (W/m.K)	Reference
PEG	24.98	189.6	-	-	0.212 ± 0.02	This work
5SrBaCO ₃ /PEG	21.11	148.8	81.68	78.48	0.298 ± 0.03	This work
10SrBaCO ₃ /PEG	20.42	141.8	78.12	74.79	0.304 ± 0.02	This work
15SrBaCO ₃ /PEG	22.67	124.1	68.28	65.45	0.308 ± 0.02	This work
ss-CPCM1	16.95	28.56	14.01	15.60	-	[212]
ss-CPCM2	16.94	65.79	33.45	35.93	-	[212]
ss-CPCM3	14.96	104.60	54.80	57.13	-	[212]
ss-CPCM4	12.93	122.10	64.53	66.68	-	[212]
ss-CPCM4c	13.4	113.60	60.09	62.04	-	[212]
P-5-MCC	18.59	134.5	59.39	60.78	0.3389	[79]
P-10-MCC	18.63	152.5	67.94	68.91	0.5456	[79]
P-15-MCC	18.05	125.3	55.03	56.62	0.5634	[79]
PEG/EP	12.08	137.32	76.36	-	0.161	[5]
PEG/EP/CNT	8.48	129.27	71.0	-	0.479	[5]

PEG6000/SiO ₂	12.9	102.8	57.48	56.64	0.297	[275]
Cu/PEG6000/SiO ₂	12.9	121.4	68.11	66.89	0.41	[275]
FS-CPCMs-1	14.3	41.5	21.19	21.55	0.66	[276]
FS-CPCMs-2	14.5	56.4	29.09	29.28	0.61	[276]
FS-CPCMs-3	15.6	76.4	39.54	39.67	0.57	[276]
FS-CPCMs-4	16.8	115.6	59.70	60.02	0.54	[276]
GNS/PEG	23.2	176.9	95.5	95.5	0.257	[220]
Ag-GNS/PEG-1	24.3	177.2	95.8	95.6	0.317	[220]
Ag-GNS/PEG-2	24.7	173.3	93.7	93.5	0.337	[220]
Ag-GNS/PEG-3	24.2	169.6	91.7	91.5	0.367	[220]
Ag-GNS/PEG-4	24.2	166.1	89.7	89.6	0.414	[220]
OA/PEG	21.9	132.5	69.7	69.9	0.791 ± 0.03	[277]
SC/PEG	19.5	109.1	57.2	57.5	0.547 ± 0.03	[277]
ExP/PEG	18.1	150.7	79.3	79.5	0.153 ± 0.03	[277]
ExP/PEG/CNT(0.5%)	20.3	132.1	69.7	69.7	0.453 ± 0.03	[277]

4.5 Conclusions

A shape-stabilized composite was developed utilizing a simple impregnation approach employing a porous Sr^{2+} -doped BaCO_3 matrix and PEG as the functional phase. DSC, SEM imaging, FTIR, Raman spectroscopy, and TGA were used to investigate the heat storage capability, microstructure, and interactions with the $\text{SrBaCO}_3/\text{PEG}$ composites. Following conclusions can be made based on the data developed in this study.

- i. The TGA data indicate that 5% $\text{SrBaCO}_3/\text{PEG}$ PCM has outstanding thermal characteristics. A considerable amount of PEG was contained within the pores and spread throughout the surfaces of the 5% SrBaCO_3 particles, stabilized by capillary forces and surface tension, as indicated scanning electron micrographs.
- ii. The porous 5% SrBaCO_3 composite is structurally stable, preventing the leakage of liquid PEG. The thermal conductivity of composite PCMs also improved. These characteristics suggest that the produced 5% SrBaCO_3 composite is an excellent solar energy storage material with good thermal stability.
- iii. The two pore size ranges in the developed composite are expected to play a critical role in decreasing the super cooling effects and latent heat.
- iv. The excellent heat energy storage capability and strong thermal stability of the developed PCM suggest that it may also be used in several other applications.

CHAPTER 5

PREPARATION, CHARACTERIZATION AND THERMAL PERFORMANCE OF CEMENT COATED POLYETHYLENE GLYCOL/SCORIA COMPOSITE PCM FOR THERMAL ENERGY STORAGE IMPROVEMENT OF CONCRETE

5.1 Abstract

Incorporation of Form stabilized phase change materials (FS-PCM) in building materials has been verified to have significant potential to improve building energy efficiency and reduce power consumption. However, expensive PCMs used, complexity of preparation process, leakage problems and low thermal conductivity limits its use for construction applications. In this study, locally available, low-cost porous aggregates named scoria (SC) has been used as a supporting material along with PEG to develop SC/PEG composite (SCP). Moreover, cement paste coating used to develop cement coated SCP (SCPC) to prevent leakage and improve thermal conductivity. The characterization results showed that SCP is chemically stable with an optimum incorporation ratio of 47% of PEG. The developed SCPC showed outstanding thermal stability after 200 cycles of melting and solidification without sign of leakage. Moreover, SCPC has an energy storage capacity and melting enthalpy of 96.7% and 35.8 J/g, respectively. Different proportions of SCPC have been replaced by SC to prepare thermal energy storage concrete (MSCPC). It has been verified that up to 80% replacement, the MSCPC can be used as a structural concrete in

buildings. Moreover, the maximum temperature reduction and %time shifting obtained for the heating cycle is 5.49 °C and 77.8%, respectively. Thus, the prepared MSCPC has a function of reducing the energy consumption, besides, its excellent energy storage and release performance. All these favorable characteristics indicate that the prepared MSCPC can be beneficially utilized to improve the thermal efficiency of concrete in buildings.

5.2 Introduction

The sharp increase in the population rates worldwide and the high living standards have increased the energy consumptions especially in buildings, since they are responsible for about 40% of the total energy consumption in the world. Awareness of the energy needs associated with the building sector has been triggering huge research effort accordingly, aimed at developing more energy efficient constructions [196,278–280]. Air conditioning (AC), which is an essential process to maintain comfort environment in buildings is the main contributor in energy consumption in buildings. Several energy conservation measures have been implemented in building in the last decades to minimize high energy consumption rates such that the use of insulation materials [281], development of multilayered glass windows [282] and the use of phase change materials (PCMs) [283–285]. The use of insulation materials reduces the energy consumption of buildings by reducing the working times of the AC to maintain comfort temperature with lowest energy usage. However, overheating during the summer increases the energy required to maintain thermal comfort in buildings [286].

PCMs are used as a thermal storage media that storing energy in the daytime (melting process) and releasing it in the nighttime (solidification process). During the process of melting and solidification, PCM store and release solar energy that provide a stable ambient

temperature in the buildings [277]. In the gulf countries, where the temperature reaches more than 50 °C in the summer season, the demand of energy for cooling has considerably increased. Consequently, decreasing the energy demand for cooling buildings through the incorporation of methods based on renewable energy is highly appealing. According to the plentiful sunlight in these regions storing of thermal energy is one of the most promising sources of renewable energy. Using PCMs to capture and store solar energy in the form of latent heat is an intriguing method to be used in this regard. While using an appropriate PCM for providing comfort has received considerable attention [287]. However, limited resources are available on the use of PCM's in buildings for hot weather conditions. Therefore, it is necessary to develop a suitable and economical PCMs for this purpose to be used worldwide. Based on the phase transition, PCMs can be categorized mainly into, solid-liquid, liquid-gas, solid-solid, solid-gas PCM. Among the four categories the solid-liquid phase transition PCM is considered the most appropriate material to be used for energy storage in buildings due to its stability and compatibility with building materials [288]. solid-liquid PCM can be divided into three main groups, including organic, inorganic and eutectics. Among the three, organic PCM possess high latent heat of fusion, no supercooling, recyclable and compatible with building materials [195]. However, organic PCMs suffers from leakage problems during the phase transition, flammability and has low thermal conductivity values [289].

Form stabilized phase change material (FS-PCM) is a composite with a PCM impregnated in a porous supporting media to improve its thermal conductivity, chemical stability, flammability and prevent leakage of PCMs [290–293]. However, the selection of a suitable PCM along with the supporting material in concrete for hot climate conditions is essential.

It has been reported that the average maximum temperature of gulf countries could exceed 50 °C in summer period (June – August) and crossing the 60 °C in Dhahran city in Saudi Arabia at the end of 21st century [294]. In this regards, few organic PCMs can be used to serve at this temperature range including Paraffins, Fatty acids and polyethylene glycol [295]. Fatty acid which has an excellent latent heat of melting (166.6 J/g), nontoxic and chemically stable [296]. However, their high cost restricts its commercial use in building applications. On the other hand, extensive studies has been conducted on the use of paraffin with different supporting materials due to its superb enthalpy and can be used in different applications due to its wide range of working temperature [210,297–301]. Karaipekli et. al. [237] used paraffin/expanded perlite composite and used CNT's to enhance its thermal conductivity, they concluded that their developed composite revealed good stability, high latent heat of enthalpy and high thermal conductivity values. However, paraffin undergoes high volume change during phase transition which affect the long-term stability of the PCM system. Hasan et. al. reported that paraffin RT24 has a volume expansion of 12.5% [122]. Polyethylene glycol (PEG) is a better candidate PCM to be utilized with buildings for hot climate conditions. PEG is chemically stable and has a wide melting temperature range of around 3 to 69 °C, which may be controlled by its molecular weight. Additionally, PEG is non-toxic, erosion-resistant, and economical. It also has a low degree of super cooling, a high level of chemical and physical stability, and no phase segregation. Additionally, when compared to paraffin, PEG has a lower vapor pressure and a smaller volumetric change [218].

Scoria (SC) is a natural lightweight aggregate with gray to black color, which can be used in many applications, (e.g., production of lightweight concrete, filler in low-cost paint and

filtering media) [18]. Alhozaimy et. al. reported that scoria is a natural source of pozzolan that can be used in mass concretes compared to other pozzolanic materials [302]. In addition, different studies has been conducted on the use of scoria in lightweight concrete [203,303,304]. The studies have reported that using scoria in concrete improved the characteristics of cement mortar [304] reduce concrete shrinkage, improve the concrete behavior at high temperatures [203] and can be used in structural concrete [303]. Furthermore, it has been verified that scoria aggregate deposit in Saudi Arabia is suitable to be used for light weight concrete, block manufacturing and utilized as additive in Portland cement [18].

The incorporation of PCM into the supporting materials can be adopted using different techniques [251,252,305]. Vacuum impregnation method showed higher absorption capacity of PCM compared to other methods of impregnation. Ramakrishnan et. al. [207] reported that the absorption capacity of paraffin/expanded perlite composite using impregnation techniques is 30% higher than that of the same composite using direct method. However, they are heating the expanded perlite for 24 h at 105 °C, which impractical and consume high amount of energy. On the other hand, the use of fabricated FS-PCM into construction materials like mortar, concrete and bricks can be implemented using four different techniques including direct incorporation, immersion, encapsulation and form stable composite systems [306]. The first two methods suffer from leakage problems, especially after several heating-cooling cycles. The encapsulation technique can be used for PCM having a phase change temperature varying from - 10 to 80 °C. However, the encapsulated particles required to be protected during and after construction process [307]. Form stable PCM which retain an optimum volume of PCM without leaking from

the media during melting process of PCM. However, leakage occurs due to the addition of water in mixing process [308]. Surface protective layer can be applied to overcome the leakage problems. Memon et. al. [309,310] applied surface epoxy coating as a protective layer to hold the paraffin from leaking. He concluded that epoxy coating work as a barrier preventing any sign of leakage of paraffin. However, the use of epoxy coating in construction application is costly and required special care during and after mixing.

In this study the utilization of SC/PEG (SCP) composite in building applications for hot climate conditions has been discussed. SC has been used for the first time as a supporting material along with PEG using vacuum impregnation technique to develop a FS-PCM. Moreover, the feasibility of using cement paste as a special cement coating of SCP to develop FS-PCM (SCPC) has been adopted and discussed. Finally, the developed novel SCPC composite has been utilized as a coarse aggregate to improve the thermal performance of concrete.

5.3 Methodology and experimental work

5.3.1 Material

Ultrapure Polyethylene glycol with a molecular weight of 6000 (purity > 99%) was purchased from Sigma-Aldrich Co. St. Louis, MO, USA. SC was collected from a quarry in the Western Province of Saudi Arabia (Specific gravity = 1.5, thermal conductivity = 0.27 W/m.K and absorption = 11%) SC particles are shown in Fig. 2a. Ordinary Portland cement (OPC), classified as Type I by ASTM C150, with a specific weight of 3150 kg/m³ was used in the cement coating and concrete mix design. Fine sand with a specific gravity of 2.56 and water absorption of 0.60% by weight was used as fine aggregate.

5.3.2 Fabrication of SCP composite

The development of SCP composite has been conducted using the vacuum impregnation method. Various mass fractions of PEG at an increment of 20 wt.% of SC (i.e., 20%, 40%, 60%, 80% and 100%) has been used to fabricate optimum SCP composite. Vacuum impregnation process has been conducted using a vacuum pump with a vacuum pressure of 0.1 MPa. First, the SC particles were added into a conical vessel then the solid PEG was added along with SC in a conical vessel and has been vacuumed for 10 min. Then the conical vessel has been submerged into hot water bath with a temperature of 70 °C for 2 hrs. During the heating process at a temperature exceeds the melting temperature of PEG. The PEG inside the vacuumed vessel start melting and impregnating inside the pores of SC due to the applied vacuum. After 2 hrs., it has been observed that the scoria couldn't contain more PEG, this can be noticed by the disappear of the air bubbles in the conical vessel, which indicate that the SC pores fully filled with PEG. Accordingly, 2 hrs. have been selected as an optimum duration for development of SCP at 0.1 MPa vacuum pressure. The fabricated apparatus used to fabricate SCP composite is shown in Fig. 5.1. The prepared SCP composite is shown in Fig 5.2b.

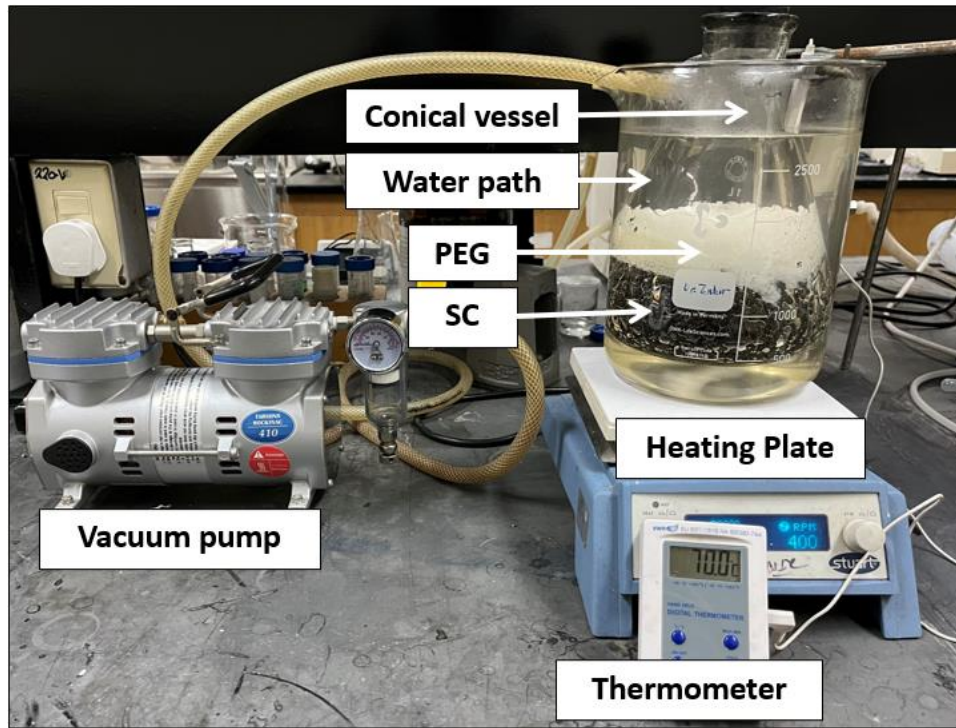


Figure 5.1 Apparatus used to fabricate SCP composite.

5.3.3 Fabrication of cement coated SCP composite (SCPC)

The preparation of cement paste to develop SCPC has been started initially by selecting the optimum SCP to cement ratio (SCP:C) by preparing several trials of mixing. The optimum SCP:C ratio selected ensures that all the SCP particles has been coated without excess of cement paste. The water to cement ratio was fixed at 0.35 for all the trial mixes. First, the cement mixed with water for 5 min. till the cement paste become homogenous. Then, the SCP particles added to cement paste and mixed for another 5 min. till all SCP particles covered with cement paste. Finally, SCPC has been segregated and kept in a room temperature for 24 h to get dried. After SCPC prepared, the water absorption and SG has been calculated according to ASTM C127 [311]. The absorption and SG of SCPC are 5.5 % and 1.8, respectively. Fig. 5.2c shoes the prepared SCPC composite prepared.

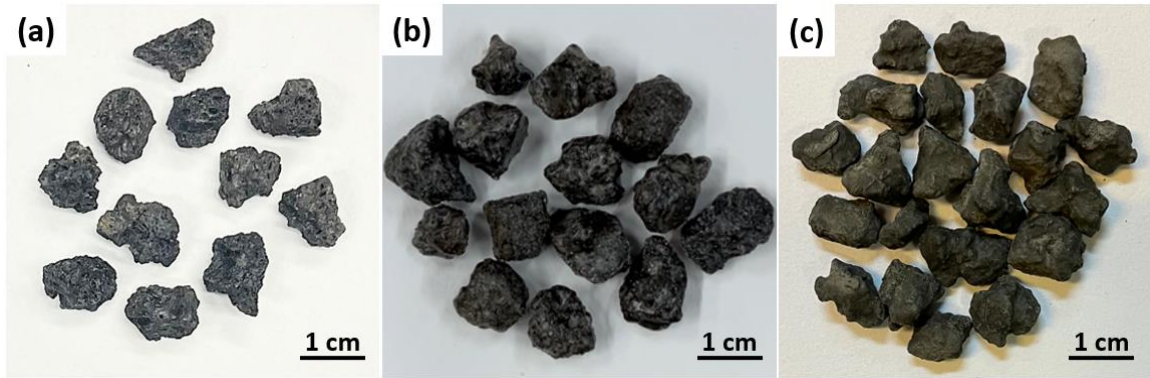


Figure 5.2 The particles of (a) SC, (b) SCP and (c) SCPC.

5.3.4 Concrete mix design mixtures

Six different concrete mixes have been prepared with different replacement of SC by SCPC. An increment of 20% replacement of SC by SCPC into concrete, starting with 20% replacement of SCPC by SC (M20SCPC) up to fully replacement of SC by SCPC (M100SCPC). In addition, a reference concrete mix has been prepared using SC only for the purpose of comparison (MSC). Table 5.1 shows the concrete mix design prepared. The water to cement ratio (w/c) used is 0.4 for all mixes, and the fine aggregate to total aggregate ratio (FA/TA) is 0.6. The selected w/c and FA/TA ratios were selected according to the reference mix after several trials and has been used for the rest of the mixtures.

Table 5.1: Concrete mix design mixtures of prepared concrete including SCPC.

Specimens	OPC (kg/m ³)	FA (kg/m ³)	SC (kg/m ³)	SCPC (kg/m ³)	Water (kg/m ³)
MSC	400	854	569	0	228
M20SCPC	400	869	464	116	223
M40SCPC	400	885	354	236	217
M60SCPC	400	902	241	361	212
M80SCPC	400	919	123	490	206
M100SCPC	400	937	0	625	200

5.3.5 Characterization

A Rigaku X-ray diffractometer (XRD) that operated at 15 mA and 30 kV at a 2°/min scanning rate and utilized Cu-K α radiation was used to determine the mineralogical composition. Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer (16F PC) spectrometer. JEOL JSM-6400F FE-SEM was used with an acceleration voltage of 10 kV to examine the morphology. In addition, an X-mass detector was used to detect the energy dispersive X-ray spectra (EDS). The structure and chemical composition of the mesoporous carriers was determined using an X-ray photoelectron spectrometer (ESCALAB-250, Thermo-VG Scientific, 1486.6 eV, USA), with Al-K α radiation and 0.5 eV instrument resolution. A thermal conductivity analyzer (C-Therm Technologies - TCi) was used to determine the thermal conductivity of the composite PCMs. Thermogravimetric analysis was performed using 10 mg samples using a Shimadzu TA-50 thermal analyzer. The heating rate was maintained at 5°C/min from room temperature

to 800 °C under argon environment. The DSC data were obtained by heating sealed samples of 10 mg in an aluminum pan with the temperature increased at a rate of 5°C/min under a fixed stream of argon at a 20 mL/min flow rate.

5.3.6 Mechanical and thermal properties of concrete incorporating SCPC

5.3.6.1 Compressive strength

The comprehensive strength test was conducted using MATEST Compression testing machine according to ASTM C109 [312] with an increasing load rate of 2 kN/sec. Cube specimens of $50 \times 50 \times 50 \text{ mm}^3$ were casted in laboratory environment, then cured for 14 days of burlap curing and tested for compressive strength after 3, 7 and 14 days, then tested at the age of 28 after exposing them to the air. Three cube replicates were used to estimate the strength of the concrete mixtures at each age of testing.

5.3.6.2 Thermal conductivity and thermal performance

The thermal conductivity of the concrete mixtures has been calculated using heat flow meter (HFM) provided by Thermtest Europe, Sweden [313]. HFM uses a Flux sensor (x 2) with an accuracy better than 3% which meet the requirement of ASTM C518 [314]. A panel size of $150 \times 150 \times 30 \text{ mm}^3$ has been prepared using the concrete mix design provided in Table 5.1. A temperature values of 60 °C and 20 °C has been set for the upper and lower HFM heating plates, respectively to measure the thermal conductivity of concrete plates.

The same HFM machine has been used to measure the temperature of the bottom plate surface with time. The temperature curves with time were obtained by changing the upper HFM plate temperature from 60 to 20 °C and vice versa which reflect the high temperatures

of hot climates in Dharan, Saudi Arabia. The HFM machine and the concrete panel arrangement are shown in Fig 5.3.

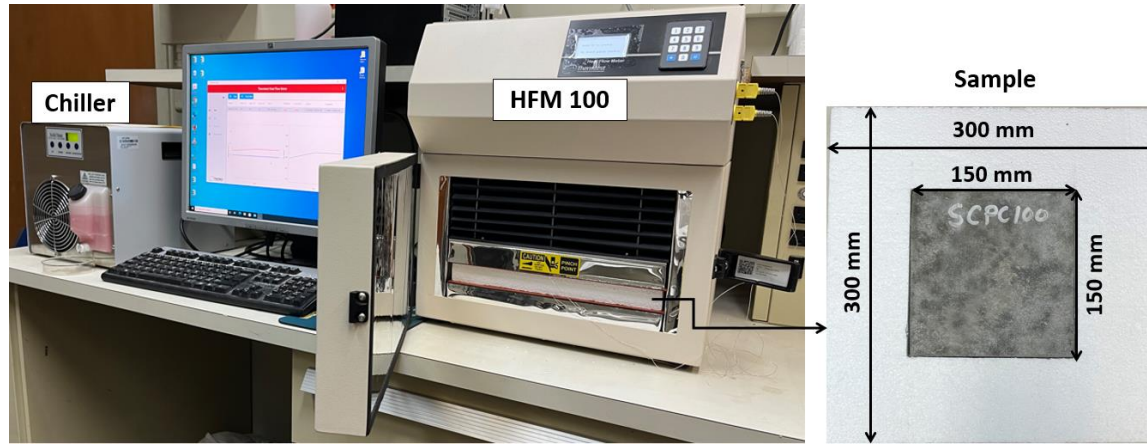


Figure 5.3 HFM machine and the concrete panel arrangement.

5.4 Results and Discussion

5.4.1 Particle size distribution of dry ingredients

The particle size distribution of SC and fine sand was obtained using sieve analysis, while that of cement was determined using laser diffraction spectroscopy (LDS) on a Microtrac® S3500 particle size analyzer as shown in Fig 5.4. The aggregate size selected of the SC is that retained on sieve #4 (4.75 mm). The % cumulative Retained of SC on sieve #4 is about 84% which used as a coarse aggregate in concrete mixtures.

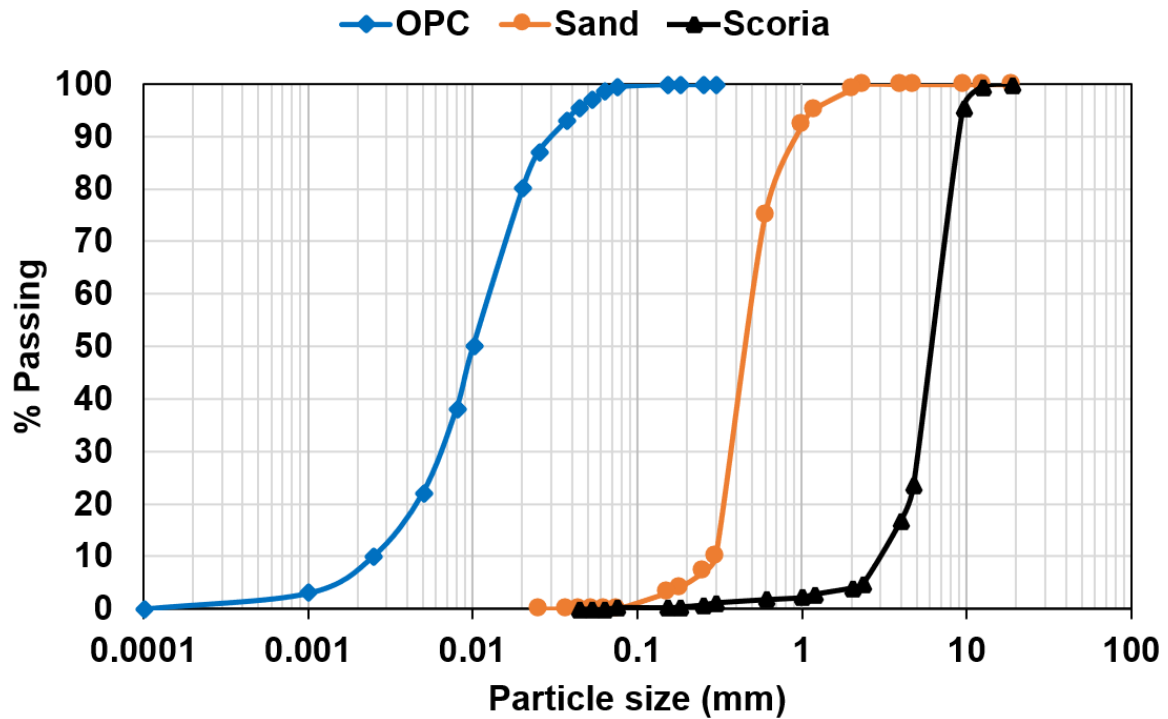


Figure 5.4 Particle size distribution of OPC, sand and scoria.

5.4.2 Selection of optimum SCP composite

The weight gained vs PEG loss has been calculated as shown in Fig 5.5 using vacuum impregnation technique. The optimum weight gained (PEG weight into SC) is about 47% at 60% PEG by weight of SC. Adding more than 60% of PEG results in higher loss of PEG than weight gained by the SC pores. The loss of PEG occurs as a result of that all the SC pores are fully occupied by PEG and SC particles can't accommodate more PEG. Accordingly, 60% PEG has been selected as an optimum percentile to develop the SCP composite.

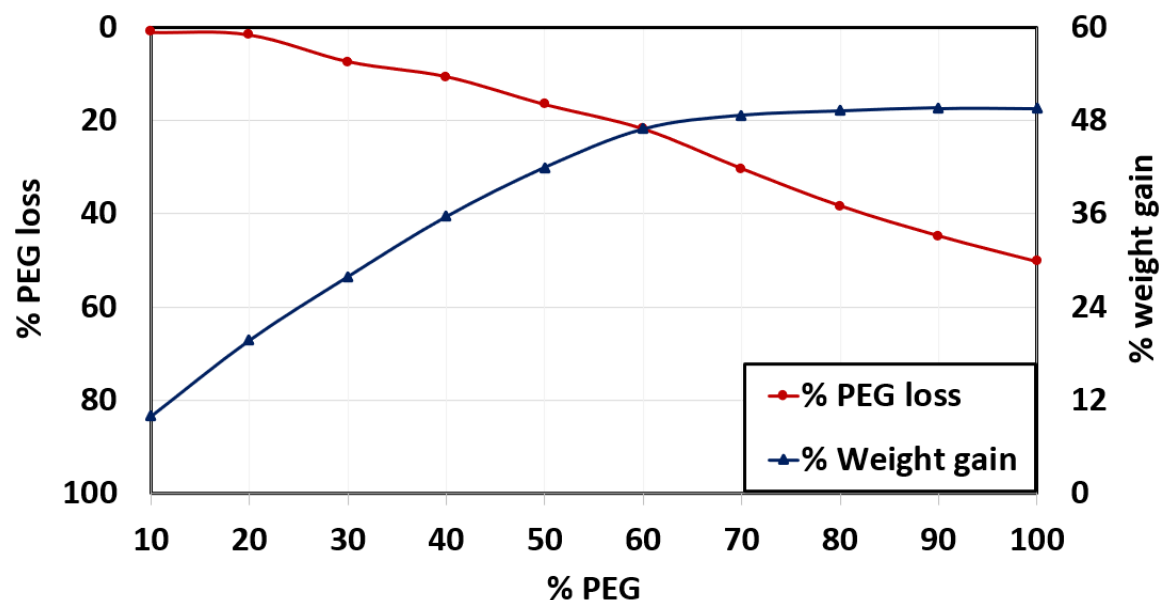


Figure 5.5 Percentiles of weight gain and PEG loss curves with different %PEG.

5.4.3 Characterization and testing of SC and SCP composite

5.4.3.1 Mineralogical composition

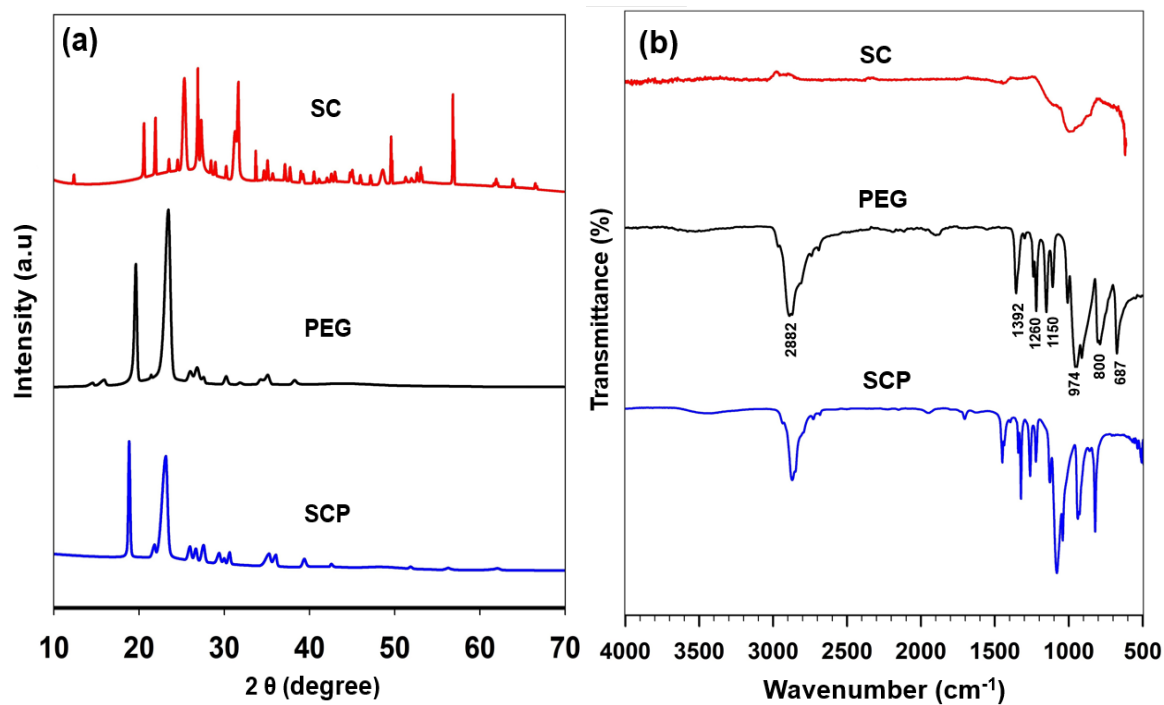


Figure 5.6 (a) XRD patterns and (b) FTIR spectra of SC, PEG and SCP.

The XRD patterns of SC, PEG and SCP are shown in Fig. 5.6a. The peaks located in the range of 20° to 30° 2θ are attributed to the presence of hematite (Fe_2O_3) and anorthite ($\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$). The peaks at an angle of 34° 2θ can be ascribed to aluminum silicate and those at 60° 2θ indicate the presence of magnetite [224–227]. The SCP composites have very intense diffraction peaks in at 18° and 23° 2θ which match with those obtained for PEG. Moreover, only PEG peaks are present in the SCP composite, indicating that the developed SCP formed without any chemical transformations during the vacuum process of PEG into SC pores.

Fig. 5.6b shows the FTIR spectrum of SC, PEG and SCP. SC has a broad band in the range of 950 cm^{-1} to 1200 cm^{-1} , which is assigned to the stretching of (Si–O–Si), confirming that SC is mostly composed of silica [225–227]. The spectra for SCP are very similar to that of PEG. The absence of any major new peaks in the spectra of the SCP compared to that of PEG, indicates that development of SCP composite takes place without any accompanied chemical reactions.

5.4.3.2 Morphology

The morphological shape of SC has a highly porous structure with an urchin-type morphology, as shown in Fig. 5.7a. The sizes of the pores in the range of the macropores with different pore sizes. The pores were fully filled with PEG after vacuum process as shown in Fig. 5.7b. The elemental weight of SC and SCP has a similar elemental composition as shown in Fig 5.7 (c and d). SC has higher Si, Fe and Al content compared to SCP, this is due to the presence of PEG that filled the SC pores.

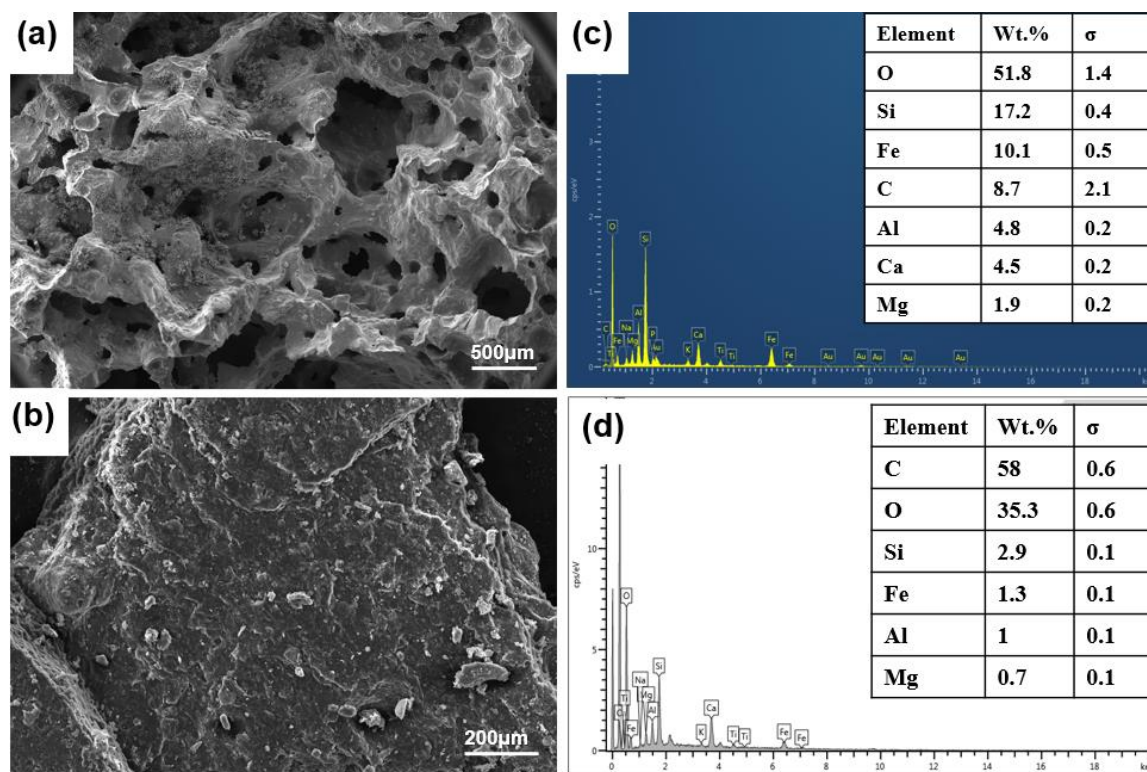


Figure 5.7 FE-SEM images of (a) SC and (b) SCP and their perspective EDS analysis (c and d), respectively.

5.4.3.3 Differential scanning calorimetry (DSC)

The DSC curves for melting and solidification of SC, PEG and SCP are shown in Fig. 5.8. The enthalpies were determined using the region under the DSC curves of melting and solidification cycles. The melting and solidification enthalpies of PEG are 192.4 J/g and 191.1 J/g, respectively. Although most of the reported values of PEG enthalpies are in same range [315,316]. Further, the developed SCP composite shows a noticeable loss of 64% and 65% of melting and solidification enthalpies respectively. The lower enthalpies of SCP compared to PEG is referred to the negligible enthalpies of the SC as shown in Fig 5.8. Consequently, the peak melting temperatures of SCP has been decreased by 5.6 % compared to that of PEG.

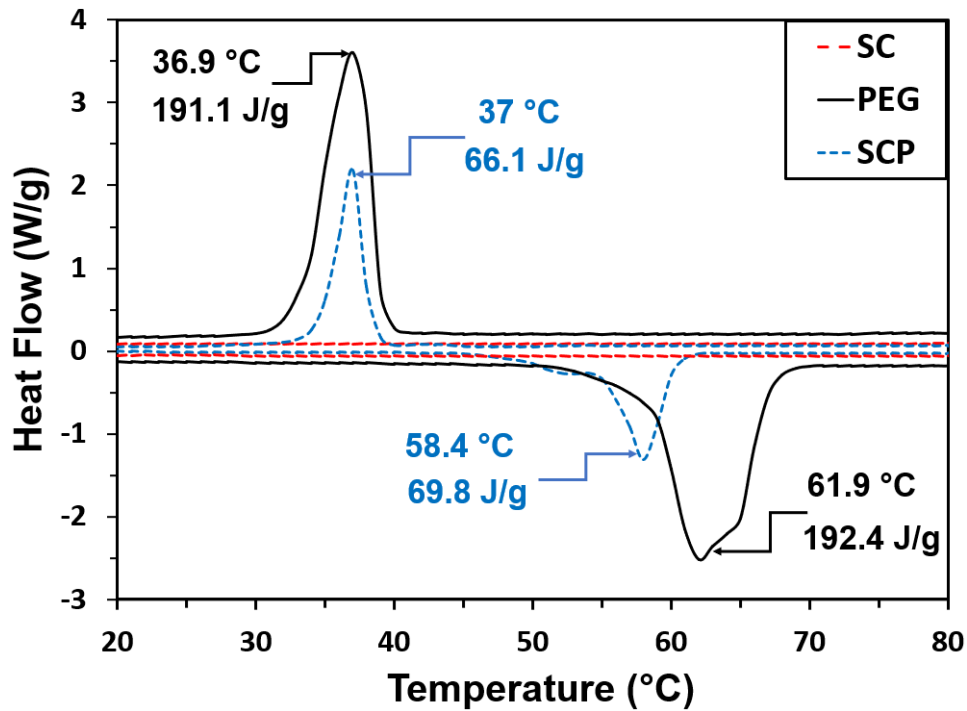


Figure 5.8 DSC analysis of SC, PEG and SCP.

5.4.4 Preparation and testing of developed cement coated SCP (SCPC)

The encapsulation process of SCP composite using cement coating to develop SCPC has been discussed in section 5.3.3. The following sections performing the performance and testing of the developed SCPC and the prepared SCPC concrete .

5.4.4.1 Leakage and morphology characteristics

Fig. 5.9 shows the PEG, SCP and SCPC before and after they have been exposed to a temperature of 70 °C in an oven for 30 min. SCPC composite did not show any leakage problems even after heating them at a temperature of 70 °C for 30 min, indicating no leakage of PEG from the developed SCPC composite. However, little leakage was observed in SCP composite due to the existence of PEG on the surface of SC particles. For SCPC the cement paste has worked as a barrier to accommodate and prevent the PEG from leaking during melting process. PEG, on the other hand, was fully decomposed when

exposed to the same conditions. This indicates that cement paste accommodates the PEG inside the matrix and prevent its leakage. The same results can be identified by the SEM image shown in Fig 5.10b.

The leakage of PEG from SCP shown in Fig. 5.9 indicate that phase change material composites must not be directly applied in cementitious mixtures because of serious loss of PEG [308].

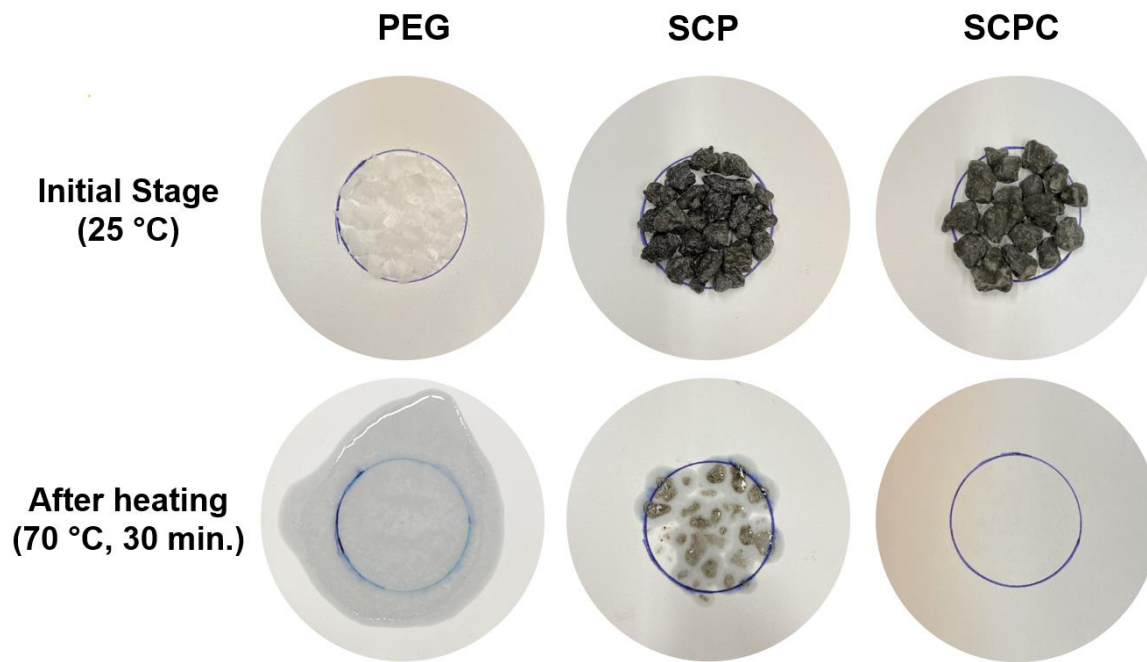


Figure 5.9 Exudation stability of PEG, SCP and SCPC.

SCPC particle has been sliced into two parts as shown in Fig. 5.10a to investigate the core and the barrier of the SCPC particles. The SEM imaging of the cross section of SCPC shown in Fig. 10b verify that cement paste creates a barrier surrounding the SCP particles which result into encapsulation the PEG and prevent its leakage. The formation of dense microstructure of C-S-H gel on the right side of Fig 10b accommodate the PEG during melting process and keep the particles stable without leakage. The EDS of SCPC (spectrum

1) in Fig. 10c shows that the elements include Oxygen, Carbon, Calcium, Silica, Alumina and iron which are the elements that producing the C-S-H gel. On the other hand, spectrum 2 shown in Fig. 10d shows that only oxygen and carbo are exist.

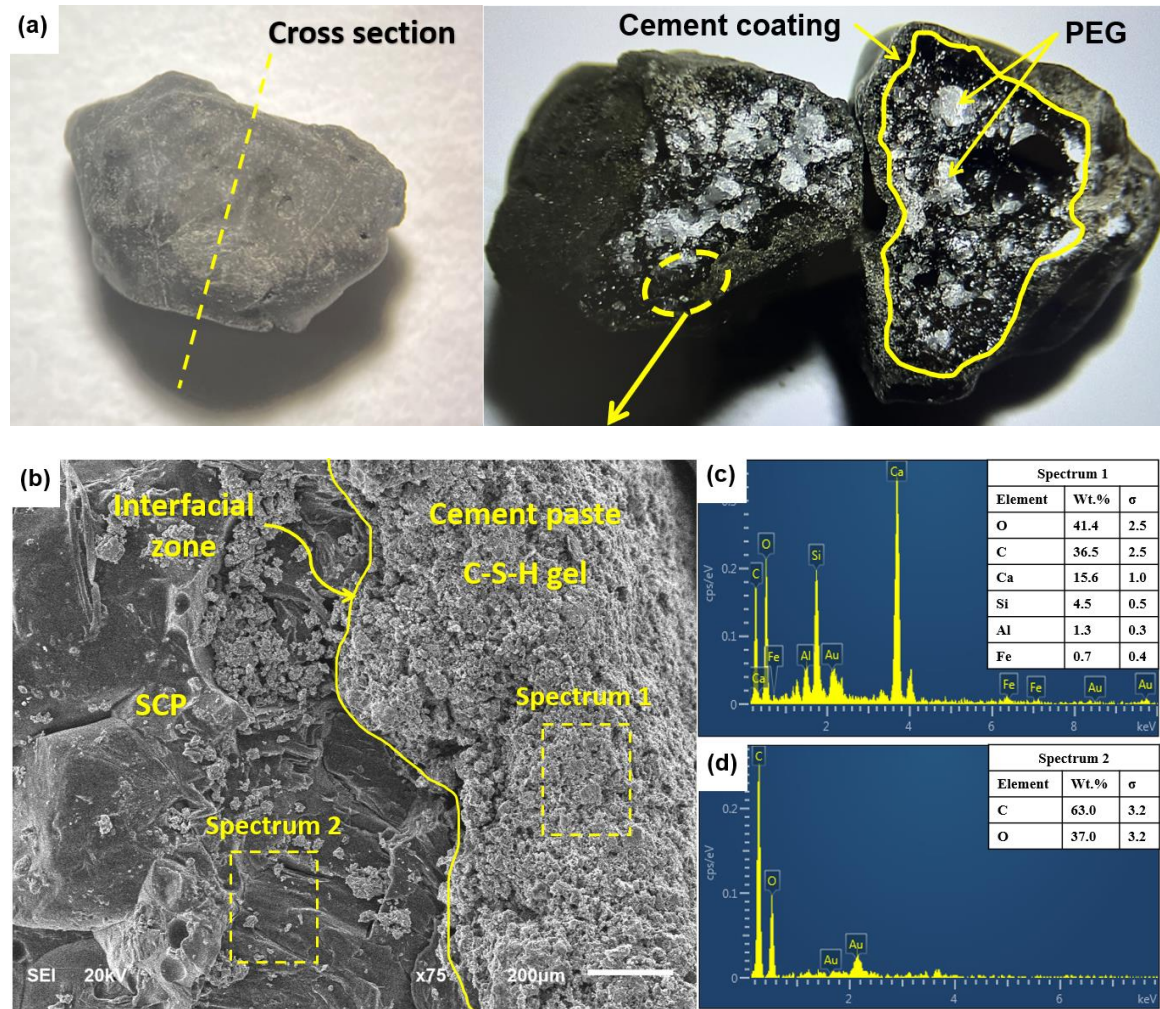


Figure 5.10 (a) Cross section of SCPC composite, (b) FE-SEM image of SCPC core and respective EDS spectrums (c and d).

5.4.4.2 Thermal reliability and thermal stability

Thermal reliability of SCPC particles was evaluated by subjecting the particles to 200 thermal cycles. The results of DSC shown in Fig. 5.11 indicate that SCPC can maintain its structure even after vigorous thermal cycling. The SCPC prepared sustained 200 cycles of melting and solidification. Furthermore, after 200 thermal cycling, the changes in the phase

change temperature and enthalpies of SCPC were less significant. Therefore, it can be concluded that the SCPC prepared has good thermal stability and can be deployed as a latent heat thermal energy storage (LHTES) materials in concrete constructions. This conclusion is crucial since a PCM's thermal stability is an essential feature for practical use in real-world applications.

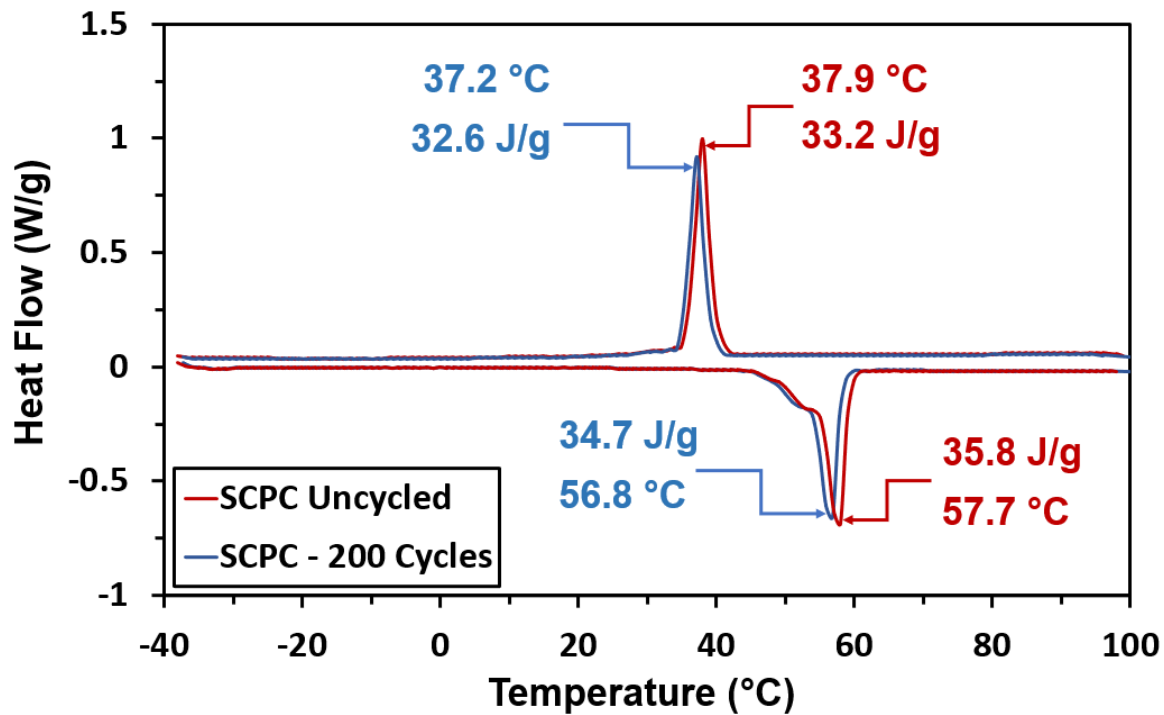


Figure 5.11 DSC before and after 200 thermal cycles of SCPC composite

TGA analysis was carried out to determine the stability of the developed composites in the working temperature range. As can be observed from Fig. 5.12, no weight loss was observed in SC particles. On the other hand, the weight loss of SCP and SCPC started at nearly 340 °C and ended at approximately 420 °C with only one step, which corresponds to the evaporation of PEG. Thereafter, the sample weights remain constant. Furthermore, the earlier occurrence of weight loss in SCP composite can be attributed to the physical

interaction between PEG and the inner porous surface of SC. Similar behavior has been observed for different PCM composites in previous studies [298,317]. Moreover, the weight loss in SCP was found to be approximately 45%, which support the results obtained earlier in Fig. 5.5. These results indicate that there is a uniform distribution of PEG in the SCP composite and the preparation of SCP particles is homogeneous. Furthermore, the weight loss of SCPC is 17.8% lower than that of SCP. This is due to the cement coating of the SCPC particles which contribute to the total weight of SCPC. Since the weight loss below 200 °C in SCPC is negligible, therefore, the developed SCPC composite can be used for thermal energy storage applications in buildings for hot weather climates.

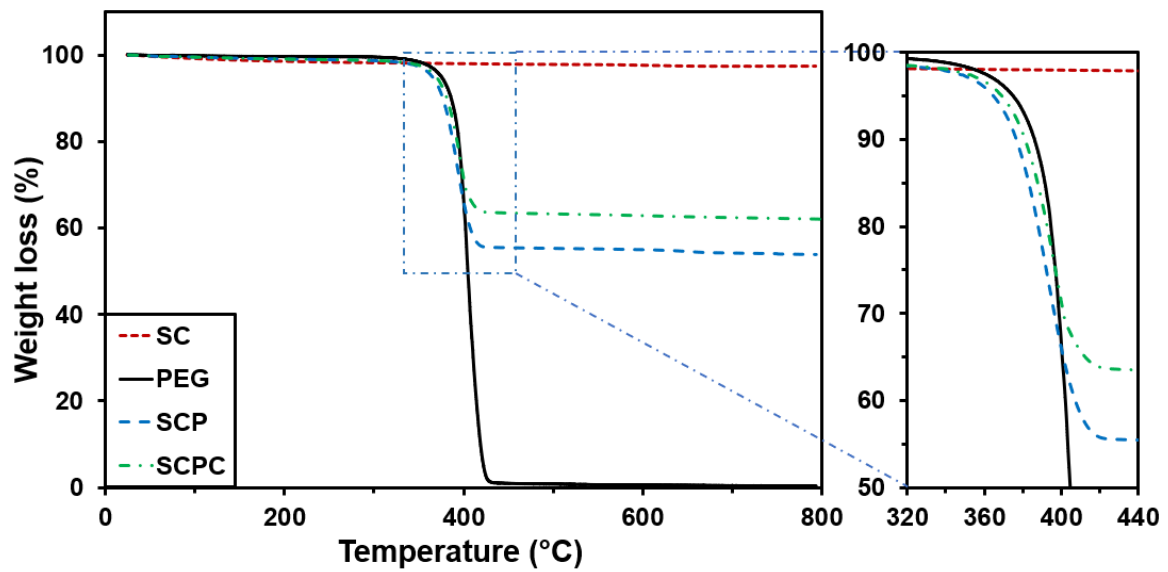


Figure 5.12 TGA curves of SC, PEG, SCP and SCPC composite

Table 5.2 lists the thermal activity values of PEG and the prepared composites with/without coating. All the parameters calculated using the formulation listed [212].

$$R = \frac{\Delta H_{m,com}}{\Delta H_{m,PEG}} \times 100\% \quad (5.1)$$

$$E_{eff} = \frac{\Delta H_{m,com}}{x_{PEG}} \quad (5.2)$$

$$E = \frac{\Delta H_{m,com} + \Delta H_{f,com}}{\Delta H_{m,PEG} + \Delta H_{f,PEG}} \times 100\% \quad (5.3)$$

$$\varphi = \frac{\frac{\Delta H_{m,com} + \Delta H_{f,com}}{R}}{\Delta H_{m,PEG} + \Delta H_{f,PEG}} \times 100\% \quad (5.4)$$

$$\gamma = \frac{\Delta H_{m,PEG}}{(x_{PEG} \times \Delta H_{m,PEG})} \times 100 \% \quad (5.5)$$

Where: T_m = melting temperature, ΔH_m = melting latent heat, T_f = solidification temperature, ΔH_f = solidification latent heat, ΔT_s = supercooling, E_{eff} = efficient energy per unit mass of PEG as shown in Equation 5.2 were calculated according to ref [238], R = impregnation ratio, E = impregnation efficiency and φ = energy storage capacity [212] and γ = Heat storage efficiency. In the listed equations, com is related to PCM composite (SCP, SCPC) and XPEG = PEG weight fraction in PCM (XPEG = 47%).

Table 5.2: Thermal activity of PEG, SCP and SCPC.

Sample	Melting process		Solidification process		Thermal properties calculations					
	T_m (°C)	ΔH_m (J/g)	T_f (°C)	ΔH_f (J/g)	ΔT_s (°C)	E_{eff} (J/g)	R (%)	E (%)	φ (%)	γ (%)
PEG	61.9	192.4	36.9	191.2	24.9	192.4	-	-	-	100
SCP	58.4	69.8	37.0	66.1	21.4	148.5	36.3	35.4	97.6	77.2
SCPC	57.7	35.8	37.9	33.2	19.8	76.2	18.6	17.9	96.7	39.6

The melting enthalpy of SCP and SCPC has been reduced by 31.1% and 63.7 % compared to That of PEG as shown in Table 5.2. This fact is because of the negligible enthalpies of SC and cement past in SCP and SCPC composite. However, compared to PEG, the supercooling values of SCPC and SCP has been reduced by 14% and 20.5%. Furthermore, high percentage of heat storage efficiency of SCPC composite are desirable. As a result, it would be feasible to use SCPC in concrete for construction material applications. The use of SCPC concrete has the potential to have substantial effects on the environment, economy, and overall life quality.

5.4.5 Development and testing of thermal energy storage concrete incorporating SCPC

5.4.5.1 Compressive strength

The compressive strength results of the prepared mixtures at different replacement ratios of SCPC (i.e., 20%, 40%, 60%, 80% and 100%) replacement by SC are presented in Fig 13. The compressive strength of MSC has been evaluated for comparison reason. The error bar of the standard deviation of each mix has been calculated for each age of testing. The strength of MSC has a relatively higher early strength values compared to SCPC concrete mixtures. These results may be attributed to the weaker bond between the SCPC particles in concrete mix, in addition to the presence of PEG which reduce the overall strength of the concrete. These findings has been reported in several previous studies [278,296,318–320]. However, the 28 days compressive strength of MSC, M20SCPC, M40SCPC, M60SCPC, M80SCPC and M100SCPC are 31.2 MPa, 28.7 MPa, 24.1 MPa, 22.8 MPa, 18.2 MPa and 16.8 MPa respectively. These results indicated that all mixtures except M100SCPC, can be used as a structural concrete according to the ACI (Section 1.1.1) and

which specify a minimum requirement of structural plain concrete above 2500 psi (17.2 MPa) [321]. Nevertheless, M100SCPC can be used as a nonstructural concrete in buildings. On the other hand, Fig. 5.13 shows that the concrete incorporating SCPC composites has slower strength development at early ages than that of late ages strength compared to MSC. The strength development from 14th to 28th days compressive strength values increased by 14.7%, 18.8%, 20.1%, 26.6% and 32% in M20SCPC, M40SCPC, M60SCPC, M80SCPC and M100SCPC mixes respectively, compared with only 11% for MSC in the same period.

Fig. 5.14 shows the percent reduction of the compressive strength during 3, 7, 14 and 28 days of testing. It's clearly shown that the increase of SCPC replacement, decrease the strength of the concrete mix. However, the strength reduction in all the SCPC concrete mixtures is reducing with time. Strength reduction of M100SCPC decreased from 77% at 3 days to 46% at 28 days of testing. The same trend has been observed for all the SCPC concrete mixes. This reveals that the SCPC concrete gain higher strength in late ages than early ages compared with reference mix (MSC). Fig. 5.15 shows the fracture pattern of the concrete mixtures after 28 days compressive strength. MSC shows that the failure in taken place in SC particles and throw the interfacial zone between the SC and cement mortar. As the SCPC has been replaced by SC, the SC particles are less appearing. This means that the failure of SCPC mixtures is taking place due to the weak bond between the SCPC particles and cement mortar.

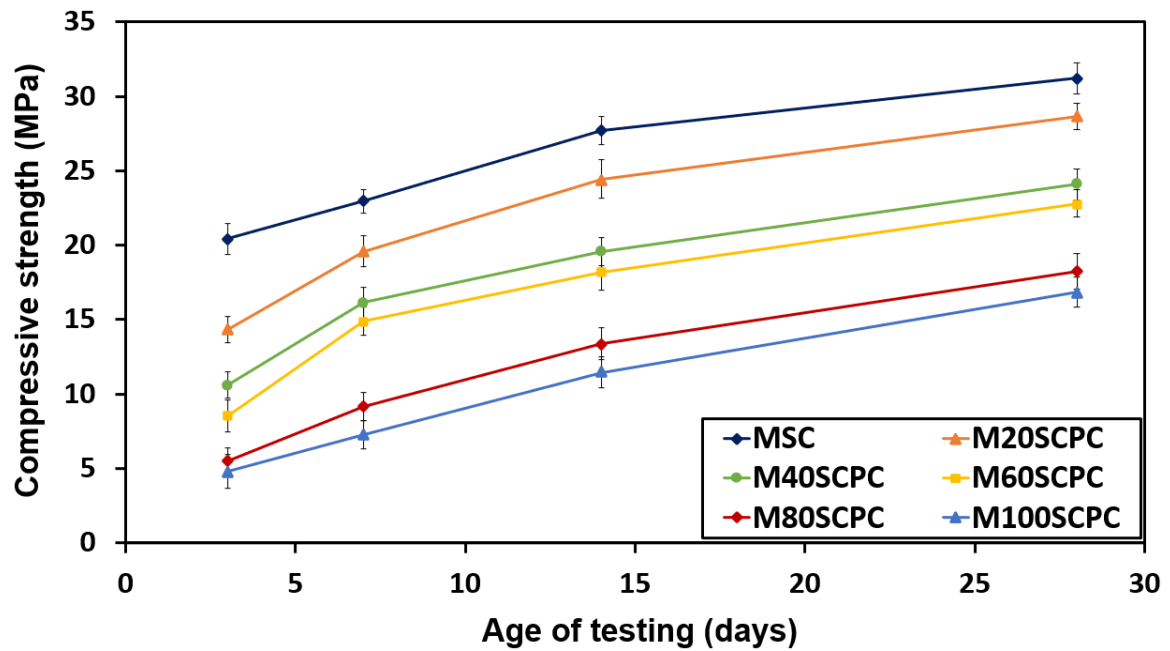


Figure 5.13 Compressive strength results of concrete mixtures at 3, 7, 14 and 28 days

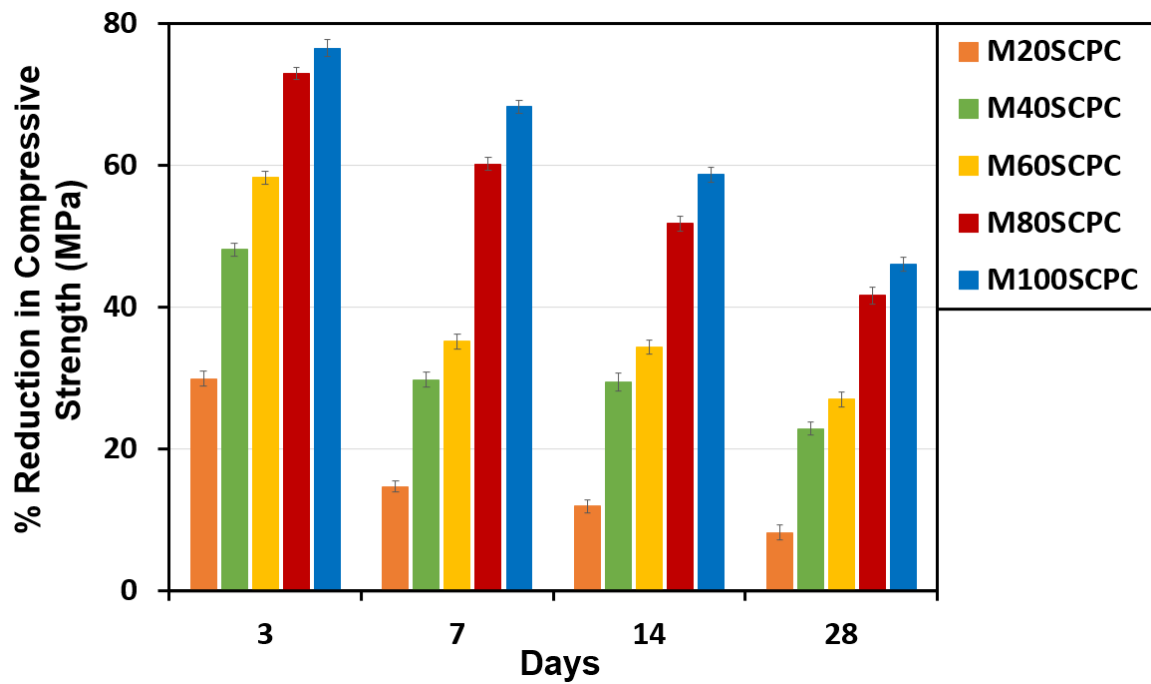


Figure 5.14 Percentage reduction in compressive strength with respect to control mix (MSC)

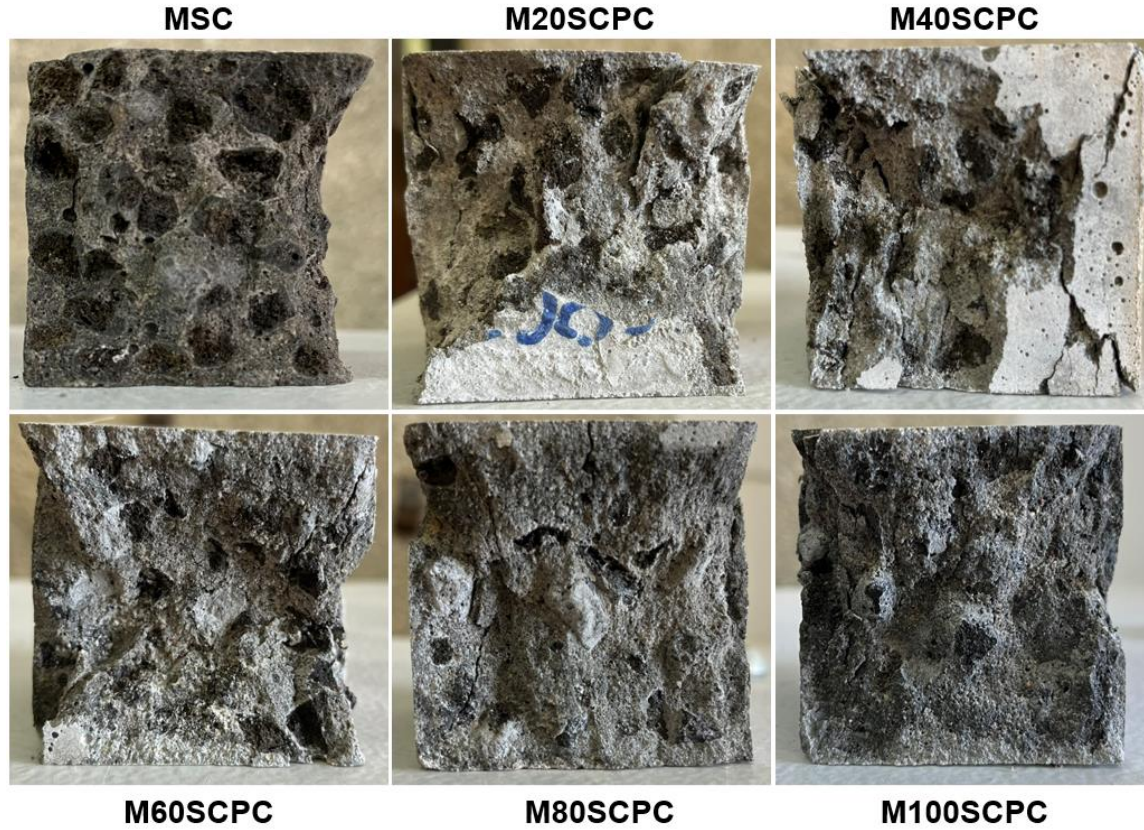


Figure 5.15 Fracture patterns of concrete samples after uniaxial compression test

5.4.5.2 Thermal conductivity and thermal performance of SCPC integrated concrete panels under repeated thermal cycles

The thermal conductivity and thermal resistivity values of the concrete panels with/without SCPC has been calculated using HFM according to the following formulations [313]:

$$\lambda = \frac{Q}{A} \times \frac{L}{\Delta T} \quad (5.6)$$

$$R = \frac{1}{\lambda} \times L \quad (5.7)$$

Where; λ : is the thermal conductivity of the samples (W/m.K), Q/A : is the heat flux measured, L : is the sample thickness, ΔT : is the temperature difference between the top and bottom plate at regular interval and R : is the thermal resistance ($m^2.K/W$).

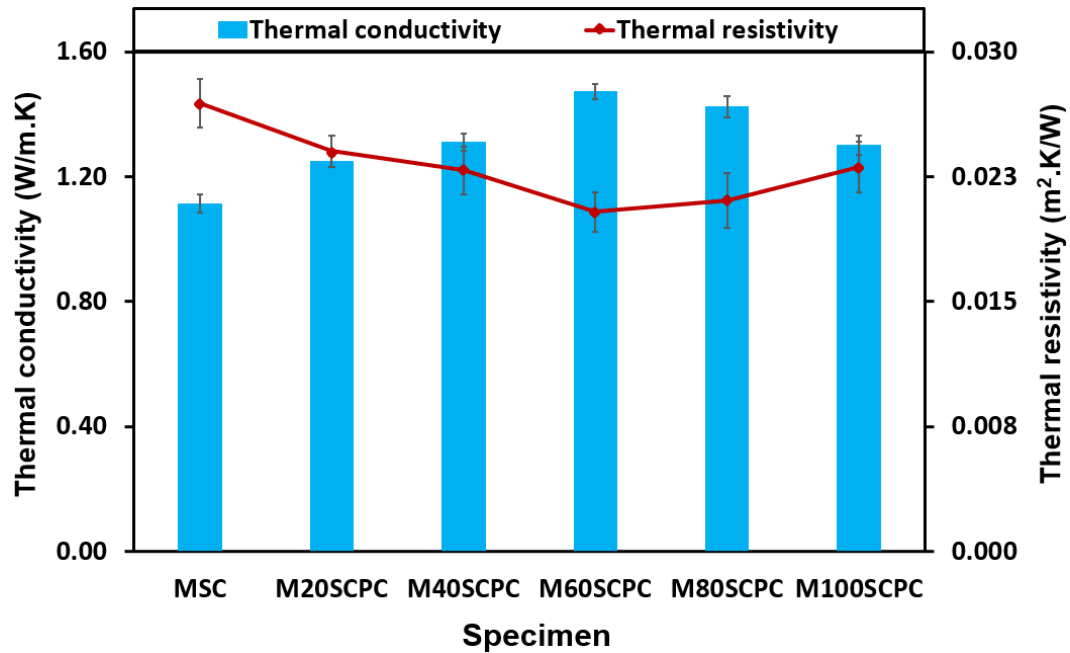
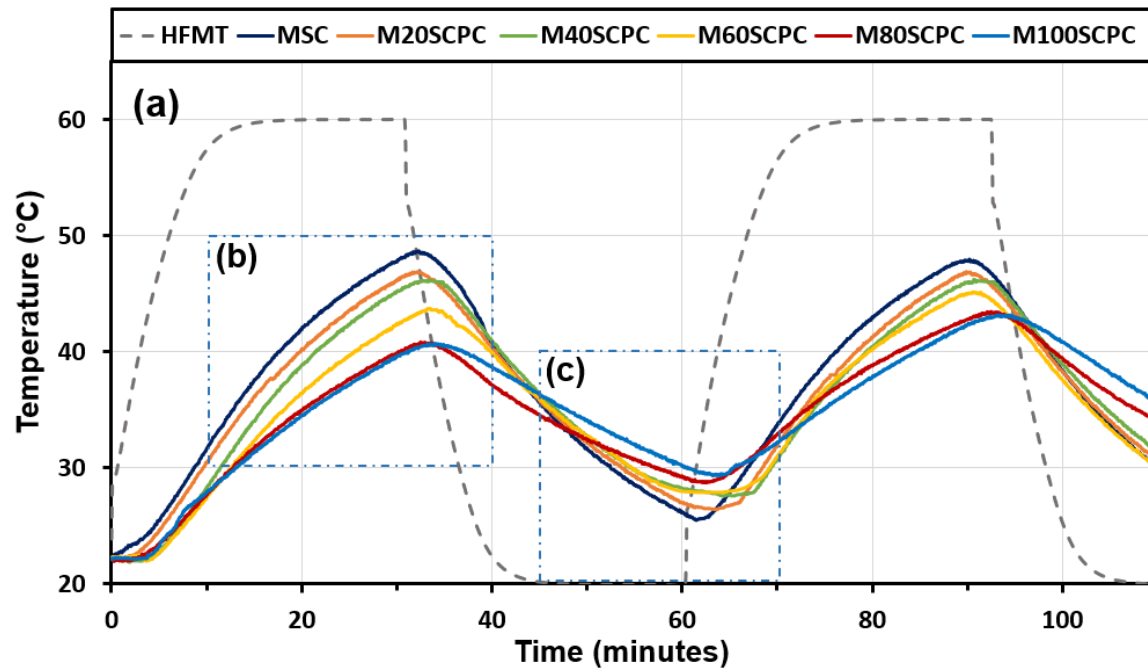


Figure 5.16 Thermal conductivity and thermal resistivity values of the concrete specimens

For thermal energy storage (TES) applications, a high thermal conductivity is preferred. Low thermal conductivity of PCMs delay the response of TES system. Therefore, the low thermal conductivity of SC and PEG are not desirable [277]. The thermal conductivity and thermal resistivity values of concrete panels with/without SCPC are shown in Fig. 5.16. The lower thermal conductivity of MSC may be attributed to the high porosity of SC in the concrete specimen. Conversely, thermal conductivity of specimens with SCPC increased with the increase in replacement of SC by SCPC, this is due to the high thermal conductivity of cement paste used for the coating of SCP particles. The cement paste improved the thermal conductivity of M60SCPC by 30.1% compared to that of MSC specimen. Moreover, as PEG are more conductive than air [318], the volume of PEG in the capillary pores of SC causes a modest increase in the heat conductivity of the SCPC concrete. Afterward, the thermal conductivity decreased for M80SCPC and M100SCPC. This may be attributed to the higher amount of PEG affected the thermal conductivity of

concrete with higher replacements. However, M100SCOP still has higher thermal conductivity than MSC specimen. The obtained vales of the thermal resistivity, which calculated using equation (5.7) are inversely proportional with that of thermal conductivity.



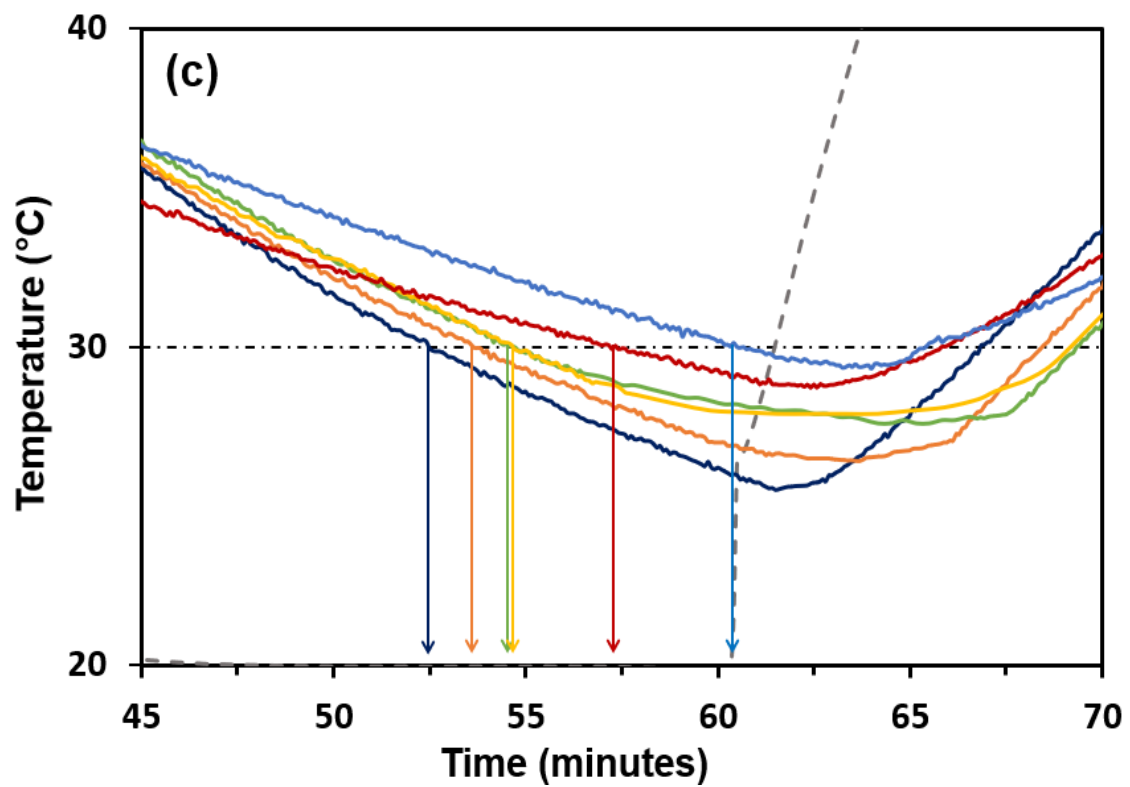
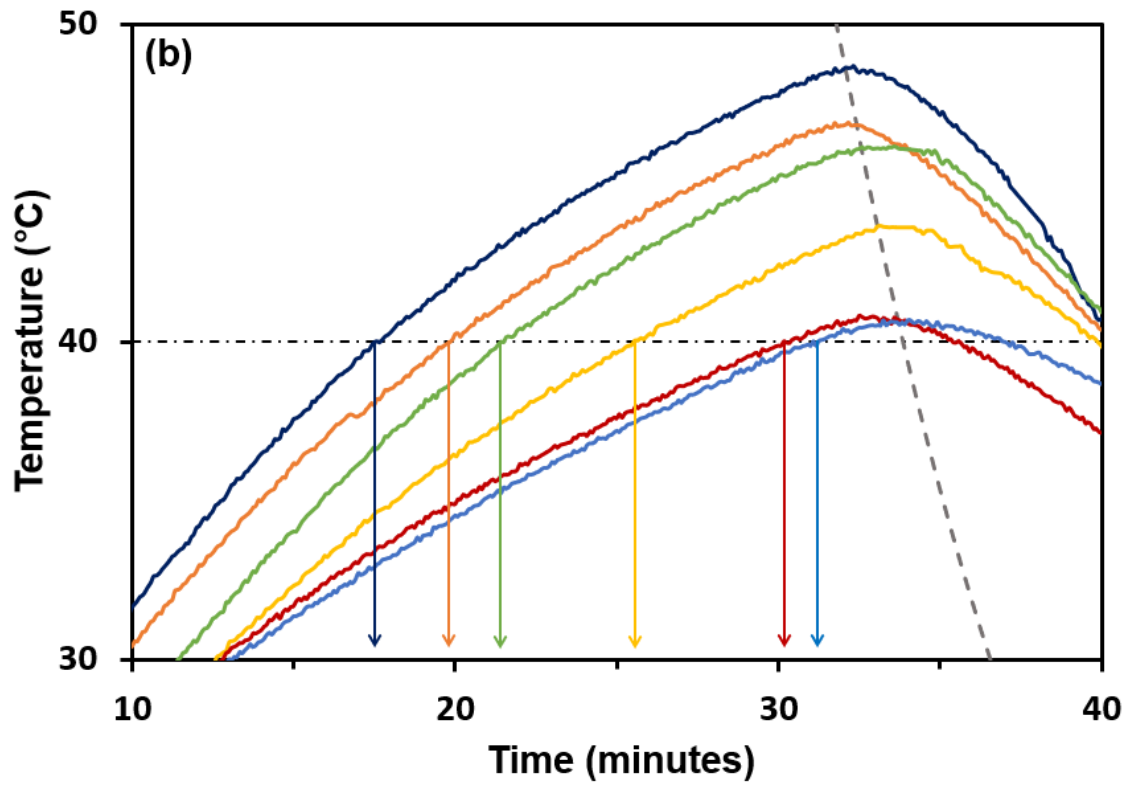
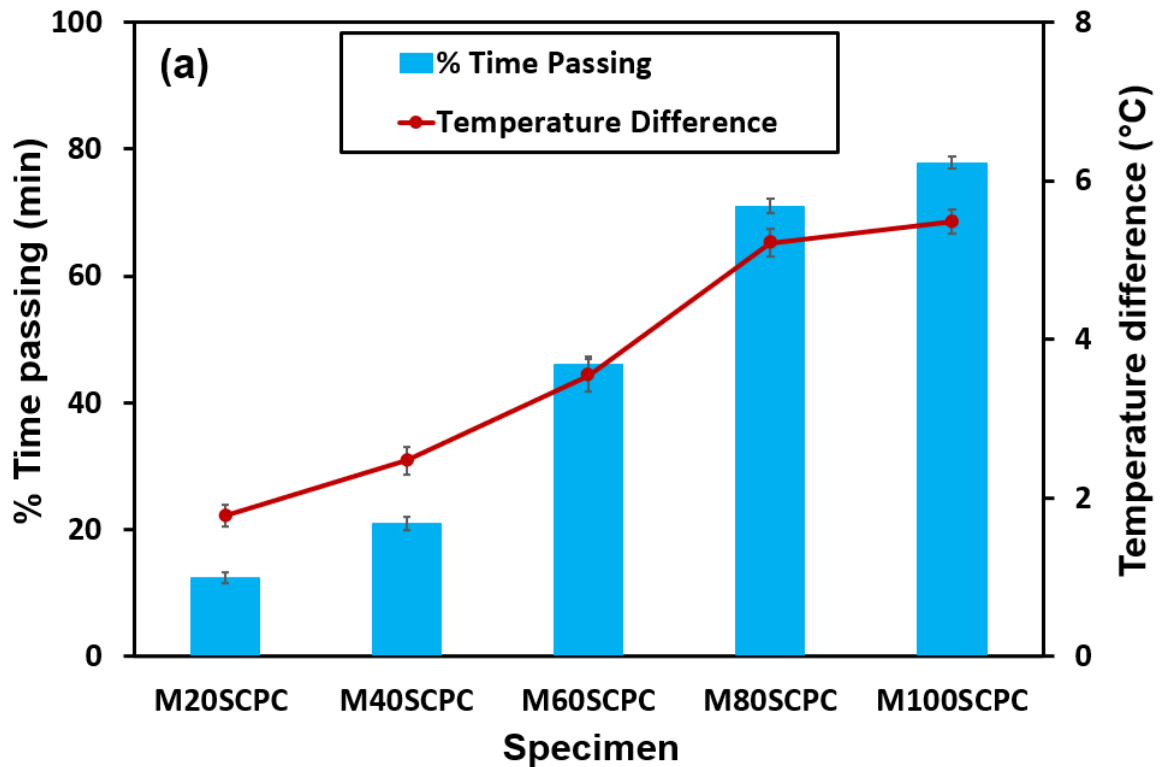


Figure 5.17 (a) Heating and cooling temperature profile cycles at the center of the bottom plate of concrete mixtures (b) and (c) close view of heating and cooling profiles, respectively.

The thermal performance of the prepared concrete panels with/without %SCPC were investigated by considering the bottom surface temperatures of the panels during both heating and cooling periods. The heat flow meter temperature (HFMT) of the top plate was set to increase up to 60 °C, then decreased to 20 °C for each thermal cycle. The bottom panel temperature was measured according to the temperature of the top HFM plate. As seen from Fig. 5.17a, the increasing rates in the bottom surface temperature of the concrete panels were not similar. To put it another way, the passing time at a temperature of 40 °C was found to be 17.6, 19.8, 21.3, 25.7, 30.1 and 31.1 min. for MSC, M20SCPC, M40SCPC, M60SCPC, M80SCPC and M100SCPC as shown in Fig. 5.17b. Moreover, that maximum temperature obtained was decreased with the increase in %SCPC in concrete panels. Overall, the higher addition of SCPC leads to the lower temperature rise or reduction during the heating or cooling period. The percent time passing of the panels containing %SCPC with respect to MSC (bar chart) and the corresponding temperature difference (line chart) of heating and cooling cycles are shown in Fig. 18a and Fig. 18b, respectively. It's clearly shown that the time passing, and temperature difference increased with the increase in the %SCPC content. The incorporation of 20% to 100% of SCPC into concrete results in the maximum temperature deviation of 1.78 to 5.49 °C and 0.93 to 3.88 °C during the heating and cooling periods, respectively. Higher temperature difference of the panels implies higher thermal inertia of concrete samples containing PCM [322]. Accordingly, higher SCPC replacement improved the thermal inertia of the prepared concrete panels. Additionally, the TES function of the concrete panels, including SCPC, and sensible heat absorption were responsible for the time delay during the temperature increase, time extension, and the established temperature difference [296,323]. Similarly, Fig. 5.17c

shows that the time needed to reduce the bottom temperatures of concrete panels at 30 °C during the cooling phase increased for the concrete panels including SCPC compared with MSC. Moreover, Fig. 5.18b shows that the temperature difference increase was calculated to be 0.93 °C, 2.08 °C, 2.47 °C, 3.32 °C and 3.88 °C for M20SCPC, M40SCPC, M60SCPC, M80SCPC and M100SCPC with respect to MSC. This increase in both cooling times passing, and temperature difference was owing to the latent heat released by SCPC into the concrete panels. From the obtained results, it can be concluded that the concrete including SCPC can be considered as a promising concrete which could reduce energy consumption and improve the thermal comfort in buildings. Moreover, SCPC concrete can reduce electricity costs by shifting the electrical load of buildings away from peak demand times.



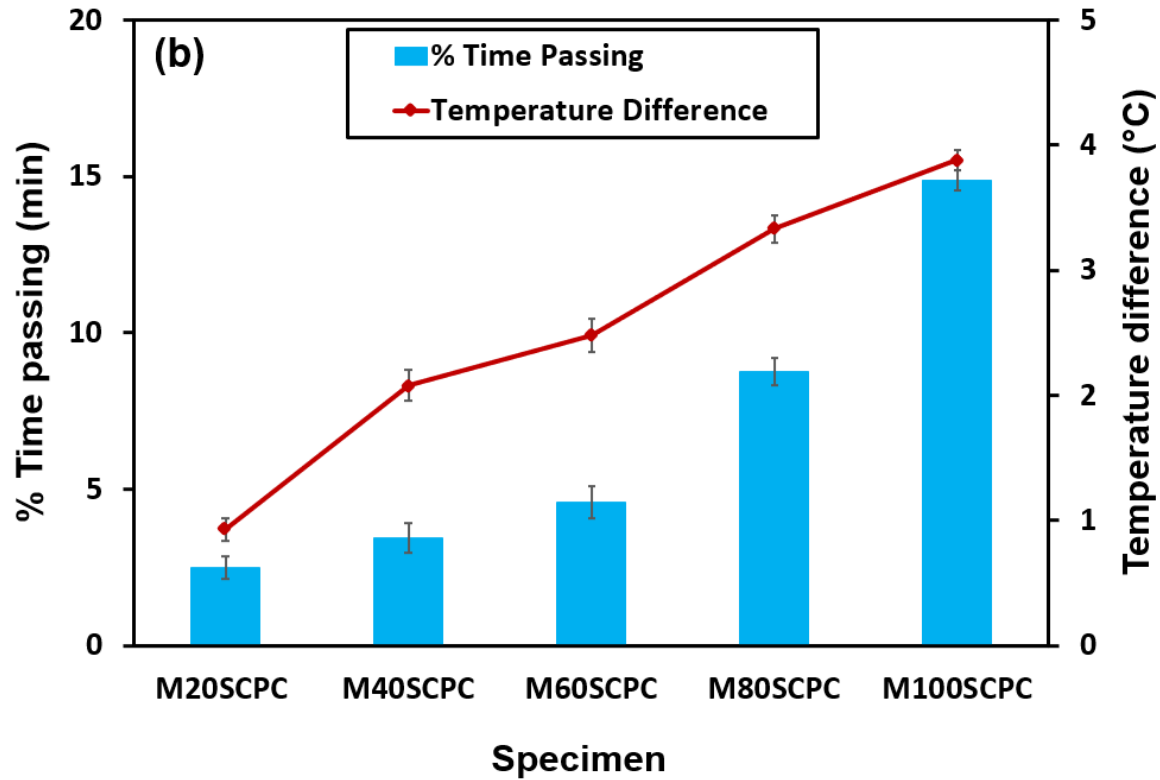


Figure 5.18 Percentage of time passing with temperature difference of SCPC panels compared with MSC for (a) heating cycle and (b) cooling cycle.

5.5 Conclusions

In this study, a novel cement coated scoria/PEG particles (SCPC) characterized and utilized for the first time to improve the thermal performance of concrete. The following conclusions can be drawn:

- Porous volcanic scoria was successfully employed as supporting material to develop a FS-PCM used in concrete. The absorption capacity SC was found to be 47% using a vacuum impregnation technique. Moreover, the XRD and FTIR results showed that SCP indicating that the developed SCP was formed without any chemical reactions during the preparation process. Although the TGA results shows

a homogeneous distribution of PEG in the SCP composite, but it suffers from leakage of PEG during melting process.

- Cement coated SCP showed superior stability, without sign of PEG leakage for a temperature exceeding the melting temperature of PEG. Moreover, after 200 cycles of melting and solidification, SCPC displays stable performance and has the ability for storing/releasing energy without any noticeable change. In addition, the cement coating enhanced the thermal conductivity of the particles which improve the TES response of concrete. The DSC results shows that SCPC composite has a heat storage efficiency value of 96.7%. Thus, SCPC could be used to enhance the thermal storage of concrete.
- The compressive strength results show that up to 80% replacement of SCPC by SC in concrete can be deployed as a structural concrete in buildings. While M100SCPC has a compressive strength value of 16.8 MPa which can be used as a non-structural concrete to improve the thermal efficiency of concrete in buildings.
- The thermal performance analysis shows that concrete panels containing SCPC has a maximum temperature reduction of 5.49 °C and 3.88 °C for the heating and cooling cycles, respectively. Which reflects the higher thermal inertia of concrete containing SCPC. Thus, the prepared SCPC concrete has a function of reducing the energy consumption by decreasing the temperature and shifting the loads away from the peak periods.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In this study, several supporting materials were investigated for their use as a supporting material to develop a form stable phase change material (FSPCM). The thermal and physico-chemical properties of the selected materials was evaluated utilizing a wide array of analytical techniques. Among the materials investigated, ExPP/CNT(0.5%) exhibited the best performance, showing that it is a viable material for thermal energy storage system. Further, the developed ExPP composite is a promising PCM for TES in energy-efficient buildings due to its remarkable ability of rapid energy storage/release combined with good chemical stability and thermal reliability. Further, ExPP does not have leakage problems, super cooling is minimized, conductivity is high and all other properties that play a crucial role in maintaining building comfort are superior. However, it has low thermal conductivity which limits its application as an energy storage system. Compared to other PCM composites, the developed ExPP/CNT(0.5%) PCM offers greater enthalpy, superior storage capacity, and minimum super cooling. The structural properties and the pore network of ExPP/CNT (0.5%) composite prevents the leakage of liquid PEG during service.

To utilize PCMs in building applications, novel cement coated scoria/PEG particles (SCPC) characterized and utilized for the first time to improve the thermal performance of concrete. Porous volcanic scoria was successfully employed as supporting material to develop a FS-PCM used in concrete. The absorption capacity SC was found to be 47%

using a vacuum impregnation technique. Moreover, the XRD and FTIR results showed that SCP indicating that the developed SCP was formed without any chemical reactions during the preparation process. Although the TGA results shows a homogeneous distribution of PEG in the SCP composite, but it suffers from leakage of PEG during melting process. Cement coated SCP showed superior stability, without sign of PEG leakage for a temperature exceeding the melting temperature of PEG. Moreover, after 200 cycles of melting and solidification, SCPC displays stable performance and has the ability for storing/releasing energy without any noticeable change. In addition, the cement coating enhanced the thermal conductivity of the particles which improve the TES response of concrete. The DSC results shows that SCPC composite has a heat storage efficiency value of 96.7%. Thus, SCPC could be used to enhance the thermal storage of concrete.

The compressive strength results show that up to 80% replacement of SCPC by SC in concrete can be deployed as a structural concrete in buildings. While M100SCPC has a compressive strength value of 16.8 MPa which can be used as a non-structural concrete to improve the thermal efficiency of concrete in buildings. In addition, the thermal performance analysis shows that concrete panels containing SCPC has a maximum temperature reduction of 5.49 °C and 3.88 °C for the heating and cooling cycles, respectively. Which reflects the higher thermal inertia of concrete containing SCPC. Thus, the prepared SCPC concrete has a function of reducing the energy consumption by decreasing the temperature and shifting the loads away from the peak periods. Based on the findings of this study, the developed novel PCM composites can be utilized to harness solar energy cleanly and efficiently and bridge the gap in the deployment of a renewable energy systems in building applications for hot climate conditions.

6.2 Recommendations for Future Investigations:

Based on the literature and the experimental work in the current study, the following recommendations can be drawn:

1. Perform the durability tests of the prepared concrete incorporated with form stabilized phase change materials.
2. Study the effect of modified cement coating with high carbon content to improve the thermal conductivity of the form stabilized phase change material.
3. Study the effect of different impregnation methods on the PCM absorption and leakage properties of FSPCM.
4. Check the effect of ExPP/CNT with different percentages of sand replacement in concrete.
5. Study other coating techniques (like epoxy coating) and its effect on thermal and mechanical performance of concrete.

References

- [1] C. Barreneche, M.E. Navarro, A.I. Fernández, L.F. Cabeza, Improvement of the thermal inertia of building materials incorporating PCM. Evaluation in the macroscale, *Applied Energy*. 109 (2013) 428–432. <https://doi.org/10.1016/j.apenergy.2012.12.055>.
- [2] S.E. Kalnæs, B.P. Jelle, Phase change materials and products for building applications: A state-of-the-art review and future research opportunities, *Energy and Buildings*. 94 (2015) 150–176. <https://doi.org/10.1016/j.enbuild.2015.02.023>.
- [3] A. Sari, A. Karaiepli, C. Alkan, Preparation, characterization and thermal properties of lauric acid/expanded perlite as novel form-stable composite phase change material, *Chemical Engineering Journal*. 155 (2009) 899–904. <https://doi.org/10.1016/j.cej.2009.09.005>.
- [4] S.A. Mohamed, F.A. Al-Sulaiman, N.I. Ibrahim, M.H. Zahir, A. Al-Ahmed, R. Saidur, B.S. Yılbaş, A.Z. Sahin, A review on current status and challenges of inorganic phase change materials for thermal energy storage systems, *Renewable and Sustainable Energy Reviews*. 70 (2017) 1072–1089. <https://doi.org/10.1016/j.rser.2016.12.012>.
- [5] X. Zhang, R. Wen, C. Tang, B. Wu, Z. Huang, X. Min, Y. Huang, Y. Liu, M. Fang, X. Wu, Thermal conductivity enhancement of polyethylene glycol/expanded perlite with carbon layer for heat storage application, *Energy and Buildings*. 130 (2016) 113–121. <https://doi.org/10.1016/j.enbuild.2016.08.049>.
- [6] E.J. B, V.A. A, A comprehensive review on latent heat and thermal conductivity of nanoparticle dispersed phase change material for low-temperature applications, (2019). <https://doi.org/10.1016/j.ensm.2019.07.031>.
- [7] W. Wang, X. Yang, Y. Fang, J. Ding, J. Yan, Preparation and thermal properties of polyethylene glycol/expanded graphite blends for energy storage, *Applied Energy*. 86 (2009) 1479–1483. <https://doi.org/10.1016/J.APENERGY.2008.12.004>.
- [8] Y. Yang, Y. Pang, Y. Liu, H. Guo, Preparation and thermal properties of polyethylene glycol/expanded graphite as novel form-stable phase change material for indoor energy saving, *Materials Letters*. 216 (2018) 220–223. <https://doi.org/10.1016/j.matlet.2018.01.025>.
- [9] D. Zhang, M. Chen, S. Wu, Q. Liu, J. Wan, Preparation of expanded graphite/polyethylene glycol composite phase change material for thermoregulation of asphalt binder, *Construction and Building Materials*. 169 (2018) 513–521. <https://doi.org/10.1016/j.conbuildmat.2018.02.167>.
- [10] Y. Lv, W. Zhou, W. Jin, Experimental and numerical study on thermal energy storage of polyethylene glycol/expanded graphite composite phase change material,

- Energy and Buildings. 111 (2016) 242–252. <https://doi.org/10.1016/j.enbuild.2015.11.042>.
- [11] L. Zhang, P. Zhang, F. Wang, M. Kang, R. Li, Y. Mou, Y. Huang, Phase change materials based on polyethylene glycol supported by graphene-based mesoporous silica sheets, *Applied Thermal Engineering*. 101 (2016) 217–223. <https://doi.org/10.1016/j.applthermaleng.2016.02.120>.
- [12] G.Q. Qi, J. Yang, R.Y. Bao, Z.Y. Liu, W. Yang, B.H. Xie, M.B. Yang, Enhanced comprehensive performance of polyethylene glycol based phase change material with hybrid graphene nanomaterials for thermal energy storage, *Carbon*. 88 (2015) 196–205. <https://doi.org/10.1016/j.carbon.2015.03.009>.
- [13] C. Wang, L. Feng, H. Yang, G. Xin, W. Li, J. Zheng, W. Tian, X. Li, Graphene oxide stabilized polyethylene glycol for heat storage, *Physical Chemistry Chemical Physics*. 14 (2012) 13233–13238. <https://doi.org/10.1039/c2cp41988b>.
- [14] L. Feng, C. Wang, P. Song, H. Wang, X. Zhang, The form-stable phase change materials based on polyethylene glycol and functionalized carbon nanotubes for heat storage, *Applied Thermal Engineering*. 90 (2015) 952–956. <https://doi.org/10.1016/j.applthermaleng.2015.07.080>.
- [15] B. Tang, Y. Wang, M. Qiu, S. Zhang, A full-band sunlight-driven carbon nanotube/PEG/SiO₂ composites for solar energy storage, *Solar Energy Materials and Solar Cells*. 123 (2014) 7–12. <https://doi.org/10.1016/j.solmat.2013.12.022>.
- [16] A. Bland, M. Khzouz, T. Statheros, E.I. Gkanas, PCMs for Residential Building Applications : A Short Future Development, (2017). <https://doi.org/10.3390/buildings7030078>.
- [17] Saudi Perlite Industries, Saudi Perlite Industries, (1984). <http://www.saudi-perlite.com.sa/>.
- [18] M.R. Moufti, A.A. Sabtan, O.R. El-Mahdy, W.M. Shehata, Assessment of the industrial utilization of scoria materials in central Harrat Rahat, Saudi Arabia, *Engineering Geology*. 57 (2000) 155–162. [https://doi.org/10.1016/S0013-7952\(00\)00024-7](https://doi.org/10.1016/S0013-7952(00)00024-7).
- [19] A.A. Sabtan, W.M. Shehata, Evaluation of engineering properties of scoria in central Harrat Rahat, Saudi Arabia, *Bulletin of Engineering Geology and the Environment*. 59 (2000) 219–225. <https://doi.org/10.1007/s100640000061>.
- [20] D. Of, L. Concrete, U.L. Materials, DEVELOPMENT OF LIGHTWEIGHT CONCRETE UTILIZING LOCAL MATERIALS, KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, n.d.
- [21] M.H. Al-Malack, G.M. Abdullah, O.S.B. Al-Amoudi, A.A. Bukhari, Stabilization of indigenous Saudi Arabian soils using fuel oil flyash, *Journal of King Saud University - Engineering Sciences*. 28 (2016) 165–173.

<https://doi.org/10.1016/j.jksues.2014.04.005>.

- [22] M. Al-Mehthel, A.S. Al-Utaibi, M.R.A. Mohammed Maslehuddin, Utilization Of Heavy Oil Ash To Produce High Quality Concrete, US 8,945,300 B2, 2015.
- [23] Mohammed Al-Mehthel Hamad I. Al-Abdul Wahhab Ibnelwaleed A. Hussein, Utilization Of Heavy Oil Fly Ash To Improve Asphalt Binder And Asphalt Concrete Performance, 2013.
- [24] Q. Meng, Y. Xi, X. Ren, H. Li, L. Jiang, L. Yang, Thermal Energy Storage Air-conditioning Demand Response Control Using Elman Neural Network Prediction Model, Sustainable Cities and Society. 76 (2022) 103480. <https://doi.org/https://doi.org/10.1016/j.scs.2021.103480>.
- [25] N. Variji, M. Siavashi, M. Tahmasbi, M. Bidabadi, Analysis of the effects of porous media parameters and inclination angle on the thermal storage and efficiency improvement of a photovoltaic-phase change material system, Journal of Energy Storage. 50 (2022) 104690. <https://doi.org/https://doi.org/10.1016/j.est.2022.104690>.
- [26] M. Frangou, M. Aryblia, S. Tournaki, T. Tsoutsos, Renewable energy performance contracting in the tertiary sector Standardization to overcome barriers in Greece, Renewable Energy. 125 (2018) 829–839. <https://doi.org/10.1016/j.renene.2018.03.001>.
- [27] A. Maturo, A. Buonomano, A. Athienitis, Design for energy flexibility in smart buildings through solar based and thermal storage systems: Modelling, simulation and control for the system optimization, Energy. 260 (2022) 125024. <https://doi.org/https://doi.org/10.1016/j.energy.2022.125024>.
- [28] K. Irshad, K. Habib, R. Saidur, M.W. Kareem, B.B. Saha, Study of thermoelectric and photovoltaic facade system for energy efficient building development: A review, Journal of Cleaner Production. 209 (2019) 1376–1395. <https://doi.org/https://doi.org/10.1016/j.jclepro.2018.09.245>.
- [29] R.A. Kishore, M.V.A. Bianchi, C. Booten, J. Vidal, R. Jackson, Modulating thermal load through lightweight residential building walls using thermal energy storage and controlled precooling strategy, Applied Thermal Engineering. 180 (2020) 115870. <https://doi.org/https://doi.org/10.1016/j.applthermaleng.2020.115870>.
- [30] A. Ghodrati, R. Zahedi, A. Ahmadi, Analysis of cold thermal energy storage using phase change materials in freezers, Journal of Energy Storage. 51 (2022) 104433. <https://doi.org/https://doi.org/10.1016/j.est.2022.104433>.
- [31] M.H. Zahir, M.M. Rahman, K. Irshad, M.M. Rahman, Shape-Stabilized Phase Change Materials for Solar Energy Storage: MgO and Mg(OH)(2) Mixed with Polyethylene Glycol., Nanomaterials (Basel, Switzerland). 9 (2019). <https://doi.org/10.3390/nano9121773>.

- [32] P.K.S. Rathore, N.K. Gupta, D. Yadav, S.K. Shukla, S. Kaul, Thermal performance of the building envelope integrated with phase change material for thermal energy storage: an updated review., *Sustainable Cities and Society*. 79 (2022) 103690. <https://doi.org/https://doi.org/10.1016/j.scs.2022.103690>.
- [33] K. Irshad, K. Habib, S. Algarni, B.B. Saha, B. Jamil, Sizing and life-cycle assessment of building integrated thermoelectric air cooling and photovoltaic wall system, *Applied Thermal Engineering*. 154 (2019) 302–314. <https://doi.org/https://doi.org/10.1016/j.applthermaleng.2019.03.027>.
- [34] Y. Cui, J. Xie, J. Liu, J. Wang, S. Chen, A review on phase change material application in building, *Advances in Mechanical Engineering*. 9 (2017) 1–15. <https://doi.org/10.1177/1687814017700828>.
- [35] Z. Rahimpour, A. Faccani, D. Azuatalam, A. Chapman, G. Verbič, Using Thermal Inertia of Buildings with Phase Change Material for Demand Response, *Energy Procedia*. 121 (2017) 102–109. <https://doi.org/10.1016/j.egypro.2017.07.483>.
- [36] A. Hasan, J. Sarwar, H. Alnoman, S. Abdelbaqi, Yearly energy performance of a photovoltaic-phase change material (PV-PCM) system in hot climate, *Solar Energy*. 146 (2017) 417–429. <https://doi.org/10.1016/j.solener.2017.01.070>.
- [37] M.A. Medina, J.B. King, M. Zhang, On the heat transfer rate reduction of structural insulated panels (SIPs) outfitted with phase change materials (PCMs), *Energy*. 33 (2008) 667–678. <https://doi.org/10.1016/j.energy.2007.11.003>.
- [38] K. Irshad, S. Algarni, N. Islam, S. Rehman, M.H. Zahir, A.A. Pasha, S.N. Pillai, Parametric analysis and optimization of a novel photovoltaic trombe wall system with venetian blinds: Experimental and computational study, *Case Studies in Thermal Engineering*. 34 (2022) 101958. <https://doi.org/10.1016/j.csite.2022.101958>.
- [39] X. Sun, Y. Zhang, K. Xie, M.A. Medina, A parametric study on the thermal response of a building wall with a phase change material (PCM) layer for passive space cooling, *Journal of Energy Storage*. 47 (2022) 103548. <https://doi.org/https://doi.org/10.1016/j.est.2021.103548>.
- [40] N. Essid, A. Eddhahak, J. Neji, Experimental and numerical analysis of the energy efficiency of PCM concrete wallboards under different thermal scenarios, *Journal of Building Engineering*. 45 (2022) 103547. <https://doi.org/https://doi.org/10.1016/j.jobbe.2021.103547>.
- [41] Y. Yang, Z. Shen, W. Wu, H. Zhang, Y. Ren, Q. Yang, Preparation of a novel diatomite-based PCM gypsum board for temperature-humidity control of buildings, *Building and Environment*. 226 (2022) 109732. <https://doi.org/https://doi.org/10.1016/j.buildenv.2022.109732>.
- [42] S. Sarkar, S. Mestry, S.T. Mhaske, Developments in phase change material (PCM) doped energy efficient polyurethane (PU) foam for perishable food cold-storage

- applications: A review, *Journal of Energy Storage*. 50 (2022) 104620. <https://doi.org/https://doi.org/10.1016/j.est.2022.104620>.
- [43] D.A. Neeper, Thermal dynamics of wallboard with latent heat storage, *Solar Energy*. 68 (2000) 393–403. [https://doi.org/10.1016/S0038-092X\(00\)00012-8](https://doi.org/10.1016/S0038-092X(00)00012-8).
- [44] S.M. HUSAIN, M. İPEK, A. ÇAĞLAYAN, T.N. AYNUR, S. KOCATÜRK, H. BEDİR, Dynamic Modelling of the Steady State and Load Processing Operation of a Domestic Refrigerator Cooled Through Natural Convection, *International Journal of Refrigeration*. (2022). <https://doi.org/https://doi.org/10.1016/j.ijrefrig.2022.08.015>.
- [45] L.F. Cabeza, A. Castell, C. Barreneche, A. De Gracia, A.I. Fernández, Materials used as PCM in thermal energy storage in buildings: A review, *Renewable and Sustainable Energy Reviews*. 15 (2011) 1675–1695. <https://doi.org/10.1016/j.rser.2010.11.018>.
- [46] V.V. Tyagi, D. Buddhi, PCM thermal storage in buildings: A state of art, *Renewable and Sustainable Energy Reviews*. 11 (2007) 1146–1166. <https://doi.org/10.1016/j.rser.2005.10.002>.
- [47] L. Liu, N. Hammami, L. Trovalet, D. Bigot, J.-P. Habas, B. Malet-Damour, Description of phase change materials (PCMs) used in buildings under various climates: A review, *Journal of Energy Storage*. 56 (2022) 105760. <https://doi.org/https://doi.org/10.1016/j.est.2022.105760>.
- [48] E.M. Alawadhi, Thermal analysis of a building brick containing phase change material, *Energy and Buildings*. 40 (2008) 351–357. <https://doi.org/10.1016/j.enbuild.2007.03.001>.
- [49] A. Castell, I. Martorell, M. Medrano, G. Pérez, L.F. Cabeza, Experimental study of using PCM in brick constructive solutions for passive cooling, *Energy and Buildings*. 42 (2010) 534–540. <https://doi.org/10.1016/j.enbuild.2009.10.022>.
- [50] P. Principi, R. Fioretti, Thermal analysis of the application of PCM and low emissivity coating in hollow bricks, *Energy and Buildings*. 51 (2012) 131–142. <https://doi.org/10.1016/j.enbuild.2012.04.022>.
- [51] T. Silva, R. Vicente, N. Soares, V. Ferreira, Experimental testing and numerical modelling of masonry wall solution with PCM incorporation: A passive construction solution, *Energy and Buildings*. 49 (2012) 235–245. <https://doi.org/10.1016/j.enbuild.2012.02.010>.
- [52] J. Kośny, K. Biswas, W. Miller, S. Kriner, Field thermal performance of naturally ventilated solar roof with PCM heat sink, *Solar Energy*. 86 (2012) 2504–2514. <https://doi.org/10.1016/j.solener.2012.05.020>.
- [53] W. Lin, Z. Ma, C. McDowell, Y. Baghi, B. Banfield, Optimal design of a thermal energy storage system using phase change materials for a net-zero energy Solar

- Decathlon house, *Energy and Buildings*. 208 (2020) 109626. <https://doi.org/https://doi.org/10.1016/j.enbuild.2019.109626>.
- [54] R. Kalbasi, B. Samali, M. Afrand, Taking benefits of using PCMs in buildings to meet energy efficiency criteria in net zero by 2050., *Chemosphere*. 311 (2022) 137100. <https://doi.org/https://doi.org/10.1016/j.chemosphere.2022.137100>.
- [55] R. Kalbasi, M. Afrand, Which one is more effective to add to building envelope: Phase change material, thermal insulation, or their combination to meet zero-carbon-ready buildings?, *Journal of Cleaner Production*. 367 (2022) 133032. <https://doi.org/https://doi.org/10.1016/j.jclepro.2022.133032>.
- [56] M.N. Ajour, M.J. Abdual, F.A. Hariri, N.H. Abu-Hamdeh, A. Karimipour, Reducing electricity demand by integrating a sustainable pack into HVAC- adding PCM in sustainable pack as well as building envelopes, *Journal of Building Engineering*. 57 (2022) 104915. <https://doi.org/https://doi.org/10.1016/j.job.2022.104915>.
- [57] M.Ç. Uludaş, E. Tunçbilek, Ç. Yıldız, M. Arıcı, D. Li, M. Krajčík, PCM-enhanced sunspace for energy efficiency and CO2 mitigation in a house in mediterranean climate, *Journal of Building Engineering*. 57 (2022) 104856. <https://doi.org/https://doi.org/10.1016/j.job.2022.104856>.
- [58] A.V. Priya, S. Shaik, Crystal mud transparent slime as a glazing material for net-zero energy buildings: Enhanced energy savings, diurnal lighting, and CO2 mitigation, *Energy for Sustainable Development*. 71 (2022) 151–166. <https://doi.org/https://doi.org/10.1016/j.esd.2022.09.018>.
- [59] C. Beji, A. Merabtine, S. Mokraoui, A. Kheiri, J. Kauffmann, N. Bouaziz, Experimental study on the effects of direct sun radiation on the dynamic thermal behavior of a floor-heating system, *Solar Energy*. 204 (2020) 1–12. <https://doi.org/https://doi.org/10.1016/j.solener.2020.04.055>.
- [60] K. Zhao, X.-H. Liu, Y. Jiang, Dynamic performance of water-based radiant floors during start-up and high-intensity solar radiation, *Solar Energy*. 101 (2014) 232–244. <https://doi.org/https://doi.org/10.1016/j.solener.2013.12.033>.
- [61] U. Stritih, E. Osterman, H. Evliya, V. Butala, H. Paksoy, Exploiting solar energy potential through thermal energy storage in Slovenia and Turkey, *Renewable and Sustainable Energy Reviews*. 25 (2013) 442–461. <https://doi.org/https://doi.org/10.1016/j.rser.2013.04.020>.
- [62] S. Ramakrishnan, X. Wang, M. Alam, J. Sanjayan, J. Wilson, Parametric analysis for performance enhancement of phase change materials in naturally ventilated buildings, *Energy and Buildings*. 124 (2016) 35–45. <https://doi.org/https://doi.org/10.1016/j.enbuild.2016.04.065>.
- [63] V. V Tyagi, A.K. Pandey, D. Buddhi, R. Kothari, Thermal performance assessment of encapsulated PCM based thermal management system to reduce peak energy

- demand in buildings, *Energy and Buildings*. 117 (2016) 44–52. <https://doi.org/https://doi.org/10.1016/j.enbuild.2016.01.042>.
- [64] A. Bastani, F. Haghighat, J. Kozinski, Designing building envelope with PCM wallboards: Design tool development, *Renewable and Sustainable Energy Reviews*. 31 (2014) 554–562. <https://doi.org/https://doi.org/10.1016/j.rser.2013.12.031>.
 - [65] M. Auzeby, S. Wei, C. Underwood, C. Chen, H. Ling, S. Pan, B. Ng, J. Tindall, R. Buswell, Using Phase Change Materials to Reduce Overheating Issues in UK Residential Buildings, *Energy Procedia*. 105 (2017) 4072–4077. <https://doi.org/https://doi.org/10.1016/j.egypro.2017.03.861>.
 - [66] N.P. Sharifi, A.A.N. Shaikh, A.R. Sakulich, Application of phase change materials in gypsum boards to meet building energy conservation goals, *Energy and Buildings*. 138 (2017) 455–467. <https://doi.org/https://doi.org/10.1016/j.enbuild.2016.12.046>.
 - [67] Y. Han, J.E. Taylor, Simulating the Inter-Building Effect on energy consumption from embedding phase change materials in building envelopes, *Sustainable Cities and Society*. 27 (2016) 287–295. <https://doi.org/https://doi.org/10.1016/j.scs.2016.03.001>.
 - [68] X. Xu, Y. Zhang, K. Lin, H. Di, R. Yang, Modeling and simulation on the thermal performance of shape-stabilized phase change material floor used in passive solar buildings, *Energy and Buildings*. 37 (2005) 1084–1091. <https://doi.org/https://doi.org/10.1016/j.enbuild.2004.12.016>.
 - [69] A.G. Entrop, H.J.H. Brouwers, A.H.M.E. Reinders, Experimental research on the use of micro-encapsulated Phase Change Materials to store solar energy in concrete floors and to save energy in Dutch houses, *Solar Energy*. 85 (2011) 1007–1020. <https://doi.org/https://doi.org/10.1016/j.solener.2011.02.017>.
 - [70] S. Lu, H. Tong, B. Pang, Study on the coupling heating system of floor radiation and sunspace based on energy storage technology, *Energy and Buildings*. 159 (2018) 441–453. <https://doi.org/https://doi.org/10.1016/j.enbuild.2017.11.027>.
 - [71] S. Pintaldi, C. Perfumo, S. Sethuvenkatraman, S. White, G. Rosengarten, A review of thermal energy storage technologies and control approaches for solar cooling, *Renewable and Sustainable Energy Reviews*. 41 (2015) 975–995. <https://doi.org/10.1016/j.rser.2014.08.062>.
 - [72] A. Pasupathy, R. Velraj, R. V. Seeniraj, Phase change material-based building architecture for thermal management in residential and commercial establishments, *Renewable and Sustainable Energy Reviews*. 12 (2008) 39–64. <https://doi.org/10.1016/j.rser.2006.05.010>.
 - [73] R. Baetens, B.P. Jelle, A. Gustavsen, Phase change materials for building applications: A state-of-the-art review, *Energy and Buildings*. 42 (2010) 1361–1368. <https://doi.org/10.1016/j.enbuild.2010.03.026>.

- [74] A. Kürklü, A. Özmerzi, S. Bilgin, Thermal performance of a water-phase change material solar collector, *Renewable Energy*. 26 (2002) 391–399. [https://doi.org/10.1016/S0960-1481\(01\)00130-6](https://doi.org/10.1016/S0960-1481(01)00130-6).
- [75] M.M. Farid, A.M. Khudhair, S.A.K. Razack, S. Al-Hallaj, A review on phase change energy storage: Materials and applications, *Energy Conversion and Management*. 45 (2004) 1597–1615. <https://doi.org/10.1016/j.enconman.2003.09.015>.
- [76] a. Jamekhorshid, S.M. Sadrameli, M. Farid, A review of microencapsulation methods of phase change materials (PCMs) as a thermal energy storage (TES) medium, *Renewable and Sustainable Energy Reviews*. 31 (2014) 531–542. <https://doi.org/10.1016/j.rser.2013.12.033>.
- [77] R. Ehid, R.D. Weinstein, A.S. Fleischer, The shape stabilization of paraffin phase change material to reduce graphite nanofiber settling during the phase change process, *Energy Conversion and Management*. 57 (2012) 60–67. <https://doi.org/10.1016/j.enconman.2011.12.008>.
- [78] S. Riffat, B. Mempo, W. Fang, Phase change material developments: a review, *International Journal of Ambient Energy*. 00 (2013) 1–14. <https://doi.org/10.1080/01430750.2013.823106>.
- [79] M.H. Zahir, M.M. Rahman, S.K.S. Basamad, K.O. Mohaisen, K. Irshad, M.M. Rahman, M.A. Aziz, A. Ali, M.M. Hossain, Preparation of a sustainable shape-stabilized phase change material for thermal energy storage based on mg₂+doped caco₃/peg composites, *Nanomaterials*. 11 (2021) 1–24. <https://doi.org/10.3390/nano11071639>.
- [80] A. Sharma, V. V. Tyagi, C.R. Chen, D. Buddhi, Review on thermal energy storage with phase change materials and applications, *Renewable and Sustainable Energy Reviews*. 13 (2009) 318–345. <https://doi.org/10.1016/j.rser.2007.10.005>.
- [81] A. Sari, C. Alkan, Ö. Lafçi, Synthesis and thermal properties of poly(styrene-co-allyl alcohol)-graft-stearic acid copolymers as novel solid-solid PCMs for thermal energy storage, *Solar Energy*. 86 (2012) 2282–2292. <https://doi.org/10.1016/j.solener.2012.04.018>.
- [82] G.A. Lane, N. Shamsundar, Solar Heat Storage: Latent Heat Materials, Vol. I: Background and Scientific Principles, *Journal of Solar Energy Engineering*. 105 (1983) 467. <https://doi.org/10.1115/1.3266412>.
- [83] A. Sari, K. Kaygusuz, Thermal performance of a eutectic mixture of lauric and stearic acids as PCM encapsulated in the annulus of two concentric pipes, *Solar Energy*. 72 (2002) 493–504. [https://doi.org/10.1016/S0038-092X\(02\)00026-9](https://doi.org/10.1016/S0038-092X(02)00026-9).
- [84] A. Sar, A. Bier, A. Karaipekli, C. Alkan, A. Karadag, Synthesis, thermal energy storage properties and thermal reliability of some fatty acid esters with glycerol as novel solidliquid phase change materials, *Solar Energy Materials and Solar Cells*.

94 (2010) 1711–1715. <https://doi.org/10.1016/j.solmat.2010.05.033>.

- [85] A. Karaipekli, A. Sari, Capric-myristic acid/expanded perlite composite as form-stable phase change material for latent heat thermal energy storage, *Renewable Energy*. 33 (2008) 2599–2605. <https://doi.org/10.1016/j.renene.2008.02.024>.
- [86] A. Al-Ahmed, M.A.J. Mazumder, B. Salhi, A. Sari, M. Afzaal, F.A. Al-Sulaiman, Effects of carbon-based fillers on thermal properties of fatty acids and their eutectics as phase change materials used for thermal energy storage: A Review, *Journal of Energy Storage*. 35 (2021) 102329. <https://doi.org/10.1016/j.est.2021.102329>.
- [87] S. Scalat, D. Banu, D. Hawes, J. Paris, F. Haghighata, D. Feldman, Full scale thermal testing of latent heat storage in wallboard, *Solar Energy Materials and Solar Cells*. 44 (1996) 49–61. [https://doi.org/10.1016/0927-0248\(96\)00017-7](https://doi.org/10.1016/0927-0248(96)00017-7).
- [88] A. De Gracia, L.F. Cabeza, Phase change materials and thermal energy storage for buildings, *Energy and Buildings*. 103 (2015) 414–419. <https://doi.org/10.1016/j.enbuild.2015.06.007>.
- [89] Q. Al-Yasiri, M. Szabó, Incorporation of phase change materials into building envelope for thermal comfort and energy saving: A comprehensive analysis, *Journal of Building Engineering*. 36 (2021). <https://doi.org/10.1016/j.jobbe.2020.102122>.
- [90] R.J. Khan, M.Z.H. Bhuiyan, D.H. Ahmed, Investigation of heat transfer of a building wall in the presence of phase change material (PCM), *Energy and Built Environment*. 1 (2020) 199–206. <https://doi.org/10.1016/j.enbenv.2020.01.002>.
- [91] O. Saadatian, K. Sopian, C.H. Lim, N. Asim, M.Y. Sulaiman, Trombe walls: A review of opportunities and challenges in research and development, *Renewable and Sustainable Energy Reviews*. 16 (2012) 6340–6351. <https://doi.org/10.1016/j.rser.2012.06.032>.
- [92] K.O. Lee, M.A. Medina, X. Sun, On the use of plug-and-play walls (PPW) for evaluating thermal enhancement technologies for building enclosures: Evaluation of a thin phase change material (PCM) layer, *Energy and Buildings*. 86 (2015) 86–92. <https://doi.org/10.1016/j.enbuild.2014.10.020>.
- [93] Y. Sun, S. Wang, F. Xiao, D. Gao, Peak load shifting control using different cold thermal energy storage facilities in commercial buildings: A review, *Energy Conversion and Management*. 71 (2013) 101–114. <https://doi.org/10.1016/j.enconman.2013.03.026>.
- [94] A. Waqas, Z. Ud Din, Phase change material (PCM) storage for free cooling of buildings - A review, *Renewable and Sustainable Energy Reviews*. 18 (2013) 607–625. <https://doi.org/10.1016/j.rser.2012.10.034>.
- [95] D. Saelens, W. Parys, R. Baetens, Energy and comfort performance of thermally activated building systems including occupant behavior, *Building and Environment*. 46 (2011) 835–848. <https://doi.org/10.1016/j.buildenv.2010.10.012>.

- [96] H. Weinläder, W. Körner, B. Strieder, A ventilated cooling ceiling with integrated latent heat storage - Monitoring results, *Energy and Buildings*. 82 (2014) 65–72. <https://doi.org/10.1016/j.enbuild.2014.07.013>.
- [97] A. De Gracia, L. Navarro, A. Castell, Á. Ruiz-Pardo, S. Álvarez, L.F. Cabeza, Thermal analysis of a ventilated facade with PCM for cooling applications, *Energy and Buildings*. 65 (2013) 508–515. <https://doi.org/10.1016/j.enbuild.2013.06.032>.
- [98] A. de Gracia, L. Navarro, A. Castell, Á. Ruiz-Pardo, S. Álvarez, L.F. Cabeza, Experimental study of a ventilated facade with PCM during winter period, *Energy and Buildings*. 58 (2013) 324–332. <https://doi.org/10.1016/j.enbuild.2012.10.026>.
- [99] G. Fraisse, K. Johannes, V. Trillat-Berdal, G. Achard, The use of a heavy internal wall with a ventilated air gap to store solar energy and improve summer comfort in timber frame houses, *Energy and Buildings*. 38 (2006) 293–302. <https://doi.org/10.1016/j.enbuild.2005.06.010>.
- [100] A. Arteconi, N.J. Hewitt, F. Polonara, Domestic demand-side management (DSM): Role of heat pumps and thermal energy storage (TES) systems, *Applied Thermal Engineering*. 51 (2013) 155–165. <https://doi.org/10.1016/j.applthermaleng.2012.09.023>.
- [101] P. Moreno, C. Solé, A. Castell, L.F. Cabeza, The use of phase change materials in domestic heat pump and air-conditioning systems for short term storage: A review, *Renewable and Sustainable Energy Reviews*. 39 (2014) 1–13. <https://doi.org/10.1016/j.rser.2014.07.062>.
- [102] F. Kuznik, D. David, K. Johannes, J.J. Roux, A review on phase change materials integrated in building walls, *Renewable and Sustainable Energy Reviews*. 15 (2011) 379–391. <https://doi.org/10.1016/j.rser.2010.08.019>.
- [103] F. Kuznik, J. Virgone, K. Johannes, In-situ study of thermal comfort enhancement in a renovated building equipped with phase change material wallboard, *Renewable Energy*. 36 (2011) 1458–1462. <https://doi.org/10.1016/j.renene.2010.11.008>.
- [104] K. Biswas, J. Lu, P. Soroushian, S. Shrestha, Combined experimental and numerical evaluation of a prototype nano-PCM enhanced wallboard, *Applied Energy*. 131 (2014) 517–529. <https://doi.org/10.1016/j.apenergy.2014.02.047>.
- [105] C.M. Lai, S. Hokoi, Thermal performance of an aluminum honeycomb wallboard incorporating microencapsulated PCM, *Energy and Buildings*. 73 (2014) 37–47. <https://doi.org/10.1016/j.enbuild.2014.01.017>.
- [106] T. Lee, D.W. Hawes, D. Banu, D. Feldman, Control aspects of latent heat storage and recovery in concrete, *Solar Energy Materials and Solar Cells*. 62 (2000) 217–237. [https://doi.org/10.1016/S0927-0248\(99\)00128-2](https://doi.org/10.1016/S0927-0248(99)00128-2).
- [107] M. Hadjieva, R. Stoykov, T. Filipova, Composite salt-hydrate concrete system for building energy storage, *Renewable Energy*. 19 (2000) 111–115.

[https://doi.org/10.1016/S0960-1481\(99\)00024-5](https://doi.org/10.1016/S0960-1481(99)00024-5).

- [108] W. Lin, Z. Ma, P. Cooper, M.I. Sohel, L. Yang, Thermal performance investigation and optimization of buildings with integrated phase change materials and solar photovoltaic thermal collectors, *Energy and Buildings*. 116 (2016) 562–573. <https://doi.org/10.1016/j.enbuild.2016.01.041>.
- [109] X. Jin, M.A. Medina, X. Zhang, On the placement of a phase change material thermal shield within the cavity of buildings walls for heat transfer rate reduction, *Energy*. 73 (2014) 780–786. <https://doi.org/10.1016/j.energy.2014.06.079>.
- [110] <https://phasechange.com/enrgblanket/>, (n.d.).
- [111] M. Ahmad, A. Bontemps, H. Sallée, D. Quenard, Experimental investigation and computer simulation of thermal behaviour of wallboards containing a phase change material, *Energy and Buildings*. 38 (2006) 357–366. <https://doi.org/10.1016/j.enbuild.2005.07.008>.
- [112] M. Ahmad, A. Bontemps, H. Sallée, D. Quenard, Thermal testing and numerical simulation of a prototype cell using light wallboards coupling vacuum isolation panels and phase change material, *Energy and Buildings*. 38 (2006) 673–681. <https://doi.org/10.1016/j.enbuild.2005.11.002>.
- [113] A. Carbonari, M. De Grassi, C. Di Perna, P. Principi, Numerical and experimental analyses of PCM containing sandwich panels for prefabricated walls, *Energy and Buildings*. 38 (2006) 472–483. <https://doi.org/10.1016/j.enbuild.2005.08.007>.
- [114] Y. Konuklu, H.Ö. Paksoy, Phase change material sandwich panels for managing solar gain in buildings, *Journal of Solar Energy Engineering*. 131 (2009).
- [115] C. Voelker, O. Kornadt, M. Ostry, Temperature reduction due to the application of phase change materials, *Energy and Buildings*. 40 (2008) 937–944. <https://doi.org/10.1016/j.enbuild.2007.07.008>.
- [116] M. Zhang, M.A. Medina, J.B. King, Development of a thermally enhanced frame wall with phase-change materials for on-peak air conditioning demand reduction and energy savings in residential buildings, *International Journal of Energy Research*. 29 (2005) 795–809. <https://doi.org/10.1002/er.1082>.
- [117] S.I. Güçeri, S.F. Faunce, Modeling of a thermal wall panel using phase change materials, *Energy*. 4 (1979) 695–699. [https://doi.org/10.1016/0360-5442\(79\)90091-4](https://doi.org/10.1016/0360-5442(79)90091-4).
- [118] A. Pasupathy, L. Athanasius, R. Velraj, R. V. Seeniraj, Experimental investigation and numerical simulation analysis on the thermal performance of a building roof incorporating phase change material (PCM) for thermal management, *Applied Thermal Engineering*. 28 (2008) 556–565. <https://doi.org/10.1016/j.applthermaleng.2007.04.016>.
- [119] K.A. Al-Sallal, Comparison between polystyrene and fiberglass roof insulation in

- warm and cold climates, *Renewable Energy*. 28 (2003) 603–611. [https://doi.org/10.1016/S0960-1481\(02\)00065-4](https://doi.org/10.1016/S0960-1481(02)00065-4).
- [120] E.M. Alawadhi, H.J. Alqallaf, Building roof with conical holes containing PCM to reduce the cooling load: Numerical study, *Energy Conversion and Management*. 52 (2011) 2958–2964. <https://doi.org/10.1016/j.enconman.2011.04.004>.
- [121] W. Al-Nassar, S. Alhajraf, A. Al-Enizi, L. Al-Awadhi, Potential wind power generation in the State of Kuwait, *Renewable Energy*. 30 (2005) 2149–2161. <https://doi.org/10.1016/j.renene.2005.01.002>.
- [122] A. Hasan, K.A. Al-Sallal, H. Alnoman, Y. Rashid, S. Abdelbaqi, Effect of phase change materials (PCMs) integrated into a concrete block on heat gain prevention in a hot climate, *Sustainability (Switzerland)*. 8 (2016). <https://doi.org/10.3390/su8101009>.
- [123] N. A. Nader, Application of Phase-Change Materials in Buildings, *American Journal of Energy Engineering*. 3 (2015) 46. <https://doi.org/10.11648/j.ajee.20150303.13>.
- [124] D. Mazzeo, G. Oliveti, N. Arcuri, A method for thermal dimensioning and for energy behavior evaluation of a building envelope PCM layer by using the characteristic days, *Energies*. 10 (2017). <https://doi.org/10.3390/en10050659>.
- [125] F. Chen, J. Mao, S. Chen, C. Li, P. Hou, L. Liao, Efficiency analysis of utilizing phase change materials as grout for a vertical U-tube heat exchanger coupled ground source heat pump system, *Applied Thermal Engineering*. 130 (2018) 698–709. <https://doi.org/10.1016/j.applthermaleng.2017.11.062>.
- [126] M.J. Huang, P.C. Eames, N.J. Hewitt, The application of a validated numerical model to predict the energy conservation potential of using phase change materials in the fabric of a building, *Solar Energy Materials and Solar Cells*. 90 (2006) 1951–1960. <https://doi.org/10.1016/j.solmat.2006.02.002>.
- [127] K. Nagano, S. Takeda, T. Mochida, K. Shimakura, T. Nakamura, Study of a floor supply air conditioning system using granular phase change material to augment building mass thermal storage - Heat response in small scale experiments, *Energy and Buildings*. 38 (2006) 436–446. <https://doi.org/10.1016/j.enbuild.2005.07.010>.
- [128] C. Arkar, S. Medved, Influence of accuracy of thermal property data of a phase change material on the result of a numerical model of a packed bed latent heat storage with spheres, *Thermochimica Acta*. 438 (2005) 192–201. <https://doi.org/10.1016/j.tca.2005.08.032>.
- [129] U. Stritih, P. Novak, Thermal Storage Of Solar Energy In The Wall For Building Ventilation, *International IEA Workshop (Annex 17), Advanced Thermal Energy Storage Techniques*. (2002) 3–5.
- [130] E.M. Alawadhi, Using phase change materials in window shutter to reduce the solar

- heat gain, *Energy and Buildings*. 47 (2012) 421–429. <https://doi.org/10.1016/j.enbuild.2011.12.009>.
- [131] K.A.R. Ismail, J.R. Henríquez, Thermally effective windows with moving phase change material curtains, *Applied Thermal Engineering*. 21 (2001) 1909–1923. [https://doi.org/10.1016/s1359-4311\(01\)00058-8](https://doi.org/10.1016/s1359-4311(01)00058-8).
- [132] K.A.R. Ismail, C.T. Salinas, J.R. Henriquez, Comparison between PCM filled glass windows and absorbing gas filled windows, *Energy and Buildings*. 40 (2008) 710–719. <https://doi.org/10.1016/j.enbuild.2007.05.005>.
- [133] J. Szimmat, Numerical simulation of solidification processes in enclosures, *Heat and Mass Transfer/Waerme- Und Stoffuebertragung*. 38 (2002) 279–293. <https://doi.org/10.1007/s00231-001-0282-7>.
- [134] Q. Duan, F.L. Tan, K.C. Leong, A numerical study of solidification of n-hexadecane based on the enthalpy formulation, *Journal of Materials Processing Technology*. 120 (2002) 249–258. [https://doi.org/10.1016/S0924-0136\(01\)01188-8](https://doi.org/10.1016/S0924-0136(01)01188-8).
- [135] Z. Liu, C. Ma, Numerical analysis of melting with constant heat flux heating in a thermal energy storage system, *Energy Conversion and Management*. 43 (2002) 2521–2538. [https://doi.org/10.1016/S0196-8904\(01\)00190-X](https://doi.org/10.1016/S0196-8904(01)00190-X).
- [136] C.J. Ho, C.H. Chu, Periodic melting within a square enclosure with an oscillatory surface temperature, *International Journal of Heat and Mass Transfer*. 36 (1993) 725–733. [https://doi.org/10.1016/0017-9310\(93\)80048-Y](https://doi.org/10.1016/0017-9310(93)80048-Y).
- [137] E.M. Alawadhi, Effect of an incompletely closed window shutter on indoor illuminance level and heat gain, *Energy and Buildings*. 110 (2016) 112–119. <https://doi.org/10.1016/j.enbuild.2015.10.040>.
- [138] S. Agrawal, G.N. Tiwari, Energy and exergy analysis of hybrid micro-channel photovoltaic thermal module, *Solar Energy*. 85 (2011) 356–370. <https://doi.org/10.1016/j.solener.2010.11.013>.
- [139] K. Hassouneh, A. Alshboul, A. Al-Salaymeh, Influence of windows on the energy balance of apartment buildings in Amman, *Energy Conversion and Management*. 51 (2010) 1583–1591. <https://doi.org/10.1016/j.enconman.2009.08.037>.
- [140] R.P. Chasar, F. Armin, S. Measured, D. Chasar, N. Moyer, A.F. Rudd, D. Parker, S. Chandra, Measured and Simulated Cooling Performance Comparison ; Insulated Concrete Form Versus Frame Construction, (2002) 1–11.
- [141] J.L. Wright, Calculating Center-Glass Performance Indices of Glazing Systems with Shading Devices, *ASHRAE Transactions*. 114 (2008) 199–209.
- [142] D. Saelens, W. Parys, J. Roofthoof, A.T. De La Torre, Reprint of “assessment of approaches for modeling louver shading devices in building energy simulation programs,” *Energy and Buildings*. 68 (2014) 799–810. <https://doi.org/10.1016/j.enbuild.2013.11.031>.

- [143] K.A.R. Ismail, J.R. Henríquez, Modeling and simulation of a simple glass window, *Solar Energy Materials and Solar Cells*. 80 (2003) 355–374. <https://doi.org/10.1016/j.solmat.2003.08.010>.
- [144] O. Aydin, Conjugate heat transfer analysis of double pane windows, *Building and Environment*. 41 (2006) 109–116. <https://doi.org/10.1016/j.buildenv.2005.01.011>.
- [145] A.E. Ben-Nakhi, Minimizing thermal bridging through window systems in buildings of hot regions, *Applied Thermal Engineering*. 22 (2002) 989–998. [https://doi.org/10.1016/S1359-4311\(01\)00121-1](https://doi.org/10.1016/S1359-4311(01)00121-1).
- [146] C. Cuevas, A. Fissore, N. Fonseca, Natural convection at an indoor glazing surface with different window blinds, *Energy and Buildings*. 42 (2010) 1685–1691. <https://doi.org/10.1016/j.enbuild.2010.05.003>.
- [147] R. Dalal, D. Naylor, D. Roeleveld, A CFD study of convection in a double glazed window with an enclosed pleated blind, *Energy and Buildings*. 41 (2009) 1256–1262. <https://doi.org/10.1016/j.enbuild.2009.07.024>.
- [148] D. Naylor, M. Collins, Evaluation of an approximate method for predicting the u-value of a window with a between-panes louvered shade, *International Symposium on Advances in Computational Heat Transfer*. (2008). <https://doi.org/10.1615/ichmt.2004.cht-04.710>.
- [149] K.A.R. Ismail, C.T. Salinas, J.R. Henriquez, A comparative study of naturally ventilated and gas filled windows for hot climates, *Energy Conversion and Management*. 50 (2009) 1691–1703. <https://doi.org/10.1016/j.enconman.2009.03.026>.
- [150] B. Bueno, J. Wienold, A. Katsifaraki, T.E. Kuhn, Fener: A Radiance-based modelling approach to assess the thermal and daylighting performance of complex fenestration systems in office spaces, *Energy and Buildings*. 94 (2015) 10–20. <https://doi.org/10.1016/j.enbuild.2015.02.038>.
- [151] C. Oleskowicz-Popiel, M. Sobczak, Effect of the roller blinds on heat losses through a double-glazing window during heating season in Central Europe, *Energy and Buildings*. 73 (2014) 48–58. <https://doi.org/10.1016/j.enbuild.2013.12.032>.
- [152] F. Hammad, B. Abu-Hijleh, The energy savings potential of using dynamic external louvers in an office building, *Energy and Buildings*. 42 (2010) 1888–1895. <https://doi.org/10.1016/j.enbuild.2010.05.024>.
- [153] A.I. Palmero-Marrero, A.C. Oliveira, Effect of louver shading devices on building energy requirements, *Applied Energy*. 87 (2010) 2040–2049. <https://doi.org/10.1016/j.apenergy.2009.11.020>.
- [154] F. Yazicioglu, A comparative analysis of the energy performance of traditional wooden shutters and contemporary aluminium roller shutters in Istanbul, a case study, *Energy Procedia*. 42 (2013) 483–492.

<https://doi.org/10.1016/j.egypro.2013.11.049>.

- [155] A.A.Y. Freewan, Impact of external shading devices on thermal and daylighting performance of offices in hot climate regions, *Solar Energy*. 102 (2014) 14–30. <https://doi.org/10.1016/j.solener.2014.01.009>.
- [156] P.R. Defaix, W.G.J.H.M. van Sark, E. Worrell, E. de Visser, Technical potential for photovoltaics on buildings in the EU-27, *Solar Energy*. 86 (2012) 2644–2653. <https://doi.org/10.1016/J.SOLENER.2012.06.007>.
- [157] A. Hasan, H. Alnoman, Y. Rashid, Impact of integrated photovoltaic-phase change material system on building energy efficiency in hot climate, *Energy and Buildings*. 130 (2016) 495–505. <https://doi.org/10.1016/j.enbuild.2016.08.059>.
- [158] M.J. Huang, P.C. Eames, B. Norton, Thermal regulation of building-integrated photovoltaics using phase change materials, *International Journal of Heat and Mass Transfer*. 47 (2004) 2715–2733. <https://doi.org/10.1016/J.IJHEATMASSTRANSFER.2003.11.015>.
- [159] M.J. Huang, P.C. Eames, B. Norton, Phase change materials for limiting temperature rise in building integrated photovoltaics, *Solar Energy*. 80 (2006) 1121–1130. <https://doi.org/10.1016/J.SOLENER.2005.10.006>.
- [160] A. Hasan, S.J. McCormack, M.J. Huang, B. Norton, Evaluation of phase change materials for thermal regulation enhancement of building integrated photovoltaics, *Solar Energy*. 84 (2010) 1601–1612. <https://doi.org/10.1016/j.solener.2010.06.010>.
- [161] A. Hasan, S.J. McCormack, M.J. Huang, J. Sarwar, B. Norton, Increased photovoltaic performance through temperature regulation by phase change materials: Materials comparison in different climates, *Solar Energy*. 115 (2015) 264–276. <https://doi.org/10.1016/j.solener.2015.02.003>.
- [162] P.A. Fokaides, A. Kylili, S.A. Kalogirou, Phase change materials (PCMs) integrated into transparent building elements: A review, *Materials for Renewable and Sustainable Energy*. 4 (2015). <https://doi.org/10.1007/s40243-015-0047-8>.
- [163] I. Vigna, L. Bianco, F. Goia, V. Serra, Phase change materials in transparent building envelopes: A Strengths, Weakness, Opportunities and Threats (SWOT) analysis, *Energies*. 11 (2018). <https://doi.org/10.3390/en11010111>.
- [164] M.A. Kibria, R. Saidur, F.A. Al-Sulaiman, M.M.A. Aziz, Development of a thermal model for a hybrid photovoltaic module and phase change materials storage integrated in buildings, *Solar Energy*. 124 (2016) 114–123. <https://doi.org/10.1016/j.solener.2015.11.027>.
- [165] S. Li, Y. Zhou, K. Zhong, X. Zhang, X. Jin, Thermal analysis of PCM-filled glass windows in hot summer and cold winter area, *International Journal of Low-Carbon Technologies*. 11 (2016) 275–282. <https://doi.org/10.1093/ijlct/ctt073>.
- [166] P.H. Biwole, P. Achard, P.H. Biwole, P. Achard, Thermal behavior of a passive

- solar wall with silica aerogel and phase change materials, *Proceedings of Energy Forum on Advanced Building Skins*. (2015) 197–207.
- [167] H. Weinläder, A. Beck, J. Fricke, PCM-facade-panel for daylighting and room heating, *Solar Energy*. 78 (2005) 177–186. <https://doi.org/10.1016/j.solener.2004.04.013>.
- [168] B. Faircloth, R. Welch, M. Tamke, P. Nicholas, P. Ayres, Y. Sinke, B. Cuffy, M. Ramsgaard Thomsen, Multiscale modeling frameworks for architecture: Designing the unseen and invisible with phase change materials, *International Journal of Architectural Computing*. 16 (2018) 104–122. <https://doi.org/10.1177/1478077118778599>.
- [169] M. Shafiullah, S.D. Ahmed, F.A. Al-Sulaiman, Grid Integration Challenges and Solution Strategies for Solar PV Systems: A Review, *IEEE Access*. 10 (2022) 52233–52257. <https://doi.org/10.1109/ACCESS.2022.3174555>.
- [170] S.M. Rahman, F.S. Al-Ismail, M.E. Haque, M. Shafiullah, M.R. Islam, M.T. Chowdhury, M.S. Alam, S.A. Razzak, A. Ali, Z.A. Khan, Electricity generation in Saudi Arabia: Tracing opportunities and challenges to reducing greenhouse gas emissions, *IEEE Access*. (2021). <https://doi.org/10.1109/ACCESS.2021.3105378>.
- [171] S.D. Ahmed, F.S.M. Al-Ismail, M. Shafiullah, F.A. Al-Sulaiman, I.M. El-Amin, Grid Integration Challenges of Wind Energy: A Review, *IEEE Access*. 8 (2020) 10857–10878. <https://doi.org/10.1109/ACCESS.2020.2964896>.
- [172] H. Ritchie, M. Roser, P. Rosado, *Energy, Our World in Data*. (2022).
- [173] H. Ritchie, M. Roser, *Greenhouse gas emissions, Our World in Data*. (2022).
- [174] International Energy Agency, *Buildings*, International Energy Agency. (2022).
- [175] T. Wilberforce, A.G. Olabi, E.T. Sayed, K. Elsaid, H.M. Maghrabie, M.A. Abdelkareem, A review on zero energy buildings – Pros and cons, *Energy and Built Environment*. (2021). <https://doi.org/10.1016/J.ENBENV.2021.06.002>.
- [176] R. Parameshwaran, S. Kalaiselvam, S. Harikrishnan, A. Elayaperumal, Sustainable thermal energy storage technologies for buildings: A review, *Renewable and Sustainable Energy Reviews*. 16 (2012) 2394–2433. <https://doi.org/10.1016/j.rser.2012.01.058>.
- [177] L. Zhu, R. Hurt, D. Correia, R. Boehm, Detailed energy saving performance analyses on thermal mass walls demonstrated in a zero energy house, *Energy and Buildings*. 41 (2009) 303–310. <https://doi.org/10.1016/J.ENBUILD.2008.10.003>.
- [178] V.D. Cao, T.Q. Bui, A.L. Kjøniksen, Thermal analysis of multi-layer walls containing geopolymers concrete and phase change materials for building applications, *Energy*. 186 (2019) 115792. <https://doi.org/10.1016/J.ENERGY.2019.07.122>.

- [179] H.S. Khan, M. Asif, M.A. Mohammed, Case Study of a Nearly Zero Energy Building in Italian Climatic Conditions, *Infrastructures* 2017, Vol. 2, Page 19. 2 (2017) 19. <https://doi.org/10.3390/INFRASTRUCTURES2040019>.
- [180] M. Ozel, Effect of indoor design temperature on the heating and cooling transmission loads, *Journal of Building Engineering*. 7 (2016) 46–52. <https://doi.org/10.1016/J.JOBE.2016.05.001>.
- [181] K.J. Kontoleon, E.A. Eumorfopoulou, The influence of wall orientation and exterior surface solar absorptivity on time lag and decrement factor in the Greek region, *Renewable Energy*. 33 (2008) 1652–1664. <https://doi.org/10.1016/J.RENENE.2007.09.008>.
- [182] K.J. Kontoleon, D.K. Bikas, The effect of south wall's outdoor absorption coefficient on time lag, decrement factor and temperature variations, *Energy and Buildings*. 39 (2007) 1011–1018. <https://doi.org/10.1016/J.ENBUILD.2006.11.006>.
- [183] S. Verbeke, A. Audenaert, Thermal inertia in buildings: A review of impacts across climate and building use, *Renewable and Sustainable Energy Reviews*. 82 (2018) 2300–2318. <https://doi.org/10.1016/J.RSER.2017.08.083>.
- [184] G. Alessio, M. De Carli, A. Zarrella, A. di Bella, Efficiency in Heating Operation of Low-Temperature Radiant Systems Working under Dynamic Conditions in Different Kinds of Buildings, *Applied Sciences* 2018, Vol. 8, Page 2399. 8 (2018) 2399. <https://doi.org/10.3390/APP8122399>.
- [185] A. Laaouatni, N. Martaj, R. Bennacer, M. El Omari, M. El Ganaoui, Phase change materials for improving the building thermal inertia, *Energy Procedia*. 139 (2017) 744–749. <https://doi.org/10.1016/j.egypro.2017.11.281>.
- [186] N. Hichem, S. Noureddine, S. Nadia, D. Djamila, Experimental and Numerical Study of a Usual Brick Filled with PCM to Improve the Thermal Inertia of Buildings, *Energy Procedia*. 36 (2013) 766–775. <https://doi.org/10.1016/J.EGYPRO.2013.07.089>.
- [187] A. Adesina, Use of phase change materials in concrete: current challenges, *Renewable Energy and Environmental Sustainability*. 4 (2019) 9. <https://doi.org/10.1051/REES/2019006>.
- [188] N.A. Nader, R.S. Alsayed, Net-Zero Energy Building – Case Study Al Khobar City, Saudi Arabia, *International Journal of Sustainable Energy and Environmental Research*. 5 (2016) 70–78. <https://doi.org/10.18488/journal.13/2016.5.4/13.4.70.78>.
- [189] G.P. Panayiotou, S.A. Kalogirou, S.A. Tassou, Evaluation of the application of Phase Change Materials (PCM) on the envelope of a typical dwelling in the Mediterranean region, *Renewable Energy*. 97 (2016) 24–32. <https://doi.org/10.1016/j.renene.2016.05.043>.
- [190] A. Bland, M. Khzouz, T. Statheros, E.I. Gkanas, PCMs for residential building

- applications: A short review focused on disadvantages and proposals for future development, *Buildings*. 7 (2017). <https://doi.org/10.3390/buildings7030078>.
- [191] C. Alkan, Enthalpy of melting and solidification of sulfonated paraffins as phase change materials for thermal energy storage, *Thermochimica Acta*. 451 (2006) 126–130. <https://doi.org/10.1016/J.TCA.2006.09.010>.
- [192] A. Biçer, A. Sari, New kinds of energy-storing building composite PCMs for thermal energy storage, *Energy Conversion and Management*. 69 (2013) 148–156. <https://doi.org/10.1016/j.enconman.2013.01.027>.
- [193] M.H. Zahir, K. Irshad, M.A. Aziz, M. Shafiullah, M.M. Rahman, M.M. Hossain, Shape-Stabilized Phase Change Material for Solar Thermal Energy Storage: CaO Containing MgCO₃ Mixed with Polyethylene Glycol, *Energy and Fuels*. (2019). <https://doi.org/10.1021/acs.energyfuels.9b02885>.
- [194] M.A. Boda, R. V. Phand, A.C. Kotali, Various Applications of Phase Change Materials: Thermal Energy Storing Materials, *International Journal of Emerging Research in Management and Technology*. 6 (2017) 167–171. <https://doi.org/10.23956/ijermt/sv6n4/114>.
- [195] M.H. Zahir, S.A. Mohamed, R. Saidur, F.A. Al-Sulaiman, Supercooling of phase-change materials and the techniques used to mitigate the phenomenon, *Applied Energy*. 240 (2019) 793–817. <https://doi.org/10.1016/j.apenergy.2019.02.045>.
- [196] J. Heier, C. Bales, V. Martin, Combining thermal energy storage with buildings - A review, *Renewable and Sustainable Energy Reviews*. 42 (2015) 1305–1325. <https://doi.org/10.1016/j.rser.2014.11.031>.
- [197] M.M. Kenisarin, K.M. Kenisarina, Form-stable phase change materials for thermal energy storage, *Renewable and Sustainable Energy Reviews*. 16 (2012) 1999–2040. <https://doi.org/10.1016/j.rser.2012.01.015>.
- [198] X. Huang, L. Liu, H. Gao, W. Dong, M. Yang, G. Wang, Hierarchically nanostructured MnCo₂O₄ as active catalysts for the synthesis of N-benzylideneaniline from benzyl alcohol and aniline, *Green Chemistry*. 19 (2017) 769–777. <https://doi.org/10.1039/c6gc02065h>.
- [199] Y. Zhang, G.G. Gurzadyan, M.M. Umair, W. Wang, R. Lu, S. Zhang, B. Tang, Ultrafast and efficient photothermal conversion for sunlight-driven thermal-electric system, *Chemical Engineering Journal*. 344 (2018) 402–409. <https://doi.org/10.1016/j.cej.2018.03.098>.
- [200] Z. Aslam, R.A. Shawabkeh, I.A. Hussein, N. Al-Baghli, M. Eic, Synthesis of activated carbon from oil fly ash for removal of H₂S from gas stream, *Applied Surface Science*. 327 (2015) 107–115. <https://doi.org/10.1016/j.apsusc.2014.11.152>.
- [201] Y.S. Al-Degs, A. Ghir, H. Khoury, G.M. Walker, M. Sunjuk, M.A. Al-Ghouti,

- Characterization and utilization of fly ash of heavy fuel oil generated in power stations, *Fuel Processing Technology*. 123 (2014) 41–46. <https://doi.org/10.1016/j.fuproc.2014.01.040>.
- [202] M. Maslehuddin, M.R.A. Salah U . Al - Dulaijan, Structural Lightweight Concrete With Superior Thermal Insulation, US 2017 / 0283319 A1, 2017.
- [203] J.A. Bogas, D. Cunha, Non-structural lightweight concrete with volcanic scoria aggregates for lightweight fill in building's floors, *Construction and Building Materials*. 135 (2017) 151–163. <https://doi.org/10.1016/j.conbuildmat.2016.12.213>.
- [204] A.G. Celik, A.M. Kilic, G.O. Cakal, Expanded perlite aggregate characterization for use as a lightweight construction raw material, *Physicochemical Problems of Mineral Processing*. 49 (2013) 689–700. <https://doi.org/10.5277/ppmp130227>.
- [205] O. Sengul, S. Azizi, F. Karaosmanoglu, M.A. Tasdemir, Effect of expanded perlite on the mechanical properties and thermal conductivity of lightweight concrete, *Energy and Buildings*. 43 (2011) 671–676. <https://doi.org/10.1016/j.enbuild.2010.11.008>.
- [206] R. Jahanshahi, B. Akhlaghinia, Expanded perlite: An inexpensive natural efficient heterogeneous catalyst for the green and highly accelerated solvent-free synthesis of 5-substituted-1H-tetrazoles using [bmim]N3 and nitriles, *RSC Advances*. 5 (2015) 104087–104094. <https://doi.org/10.1039/c5ra21481e>.
- [207] S. Ramakrishnan, J. Sanjayan, X. Wang, M. Alam, J. Wilson, A novel paraffin/expanded perlite composite phase change material for prevention of PCM leakage in cementitious composites, *Applied Energy*. 157 (2015) 85–94. <https://doi.org/10.1016/j.apenergy.2015.08.019>.
- [208] S.A. Mohamed, F.A. Al-Sulaiman, N.I. Ibrahim, M.H. Zahir, A. Al-Ahmed, R. Saidur, B.S. Yılbaş, A.Z. Sahin, A review on current status and challenges of inorganic phase change materials for thermal energy storage systems, *Renewable and Sustainable Energy Reviews*. 70 (2017) 1072–1089. <https://doi.org/10.1016/j.rser.2016.12.012>.
- [209] V. V. Tyagi, S.C. Kaushik, S.K. Tyagi, T. Akiyama, Development of phase change materials based microencapsulated technology for buildings: A review, *Renewable and Sustainable Energy Reviews*. 15 (2011) 1373–1391. <https://doi.org/10.1016/j.rser.2010.10.006>.
- [210] P. Lv, C. Liu, Z. Rao, Experiment study on the thermal properties of paraffin/kaolin thermal energy storage form-stable phase change materials, *Applied Energy*. 182 (2016) 475–487. <https://doi.org/10.1016/j.apenergy.2016.08.147>.
- [211] A. Sari, Thermal energy storage properties of mannitol-fatty acid esters as novel organic solid-liquid phase change materials, *Energy Conversion and Management*. 64 (2012) 68–78. <https://doi.org/10.1016/j.enconman.2012.07.003>.

- [212] T. Qian, J. Li, X. Min, Y. Deng, W. Guan, H. Ma, Polyethylene glycol/mesoporous calcium silicate shape-stabilized composite phase change material: Preparation, characterization, and adjustable thermal property, *Energy*. 82 (2015) 333–340. <https://doi.org/10.1016/j.energy.2015.01.043>.
- [213] S. Ramakrishnan, X. Wang, J. Sanjayan, J. Wilson, Heat Transfer Performance Enhancement of Paraffin/Expanded Perlite Phase Change Composites with Graphene Nano-platelets, *Energy Procedia*. 105 (2017) 4866–4871. <https://doi.org/10.1016/j.egypro.2017.03.964>.
- [214] L. Jiesheng, L. Faping, G. Xiaoqiang, Z. Rongtang, Experimental research in the phase change materials based on paraffin and expanded perlite, *Phase Transitions*. 1594 (2018) 1–7. <https://doi.org/10.1080/01411594.2018.1424338>.
- [215] S.D. Sharma, D. Buddhi, R.L. Sawhney, Accelerated thermal cycle test of latent heat-storage materials, *Solar Energy*. 66 (1999) 483–490. [https://doi.org/10.1016/S0038-092X\(99\)00045-6](https://doi.org/10.1016/S0038-092X(99)00045-6).
- [216] R. Baetens, B.P. Jelle, A. Gustavsen, Phase change materials for building applications: A state-of-the-art review, *Energy and Buildings*. 42 (2010) 1361–1368. <https://doi.org/10.1016/j.enbuild.2010.03.026>.
- [217] L. Feng, W. Zhao, J. Zheng, S. Frisco, P. Song, X. Li, The shape-stabilized phase change materials composed of polyethylene glycol and various mesoporous matrices (AC, SBA-15 and MCM-41), *Solar Energy Materials and Solar Cells*. 95 (2011) 3550–3556. <https://doi.org/10.1016/j.solmat.2011.08.020>.
- [218] Y. Kou, S. Wang, J. Luo, K. Sun, J. Zhang, Z. Tan, Q. Shi, Thermal analysis and heat capacity study of polyethylene glycol (PEG) phase change materials for thermal energy storage applications, *Journal of Chemical Thermodynamics*. 128 (2019) 259–274. <https://doi.org/10.1016/j.jct.2018.08.031>.
- [219] N. Mekaddem, S. Ben Ali, M. Fois, A. Hannachi, Paraffin/expanded perlite/plaster as thermal energy storage composite, *Energy Procedia*. 157 (2019) 1118–1129. <https://doi.org/10.1016/j.egypro.2018.11.279>.
- [220] Y. Zhang, J. Wang, J. Qiu, X. Jin, M.M. Umair, R. Lu, S. Zhang, B. Tang, Ag-graphene/PEG composite phase change materials for enhancing solar-thermal energy conversion and storage capacity, *Applied Energy*. 237 (2019) 83–90. <https://doi.org/10.1016/j.apenergy.2018.12.075>.
- [221] Z. Lu, B. Xu, J. Zhang, Y. Zhu, G. Sun, Z. Li, Preparation and characterization of expanded perlite/paraffin composite as form-stable phase change material, *Solar Energy*. 108 (2014) 460–466. <https://doi.org/10.1016/j.solener.2014.08.008>.
- [222] J. Morkel, S.J. Kruger, M.K.G. Vermaak, Characterization of clay mineral fractions in tuffisitic kimberlite breccias by X-ray diffraction, *Journal of the Southern African Institute of Mining and Metallurgy*. 106 (2006) 397–406.

- [223] R.A. Shawabkeh, Z. Aslam, I.A. Hussien, Thermochemical treatment of fly ash for synthesis of mesoporous activated carbon, *Journal of Thermal Analysis and Calorimetry*. 122 (2015) 1191–1201. <https://doi.org/10.1007/s10973-015-4964-7>.
- [224] J.S. Kwon, S.T. Yun, J.H. Lee, S.O. Kim, H.Y. Jo, Removal of divalent heavy metals (Cd, Cu, Pb, and Zn) and arsenic(III) from aqueous solutions using scoria: Kinetics and equilibria of sorption, *Journal of Hazardous Materials*. 174 (2010) 307–313. <https://doi.org/10.1016/j.jhazmat.2009.09.052>.
- [225] S. Seyfi, A.R. Azadmehr, M. Gharabaghi, A. Maghsoudi, Usage of Iranian scoria for copper and cadmium removal from aqueous solutions, *Journal of Central South University*. 22 (2015) 3760–3769. <https://doi.org/10.1007/s11771-015-2920-0>.
- [226] T. Depci, T. Efe, M. Tapan, A. Ozvan, M. Aclan, T. Uner, Chemical characterization of Patnos scoria (Ağrı, Turkey) and its usability for production of blended cement, *Physicochemical Problems of Mineral Processing*. 48 (2012) 303–315.
- [227] J.N.Y. Djobo, L.N. Tchadjié, H.K. Tchakoute, B.B.D. Kenne, A. Elimbi, D. Njopwouo, Synthesis of geopolymer composites from a mixture of volcanic scoria and metakaolin, *Journal of Asian Ceramic Societies*. 2 (2014) 387–398. <https://doi.org/10.1016/j.jascr.2014.08.003>.
- [228] L.D. Maxim, R. Niebo, E.E. Mcconnell, Perlite toxicology and epidemiology - A review, *Inhalation Toxicology*. 26 (2014) 259–270. <https://doi.org/10.3109/08958378.2014.881940>.
- [229] P.F. Corregidor, P.M. Cuesta, D.E. Acosta, H.A. Destéfanis, Composite ZSM-5/MCM-41 material obtained from a green resource and its enhanced catalytic performance in the reaction of vinyl acetate and isoamyl alcohol, *Applied Catalysis A: General*. 587 (2019) 117262. <https://doi.org/10.1016/j.apcata.2019.117262>.
- [230] K.A. Publishers, Preparation of fine expanded perlite, 4 (1999) 2461–2468.
- [231] A. Chakir, J. Bessiere, K. El, A comparative study of the removal of trivalent chromium from aqueous solutions by bentonite and expanded perlite, 95 (2002) 29–46.
- [232] S. Kabra, S. Katara, A. Rani, Characterization and Study of Turkish Perlite, *International Journal of Innovative Research in Science, Engineering and Technology*. 2 (2013) 4319–4326.
- [233] M. Rabbani, M. Haghverdi, M. Heidari-golafzani, Preparation of a new adsorbent expanded perlite @ ZnO @ reduced graphene oxide for the synergistic photocatalytic – adsorption removal, (2017) 8011–8015. <https://doi.org/10.1039/c7nj00482f>.
- [234] M. Taxiarchou, D. Panias, Study on the Suitability of Volcanic Amorphous Aluminosilicate Rocks (Perlite) for the Synthesis of Geopolymer-Based Concrete, (2013). <https://doi.org/10.1520/STP156620120077>.

- [235] R. Li, J. Zhu, W. Zhou, X. Cheng, Y. Li, Thermal compatibility of Sodium Nitrate/Expanded Perlite composite phase change materials, *Applied Thermal Engineering*. 103 (2016) 452–458. <https://doi.org/10.1016/j.applthermaleng.2016.03.108>.
- [236] S. Edebalı, Alternative Composite Nanosorbents Based on Turkish Perlite for the Removal of Cr(VI) from Aqueous Solution, *Journal of Nanomaterials*. 2015 (2015) 18–20. <https://doi.org/10.1155/2015/697026>.
- [237] A. Karaipekli, A. Biçer, A. Sarı, V.V. Tyagi, Thermal characteristics of expanded perlite/paraffin composite phase change material with enhanced thermal conductivity using carbon nanotubes, *Energy Conversion and Management*. 134 (2017) 373–381. <https://doi.org/10.1016/j.enconman.2016.12.053>.
- [238] C. Li, B. Zhang, B. Xie, X. Zhao, J. Chen, Tailored phase change behavior of Na₂SO₄·10H₂O/expanded graphite composite for thermal energy storage, *Energy Conversion and Management*. 208 (2020) 112586. <https://doi.org/10.1016/j.enconman.2020.112586>.
- [239] M.H. Zahir, M.M. Rahman, K. Irshad, M.M. Rahman, Shape-stabilized phase change materials for solar energy storage: MgO and mg(OH)₂ mixed with polyethylene glycol, *Nanomaterials*. 9 (2019) 1–21. <https://doi.org/10.3390/nano9121773>.
- [240] Y. Hao, X. Shao, T. Liu, B. Li, S. Nie, Porous MgO material with ultrahigh surface area as the matrix for phase change composite, *Thermochimica Acta*. 604 (2015) 45–51. <https://doi.org/10.1016/j.tca.2015.01.020>.
- [241] W. Wang, X. Yang, Y. Fang, J. Ding, Preparation and performance of form-stable polyethylene glycol/silicon dioxide composites as solid-liquid phase change materials, *Applied Energy*. 86 (2009) 170–174. <https://doi.org/10.1016/j.apenergy.2007.12.003>.
- [242] A. Al-Ahmed, A. Sarı, M.A.J. Mazumder, G. Hekimoğlu, F.A. Al-Sulaiman, Inamuddin, Thermal energy storage and thermal conductivity properties of Octadecanol-MWCNT composite PCMs as promising organic heat storage materials, *Scientific Reports*. 10 (2020) 1–15. <https://doi.org/10.1038/s41598-020-64149-3>.
- [243] L. Chen, R. Zou, W. Xia, Z. Liu, Y. Shang, J. Zhu, Y. Wang, J. Lin, D. Xia, A. Cao, Electro- and photodriven phase change composites based on wax-infiltrated carbon nanotube sponges, *ACS Nano*. 6 (2012) 10884–10892. <https://doi.org/10.1021/nn304310n>.
- [244] A. Sarı, A. Karaipekli, Preparation, thermal properties and thermal reliability of palmitic acid/expanded graphite composite as form-stable PCM for thermal energy storage, *Solar Energy Materials and Solar Cells*. 93 (2009) 571–576. <https://doi.org/10.1016/j.solmat.2008.11.057>.

- [245] I. Sarbu, C. Sebarchievici, A comprehensive review of thermal energy storage, Sustainability (Switzerland). 10 (2018). <https://doi.org/10.3390/su10010191>.
- [246] V. V. Tyagi, S.C. Kaushik, S.K. Tyagi, T. Akiyama, Development of phase change materials based microencapsulated technology for buildings: A review, Renewable and Sustainable Energy Reviews. 15 (2011) 1373–1391. <https://doi.org/10.1016/j.rser.2010.10.006>.
- [247] Y. Zhang, G.G. Gurzadyan, M.M. Umair, W. Wang, R. Lu, S. Zhang, B. Tang, Ultrafast and efficient photothermal conversion for sunlight-driven thermal-electric system, Chemical Engineering Journal. 344 (2018) 402–409. <https://doi.org/10.1016/j.cej.2018.03.098>.
- [248] L. Liu, G. Alva, X. Huang, G. Fang, Preparation, heat transfer and flow properties of microencapsulated phase change materials for thermal energy storage, Renewable and Sustainable Energy Reviews. 66 (2016) 399–414. <https://doi.org/10.1016/j.rser.2016.08.035>.
- [249] S. Zhang, M. Zhou, X. Lu, C. Wu, Y. Sun, Y. Xie, Macroscaled mesoporous calcium carbonate tetragonal prisms: Top-down solid-phase fabrication and applications of phase-change material support matrices, CrystEngComm. 12 (2010) 3571–3578. <https://doi.org/10.1039/b925283e>.
- [250] D.C. Hyun, N.S. Levinson, U. Jeong, Y. Xia, Emerging applications of phase-change materials (PCMs): Teaching an old dog new tricks, Angewandte Chemie - International Edition. 53 (2014) 3780–3795. <https://doi.org/10.1002/anie.201305201>.
- [251] N. Soares, J.J. Costa, A.R. Gaspar, P. Santos, Review of passive PCM latent heat thermal energy storage systems towards buildings' energy efficiency, Energy and Buildings. 59 (2013) 82–103. <https://doi.org/10.1016/j.enbuild.2012.12.042>.
- [252] M. Song, F. Niu, N. Mao, Y. Hu, S. Deng, Review on building energy performance improvement using phase change materials, Energy and Buildings. 158 (2018) 776–793. <https://doi.org/10.1016/j.enbuild.2017.10.066>.
- [253] O. Mesalhy, K. Lafdi, A. Elgafy, K. Bowman, Numerical study for enhancing the thermal conductivity of phase change material (PCM) storage using high thermal conductivity porous matrix, Energy Conversion and Management. 46 (2005) 847–867. <https://doi.org/10.1016/j.enconman.2004.06.010>.
- [254] Z.G. Wu, C.Y. Zhao, Experimental investigations of porous materials in high temperature thermal energy storage systems, Solar Energy. 85 (2011) 1371–1380. <https://doi.org/10.1016/j.solener.2011.03.021>.
- [255] T. Mott, Nature 457, (1890) 1890–1892.
- [256] C. Xiong, W. Li, L. Jiang, W. Wang, Q. Guo, Use of grounded iron ore tailings (GIOTs) and BaCO₃ to improve sulfate resistance of pastes, Construction and

- Building Materials. 150 (2017) 66–76.
<https://doi.org/10.1016/j.conbuildmat.2017.05.209>.
- [257] P.M. Carmona-Quiroga, C. Mota-Heredia, M. Torres-Carrasco, J.F. Fernández, M.T. Blanco-Varela, Effect of BaCO₃ reactivity and mixing procedure on sulfate-resistant cement performance, *Cement and Concrete Composites*. 120 (2021).
<https://doi.org/10.1016/j.cemconcomp.2021.104038>.
- [258] P.M. Carmona-Quiroga, M.T. Blanco-Varela, Use of barium carbonate to inhibit sulfate attack in cements, *Cement and Concrete Research*. 69 (2015) 96–104.
<https://doi.org/10.1016/j.cemconres.2014.12.006>.
- [259] A. Jamaluddin, Suwarni, A. Supriyanto, Y. Iriani, Properties of strontium doped barium titanate powder prepared by solid state reaction, *Journal of Physics: Conference Series*. 776 (2016). <https://doi.org/10.1088/1742-6596/776/1/012052>.
- [260] M. Arshad, H. Du, M.S. Javed, A. Maqsood, I. Ashraf, S. Hussain, W. Ma, H. Ran, Fabrication, structure, and frequency-dependent electrical and dielectric properties of Sr-doped BaTiO₃ ceramics, *Ceramics International*. 46 (2020) 2238–2246.
<https://doi.org/10.1016/j.ceramint.2019.09.208>.
- [261] J. Liu, X. Wei, Y. Lian, Q. Liu, X. Xu, D. Lu, Influence of Sr ions on the structure and dielectric properties of Cu/Nb Co-doped BaTiO₃ ceramics, *Ceramics International*. 47 (2021) 18669–18676.
<https://doi.org/10.1016/j.ceramint.2021.03.199>.
- [262] H. Shao, L. Gao, K. Liang, H. Chen, Q. Ye, J. Zhang, The effect of (Ni²⁺ + Sr²⁺) co-doping on structure and dielectric properties of Bi_{1.5}MgNb_{1.5}O₇ pyrochlores, *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*. 277 (2022) 115571. <https://doi.org/10.1016/j.mseb.2021.115571>.
- [263] S.A. Mohamed, F.A. Al-Sulaiman, N.I. Ibrahim, M.H. Zahir, A. Al-Ahmed, R. Saidur, B.S. Yilbaş, A.Z. Sahin, A review on current status and challenges of inorganic phase change materials for thermal energy storage systems, *Renewable and Sustainable Energy Reviews*. 70 (2017) 1072–1089.
<https://doi.org/10.1016/j.rser.2016.12.012>.
- [264] T. Shahid, M. Arfan, A. Zeb, T. Bibi, T.M. Khan, Preparation and physical properties of functional barium carbonate nanostructures by a facile composite-hydroxide-mediated route, *Nanomaterials and Nanotechnology*. 8 (2018) 1–8.
<https://doi.org/10.1177/1847980418761775>.
- [265] B. Sreedhar, C. Satya Vani, D. Keerthi Devi, M. V. Basaveswara Rao, C. Rambabu, Shape Controlled Synthesis of Barium Carbonate Microclusters and Nanocrystallites using Natural Polysachharide – Gum Acacia, *American Journal of Materials Science*. 2 (2012) 5–13. <https://doi.org/10.5923/j.materials.20120201.02>.
- [266] B. Sreedhar, C. Satya Vani, D. Keerthi Devi, V. Sreeram, M. V. Basaveswara Rao, Biomimetic Mineralization of BaCO₃ Microstructures By Simple

- CO₂ Diffusion Method, American Journal of Materials Science. 2 (2012) 105–109. <https://doi.org/10.5923/j.materials.20120204.02>.
- [267] A. Zelati, A. Amirabadizadeh, A. Kompany, Preparation and Characterization of Barium Carbonate Nanoparticles, International Journal of Chemical Engineering and Applications. 2 (2011) 299–303. <https://doi.org/10.7763/ijcea.2011.v2.121>.
- [268] T. Hong, F. Chen, C. Xia, Barium carbonate nanoparticle to enhance oxygen reduction activity of strontium doped lanthanum ferrite for solid oxide fuel cell, Journal of Power Sources. 278 (2015) 741–750. <https://doi.org/10.1016/j.jpowsour.2014.12.137>.
- [269] W. Kaabar, S. Bott, R. Devonshire, Raman spectroscopic study of mixed carbonate materials, Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy. 78 (2011) 136–141. <https://doi.org/10.1016/j.saa.2010.09.011>.
- [270] M.. H. Zahir, M. MizanurRahman, Calcium-doped magnesium carbonate-polymer-based synergistic phase change composite, US 10,626,238 B2, 2020.
- [271] C. Li, H. Yu, Y. Song, M. Zhao, Synthesis and characterization of PEG/ZSM-5 composite phase change materials for latent heat storage, Renewable Energy. 121 (2018) 45–52. <https://doi.org/10.1016/j.renene.2017.12.089>.
- [272] Y. Luan, M. Yang, Q. Ma, Y. Qi, H. Gao, Z. Wu, G. Wang, Introduction of an organic acid phase changing material into metal-organic frameworks and the study of its thermal properties, Journal of Materials Chemistry A. 4 (2016) 7641–7649. <https://doi.org/10.1039/c6ta01676f>.
- [273] M.H. Zahir, S.A. Mohamed, R. Saidur, F.A. Al-Sulaiman, Supercooling of phase-change materials and the techniques used to mitigate the phenomenon, Applied Energy. 240 (2019) 793–817. <https://doi.org/10.1016/j.apenergy.2019.02.045>.
- [274] Z. Liu, H. Wei, B. Tang, S. Xu, Z. Shufen, Novel light-driven CF/PEG/SiO₂ composite phase change materials with high thermal conductivity, Solar Energy Materials and Solar Cells. 174 (2018) 538–544. <https://doi.org/10.1016/j.solmat.2017.09.045>.
- [275] B. Tang, M. Qiu, S. Zhang, Thermal conductivity enhancement of PEG/SiO₂ composite PCM by in situ Cu doping, Solar Energy Materials and Solar Cells. 105 (2012) 242–248. <https://doi.org/10.1016/j.solmat.2012.06.012>.
- [276] C. Li, H. Yu, Y. Song, M. Zhao, Synthesis and characterization of PEG/ZSM-5 composite phase change materials for latent heat storage, Renewable Energy. 121 (2018) 45–52. <https://doi.org/10.1016/j.renene.2017.12.089>.
- [277] K.O. Mohaisen, M. Hasan Zahir, M. Maslehuddin, S.U. Al-Dulaijan, Development of a shape-stabilized phase change material utilizing natural and industrial byproducts for thermal energy storage in buildings, Journal of Energy Storage. 50 (2022) 104205. <https://doi.org/10.1016/j.est.2022.104205>.

- [278] A. D'Alessandro, A.L. Pisello, C. Fabiani, F. Ubertini, L.F. Cabeza, F. Cotana, Multifunctional smart concretes with novel phase change materials: Mechanical and thermo-energy investigation, *Applied Energy*. 212 (2018) 1448–1461. <https://doi.org/10.1016/j.apenergy.2018.01.014>.
- [279] A.L. Pisello, V.L. Castaldo, G. Pignatta, F. Cotana, M. Santamouris, Experimental in-lab and in-field analysis of waterproof membranes for cool roof application and urban heat island mitigation, *Energy and Buildings*. 114 (2016) 180–190. <https://doi.org/10.1016/j.enbuild.2015.05.026>.
- [280] M. Karmellos, A. Kiprakis, G. Mavrotas, A multi-objective approach for optimal prioritization of energy efficiency measures in buildings: Model, software and case studies, *Applied Energy*. 139 (2015) 131–150. <https://doi.org/10.1016/j.apenergy.2014.11.023>.
- [281] L. Aditya, T.M.I. Mahlia, B. Rismanchi, H.M. Ng, M.H. Hasan, H.S.C. Metselaar, O. Muraza, H.B. Aditiya, A review on insulation materials for energy conservation in buildings, *Renewable and Sustainable Energy Reviews*. 73 (2017) 1352–1365. <https://doi.org/10.1016/j.rser.2017.02.034>.
- [282] Y. Fang, S. Memon, J. Peng, M. Tyrer, T. Ming, Solar thermal performance of two innovative configurations of air-vacuum layered triple glazed windows, *Renewable Energy*. 150 (2020) 167–175. <https://doi.org/10.1016/j.renene.2019.12.115>.
- [283] T. Khadiran, M.Z. Hussein, Z. Zainal, R. Rusli, Advanced energy storage materials for building applications and their thermal performance characterization: A review, *Renewable and Sustainable Energy Reviews*. 57 (2016) 916–928. <https://doi.org/10.1016/j.rser.2015.12.081>.
- [284] M.A. Wahid, S.E. Hosseini, H.M. Hussien, H.J. Akeiber, S.N. Saud, A.T. Mohammad, An overview of phase change materials for construction architecture thermal management in hot and dry climate region, *Applied Thermal Engineering*. 112 (2017) 1240–1259. <https://doi.org/10.1016/j.applthermaleng.2016.07.032>.
- [285] A. Nematpour Keshteli, M. Sheikholeslami, Nanoparticle enhanced PCM applications for intensification of thermal performance in building: A review, *Journal of Molecular Liquids*. 274 (2019) 516–533. <https://doi.org/10.1016/j.molliq.2018.10.151>.
- [286] S. Sharifi, W. Saman, A. Alemu, Identification of overheating in the top floors of energy-efficient multilevel dwellings, *Energy and Buildings*. 204 (2019). <https://doi.org/10.1016/j.enbuild.2019.109452>.
- [287] F.S. Javadi, H.S.C. Metselaar, P. Ganesan, Performance improvement of solar thermal systems integrated with phase change materials (PCM), a review, *Solar Energy*. 206 (2020) 330–352. <https://doi.org/10.1016/j.solener.2020.05.106>.
- [288] D. Zhou, C.Y. Zhao, Y. Tian, Review on thermal energy storage with phase change materials (PCMs) in building applications, *Applied Energy*. 92 (2012) 593–605.

<https://doi.org/10.1016/j.apenergy.2011.08.025>.

- [289] S.S. Magendran, F.S.A. Khan, N.M. Mubarak, M. Vaka, R. Walvekar, M. Khalid, E.C. Abdullah, S. Nizamuddin, R.R. Karri, Synthesis of organic phase change materials (PCM) for energy storage applications: A review, *Nano-Structures and Nano-Objects*. 20 (2019) 100399. <https://doi.org/10.1016/j.nanoso.2019.100399>.
- [290] M. Gandhi, A. Kumar, R. Elangovan, C.S. Meena, K.S. Kulkarni, A. Kumar, G. Bhanot, N.R. Kapoor, A review on shape-stabilized phase change materials for latent energy storage in buildings, *Sustainability (Switzerland)*. 12 (2020) 1–17. <https://doi.org/10.3390/su12229481>.
- [291] N. Zhu, S. Li, P. Hu, S. Wei, R. Deng, F. Lei, A review on applications of shape-stabilized phase change materials embedded in building enclosure in recent ten years, *Sustainable Cities and Society*. 43 (2018) 251–264. <https://doi.org/10.1016/j.scs.2018.08.028>.
- [292] K. Yu, Y. Liu, Y. Yang, Review on form-stable inorganic hydrated salt phase change materials: Preparation, characterization and effect on the thermophysical properties, *Applied Energy*. 292 (2021) 116845. <https://doi.org/10.1016/j.apenergy.2021.116845>.
- [293] T.F. Phase, C. Materials, I. Materials, Expanded Graphite / Paraffin / Silicone Rubber as High Temperature Form-stabilized Phase Change Materials, *Material*. (2020).
- [294] M. Almazroui, Summer maximum temperature over the gulf cooperation council states in the twenty-first century: multimodel simulations overview, *Arabian Journal of Geosciences*. 13 (2020). <https://doi.org/10.1007/s12517-020-05537-x>.
- [295] F. Bruno, M. Belusko, M. Liu, N.H.S. Tay, Using solid-liquid phase change materials (PCMs) in thermal energy storage systems, Woodhead Publishing Limited, 2015. <https://doi.org/10.1533/9781782420965.2.201>.
- [296] R. Wang, M. Ren, X. Gao, L. Qin, Preparation and properties of fatty acids based thermal energy storage aggregate concrete, *Construction and Building Materials*. 165 (2018) 1–10. <https://doi.org/10.1016/j.conbuildmat.2018.01.034>.
- [297] J. Zhang, X. Zhang, Y. Wan, D. Mei, B. Zhang, Preparation and thermal energy properties of paraffin/halloysite nanotube composite as form-stable phase change material, *Solar Energy*. 86 (2012) 1142–1148. <https://doi.org/10.1016/j.solener.2012.01.002>.
- [298] B. Xu, Z. Li, Paraffin/diatomite composite phase change material incorporated cement-based composite for thermal energy storage, *Applied Energy*. 105 (2013) 229–237. <https://doi.org/10.1016/j.apenergy.2013.01.005>.
- [299] X. Li, J.G. Sanjayan, J.L. Wilson, Fabrication and stability of form-stable diatomite/paraffin phase change material composites, *Energy and Buildings*. 76

- (2014) 284–294. <https://doi.org/10.1016/j.enbuild.2014.02.082>.
- [300] M. Li, Z. Wu, H. Kao, J. Tan, Experimental investigation of preparation and thermal performances of paraffin/bentonite composite phase change material, *Energy Conversion and Management*. 52 (2011) 3275–3281. <https://doi.org/10.1016/j.enconman.2011.05.015>.
- [301] S.A. Memon, W. Liao, S. Yang, H. Cui, S.F.A. Shah, Development of composite PCMs by incorporation of paraffin into various building materials, *Materials*. 8 (2015) 499–518. <https://doi.org/10.3390/ma8020499>.
- [302] A. Alhozaimy, G. Fares, O.A. Alawad, A. Al-Negheimish, Heat of hydration of concrete containing powdered scoria rock as a natural pozzolanic material, *Construction and Building Materials*. 81 (2015) 113–119. <https://doi.org/10.1016/j.conbuildmat.2015.02.011>.
- [303] W.H. Juimo Tchamdjou, T. Cherradi, M.L. Abidi, L.A. Pereira-de-Oliveira, Mechanical properties of lightweight aggregates concrete made with cameroonian volcanic scoria: Destructive and non-destructive characterization, *Journal of Building Engineering*. 16 (2018) 134–145. <https://doi.org/10.1016/j.jobe.2018.01.003>.
- [304] W.H.J. Tchamdjou, S. Grigoletto, F. Michel, L. Courard, M.L. Abidi, T. Cherradi, An investigation on the use of coarse volcanic scoria as sand in Portland cement mortar, *Case Studies in Construction Materials*. 7 (2017) 191–206. <https://doi.org/10.1016/j.cscm.2017.07.005>.
- [305] Y. Konuklu, M. Ostry, H.O. Paksoy, P. Charvat, Review on using microencapsulated phase change materials (PCM) in building applications, *Energy and Buildings*. 106 (2015) 134–155. <https://doi.org/10.1016/j.enbuild.2015.07.019>.
- [306] S.A. Memon, Phase change materials integrated in building walls: A state of the art review, *Renewable and Sustainable Energy Reviews*. 31 (2014) 870–906. <https://doi.org/10.1016/j.rser.2013.12.042>.
- [307] P. Schossig, H.M. Henning, S. Gschwander, T. Haussmann, Micro-encapsulated phase-change materials integrated into construction materials, *Solar Energy Materials and Solar Cells*. 89 (2005) 297–306. <https://doi.org/10.1016/j.solmat.2005.01.017>.
- [308] H. Li, H. Chen, X. Li, J.G. Sanjayan, Development of thermal energy storage composites and prevention of PCM leakage, *Applied Energy*. 135 (2014) 225–233. <https://doi.org/10.1016/j.apenergy.2014.08.091>.
- [309] S.A. Memon, H.Z. Cui, H. Zhang, F. Xing, Utilization of macro encapsulated phase change materials for the development of thermal energy storage and structural lightweight aggregate concrete, *Applied Energy*. 139 (2015) 43–55. <https://doi.org/10.1016/j.apenergy.2014.11.022>.

- [310] S.A. Memon, H. Cui, T.Y. Lo, Q. Li, Development of structural-functional integrated concrete with macro-encapsulated PCM for thermal energy storage, *Applied Energy*. 150 (2015) 245–257. <https://doi.org/10.1016/j.apenergy.2015.03.137>.
- [311] ASTM C 127, Standard Test Method for Specific Gravity and Absorption of Coarse Aggregate, Philadelphia, PA: American Society for Testing and Materials, (2001). <https://www.astm.org/c0127-15.html>.
- [312] ASTM C127, Standard test method for compressive strength of hydraulic cement mortars (Using 2-in. or cube specimens), Annual Book of ASTM Standards. 04 (2016) 1–10. <https://doi.org/10.1520/C0109>.
- [313] “Thermtest,” HFM 100 Series - Thermal Conductivity Meter for measurement of insulation and construction materials., Sidilab. (2020). <https://thermtest.com/latinamerica/hfm-100#descargar>.
- [314] ASTM C518, Standard Test Method for Steady-State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus, ASTM International. (2015) 1–15. <https://doi.org/10.1520/C0518-21.2>.
- [315] Z. Liu, H. Wei, B. Tang, S. Xu, Z. Shufen, Novel light-driven CF/PEG/SiO₂ composite phase change materials with high thermal conductivity, *Solar Energy Materials and Solar Cells*. 174 (2018) 538–544. <https://doi.org/10.1016/j.solmat.2017.09.045>.
- [316] M.H. Zahir, M.M. Rahman, K. Irshad, Shape-Stabilized Phase Change Materials for Solar Energy Storage: MgO and Mg(OH)₂ Mixed with Polyethylene Glycol, *Nanomaterials*. 9 (2019) 1773. <https://doi.org/10.3390/nano9121773>.
- [317] S. Ramakrishnan, X. Wang, J. Sanjayan, E. Petinakis, J. Wilson, Development of thermal energy storage cementitious composites (TESC) containing a novel paraffin/hydrophobic expanded perlite composite phase change material, *Solar Energy*. 158 (2017) 626–635. <https://doi.org/10.1016/j.solener.2017.09.064>.
- [318] C. Mankel, A. Caggiano, E. Koenders, Thermal energy storage characterization of cementitious composites made with recycled brick aggregates containing PCM, *Energy and Buildings*. 202 (2019) 109395. <https://doi.org/10.1016/j.enbuild.2019.109395>.
- [319] Q. Ma, M. Bai, Mechanical behavior, energy-storing properties and thermal reliability of phase-changing energy-storing concrete, *Construction and Building Materials*. 176 (2018) 43–49. <https://doi.org/10.1016/j.conbuildmat.2018.04.226>.
- [320] H. Cui, S.A. Memon, R. Liu, Development, mechanical properties and numerical simulation of macro encapsulated thermal energy storage concrete, *Energy and Buildings*. 96 (2015) 162–174. <https://doi.org/10.1016/j.enbuild.2015.03.014>.
- [321] A.C.I. ACI, Building Code Requirements for Structural Concrete, 2014.

- [322] A. Sarı, A. Bicer, A. Karaipekli, F.A. Al-Sulaiman, Preparation, characterization and thermal regulation performance of cement based-composite phase change material, *Solar Energy Materials and Solar Cells*. 174 (2018) 523–529. <https://doi.org/10.1016/j.solmat.2017.09.049>.
- [323] A. Sarı, A. Bicer, A. Karaipekli, F.A. Al-Sulaiman, Preparation, characterization and thermal regulation performance of cement based-composite phase change material, *Solar Energy Materials and Solar Cells*. 174 (2018) 523–529. <https://doi.org/10.1016/j.solmat.2017.09.049>.

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Publications :

1. **K. O. Mohaisen**, H. Zahir, M. Maslehuddin, Shape-stabilized phase change material for thermal energy storage : Sr + 2 doped BaCO₃ matrix incorporating polyethylene glycol, Journal of Energy Storage. 58 (2023) 106369. <https://doi.org/10.1016/j.est.2022.106369>. (Journal paper, Published).
2. **K.O. Mohaisen**, M. Hasan Zahir, M. Maslehuddin, S.U. Al-Dulaijan, Development of a shape-stabilized phase change material utilizing natural and industrial byproducts for thermal energy storage in buildings, Journal of Energy Storage. 50 (2022) 104205. <https://doi.org/10.1016/j.est.2022.104205>. (Journal paper, Published).
3. H. Zahir, M.M. Rahman, **K.O. Mohaisen**, A. Helal, M.N. Shaikh, M.M. Rahman, Clarification of the Supercooling and Heat Storage Efficiency Calculation Formula

- for Shape-Stabilized Phase Change Materials, (2022) 5–8. <https://doi.org/10.1021/acsomega.2c04594>. (Journal paper, Published).
4. M.H. Zahir, M.M. Rahman, S.K.S. Basamad, **K. O. Mohaisen**, K. Irshad, M.M. Rahman, M.A. Aziz, A. Ali, M.M. Hossain, Preparation of a sustainable shape-stabilized phase change material for thermal energy storage based on mg²⁺doped caco₃/peg composites, Nanomaterials. 11 (2021) 1–24. <https://doi.org/10.3390/nano11071639> (Journal paper, Published).
 5. M.H. Zahir, M.M. Rahman, M. Shafiullah, M.M. Rahman, A. Ali, F. Khan, **K. O. Mohaisen**, M. Al-Rasheidi, LaCO₃OH nanoprisms and their luminescence and NO reduction properties, Catalysts. 10 (2020). <https://doi.org/10.3390/catal10040394> (Journal paper, Published).
 6. S. Ahmad, **K. O. Mohaisen**, S.K. Adekunle, S.U. Al-Dulaijan, M. Maslehuddin, Influence of admixing natural pozzolan as partial replacement of cement and microsilica in UHPC mixtures, Construction and Building Materials. 198 (2019) 437–444. <https://doi.org/10.1016/J.CONBUILDMAT.2018.11.260> (Journal paper, Published).
 7. **K. O. Mohaisen**, S. Ahmad , M. Maslehuddin, S. K. Adekunle, S. U. Al-Dulaijan, Use of accelerated carbonation as a viable option for curing ultra-high performance concrete, Journal of Materials in Civil Engineering (Journal paper, under review)

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