THERMAL ENERGY STORAGE AND FIRE SAFETY OF BUILDING MATERIALS

AWNİ ALKHAZALEH

A thesis submitted to the University of Bolton in partial fulfilment of the requirements for the degree of Doctor of Philosophy

Institute for Materials Research and Innovation
University of Bolton
Deane Road, Bolton, BL3 5AB

May 2018
Declaration of Authorship

I declare that the works described in this PhD thesis has not been previously presented in any form to the university or to any other institutional body, whether for assessment or for other purposes. I confirm that the intellectual content of the work is the result of my own original research and of no other person.

Signed ..........

Date ..........
Acknowledgments

I would like to express my appreciation and gratitude to my supervisor Professor Baljinder K. Kandola for her valuable support and guidance towards the development of my research. I would further like to thank the Jordanian Civil Defence for their financial support for this project. Many thanks to Prof. John Ebdon, Dr. John Milnes, Prof. Peter Myler, Dr. Navneet Soin and Dr. Mamadou Ndiaye for their help. Thanks to my colleagues Dr. Abdulla Al seiari, Maram, Chen, Rob, Nima, Sara, Gianmarco, Mohammed, Ali, Akbar and all members of the Fire Group at IMRI for their support and help to carry out this research.

I would like to thank Dr. Laila Alhusban, Dr. Waref Almanaseer, Dr. Sahar Almashaqbeh and Dr. Muna Alibrahim for their support and help. I thank all my friends in the UK for their hospitality, advice and interesting time we spent together.

Massive thanks to my mum for her support, endless love and encouragement. Special thanks go to my brothers and sisters for their constant source of support and patience. Great appreciation and enormous thank to them. This thesis is dedicated to them and to my late father, who lives in memories.
Abstract

Energy storage using organic phase change materials (PCMs) has attracted significant attention in recent years for renewable energy utilization in building materials. PCMs are capable of storing and releasing a large amount of latent heat during their phase transitions. Paraffin (PA), a eutectic mixture (EM) of capric acid (CA) and lauric acid (LA) and butyl stearate (BS) have been selected as PCMs for this work due to their melting temperatures being close to human comfort temperature, 17 - 28°C. Plaster (PL) as a building material is chosen due to its ease of construction into plaster boards and also because it is a good insulator against heat and sound. The most significant concern when using an organic PCM is its flammability. This research sets out to determine the effect of using PCMs in PL on the product’s flammability, and whether it is possible to use carrier materials and/or flame retardants to reduce their flammability while maintaining the thermal energy storage properties. Three techniques of incorporation of PCMs into PL are used to address this question. The first one is to immerse PL into hot melted PCMs using a vacuum impregnation method. The PCM however, could easily leak to the surface of PL, particularly when the temperature is above the melting temperature of PCM and also their high flammability evaluated using cone calorimetry was a limiting factor to pursuance of this route. The second method is a direct incorporation technique, i.e. adding PCM directly to PL. With this method also the leakage of PCMs was observed and all samples ignited, though the flammability parameters were less intense than those observed when the immersion method was used.

To prevent the leakage of PCM and to improve the consistency of organic PCM with building materials, form-stable PCMs composites are used in the third method. Carrier materials, namely nanoclay (NC), diatomaceous earth (DE), expanded perlite (EP), fly ash (FA) and brick dust (BD) were selected to adsorb and retain the PCMs in their pores. SEM (scanning electron microscope) demonstrated that PCMs were uniformly adsorbed in most of the carrier materials. DSC (differential scanning calorimeter) used to measure the thermal properties of PCMs showed that when these form stable composites were added to PL, they acted as PCMs, although the latent heat values were reduced. Thermal gravimetric analysis (TGA) results demonstrates that the PCMs’ decomposition was not affected by the presence of carrier materials or PL. Cone calorimetry showed that the use of carrier materials had minimal effect on the flammability of PCMs. To evaluate the thermal energy storage performance, a small environmental chamber was used, i.e. a small test “room” of
PL with dimensions of 100 mm x 100 mm x 100 mm and thickness 10 mm was set up using 6 pieces of PL. The top board of the cubic room contained PCM, and the temperature differences between the surfaces of control PL and modified PL were recorded during heating and cooling of the room. The results from heating and cooling cycles showed that the PCMs and form stable-PCM composites reduced the peak temperature and delayed the time taken to release the stored energy, the values depending on the percentage of PCMs used.

To reduce the flammability of PCMs while maintaining their energy storage performance, two approaches have been undertaken: (i) use of expanded graphite (EG) as a flame retardant carrier- material and (ii) use of a liquid flame-retardant, resorcinol bis(diphenyl phosphate) (RDP). The results demonstrated that the flame retardant did not affect the energy storage performance of the PCM. While RDP was not effective on a PA containing PL sample, the flammability of a PL+BS sample was significantly reduced with the addition of EG and RDP.
Published journal and conference papers


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## Nomenclature

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<th>Symbol</th>
<th>Designation</th>
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<tbody>
<tr>
<td>HVAC</td>
<td>Heating, ventilation and air conditioning</td>
</tr>
<tr>
<td>TES</td>
<td>Thermal energy storage</td>
</tr>
<tr>
<td>SHE</td>
<td>Sensible heat storage</td>
</tr>
<tr>
<td>LHS</td>
<td>Latent heat storage</td>
</tr>
<tr>
<td>PCMs</td>
<td>Phase change materials</td>
</tr>
<tr>
<td>CES</td>
<td>Chemical energy storage system</td>
</tr>
<tr>
<td>PL</td>
<td>Plaster</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>ASHRAE</td>
<td>Heating, Refrigeration and Air Conditioning Engineers</td>
</tr>
<tr>
<td>PA</td>
<td>Paraffin</td>
</tr>
<tr>
<td>EM</td>
<td>Eutectic mixture</td>
</tr>
<tr>
<td>CA</td>
<td>Capric acid</td>
</tr>
<tr>
<td>LA</td>
<td>Lauric acid</td>
</tr>
<tr>
<td>MC</td>
<td>Myristic acid</td>
</tr>
<tr>
<td>PAM</td>
<td>Palmitic acid</td>
</tr>
<tr>
<td>SA</td>
<td>Stearic acid</td>
</tr>
<tr>
<td>PCW</td>
<td>Phase change wallboards</td>
</tr>
<tr>
<td>NC</td>
<td>Nanoclay</td>
</tr>
<tr>
<td>BS</td>
<td>Butyl stearate</td>
</tr>
<tr>
<td>MMT</td>
<td>Organically modified montmorillonite</td>
</tr>
<tr>
<td>DE</td>
<td>Diatomaceous earth</td>
</tr>
<tr>
<td>EP</td>
<td>Expanded perlite</td>
</tr>
<tr>
<td>EG</td>
<td>Expanded graphite</td>
</tr>
<tr>
<td>SA</td>
<td>Stearic acid</td>
</tr>
<tr>
<td>GP</td>
<td>Glass powder</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>KO</td>
<td>Kaolin</td>
</tr>
<tr>
<td>GGBS</td>
<td>Ground granulated blast furnace</td>
</tr>
<tr>
<td>DA</td>
<td>Dodecyl alcohol</td>
</tr>
<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
</tr>
<tr>
<td>SBS</td>
<td>Styrene-butadiene-styrene copolymer</td>
</tr>
<tr>
<td>VIPs</td>
<td>Vacuum insulation panels</td>
</tr>
<tr>
<td>APP</td>
<td>Ammonium polyphosphate</td>
</tr>
<tr>
<td>PER</td>
<td>Pentaerythritol</td>
</tr>
<tr>
<td>MA</td>
<td>Melamine</td>
</tr>
<tr>
<td>HRR</td>
<td>Heat release rate</td>
</tr>
<tr>
<td>PHRR</td>
<td>Peak heat release rate</td>
</tr>
<tr>
<td>FSPCM</td>
<td>Flame retardant form-stable PCMs</td>
</tr>
<tr>
<td>IFR</td>
<td>Intumescent fire retardant</td>
</tr>
<tr>
<td>MPP</td>
<td>Melamine phosphate</td>
</tr>
<tr>
<td>MCA</td>
<td>Melamine Cyanurate</td>
</tr>
<tr>
<td>BPBE</td>
<td>1,2-bis (Pentabromophenyl)</td>
</tr>
<tr>
<td>AO</td>
<td>Antimony trioxide</td>
</tr>
<tr>
<td>TDE</td>
<td>Decabromo diphenyl ethane</td>
</tr>
<tr>
<td>PCNM</td>
<td>Nanocomposites materials</td>
</tr>
<tr>
<td>EVA</td>
<td>HDPE/ethylene-vinyl acetate</td>
</tr>
<tr>
<td>MRR</td>
<td>Microencapsulated red phosphorous (MRR)</td>
</tr>
<tr>
<td>MH</td>
<td>Magnesium hydroxide (MH)</td>
</tr>
<tr>
<td>FR370</td>
<td>Tris(tribromoneopentyl)phosphate</td>
</tr>
<tr>
<td>RDP</td>
<td>Resorcinol bis(diphenyl phosphate)</td>
</tr>
<tr>
<td>TTI</td>
<td>Time to ignition</td>
</tr>
<tr>
<td>TFO</td>
<td>Flame out time</td>
</tr>
<tr>
<td>EHC</td>
<td>Effective heat of combustion</td>
</tr>
</tbody>
</table>
CHAPTER ONE
INTRODUCTION

Solar energy plays an important role in our energy supply and if this infinite amount of energy is efficiently stored, it can be the promising alternative method to satisfy the large daily energy consumption in the world. Moreover, it is a cheap and environmentally friendly method. More energy from the sun falls on the earth in one hour than is used by everyone in the world in one year [1]. With the advent of growing energy crises in the 1970’s, people realised that oil is a finite resource and probably will run out within 50 years. A majority of countries introduced legislation for building regulations to encourage companies to make new buildings more energy efficient. They focused on insulation materials to be used to reduce the heat from walls, roof and floor but this method did not work very well in winter and summer seasons [2]. Therefore, air cooling systems became the alternative solution to improve the comfort of occupants. 30% of our energy supply is consumed in buildings through heating, ventilation and air conditioning (HVAC) and lighting [3], consequently, new aspects of building design have been introduced to reduce the amount of the energy consumed.

Ideally, building materials should be able to work as a heat exchanger to maintain the indoor temperature close to human comfort temperature. Thus, thermal energy storage (TES) [4] is considered the main strategy to increase energy efficiency. TES can be achieved by the following three methods [5,6] namely sensible heat storage, latent heat storage and chemical energy storage.

*Sensible heat storage system (SHS):* Thermal energy is stored by raising the temperature of a solid or a liquid such as water, rock beds and molten salt. The amount of heat stored relies on the specific heat of the medium, the temperature change and the amount of storage material [7].

*Latent heat storage system (LHS):* Latent heat storage (LHS) is based on heat absorption or release when a storage material undergoes phase change from solid to liquid or liquid to gas or vice versa. When the phase change occurs, the phase transition temperature of the material remains almost constant even though a certain amount of heat is absorbed or released by the material. Phase change materials (PCMs) are an effective way of storing a
large amount of latent heat during phase transition and could be used for storing energy in building materials.

Chemical energy storage system (CES): Energy can be stored in systems composed of one or more chemical compounds that either absorb or release energy through chemical reactions. Zhiqiang et al [6] have explained the chemical storage systems as sorption processes or reversible chemical reactions. Exemplar chemicals used include ammoniates, hydrates and metal hydrides.

Much attention has been paid to LHS among the different systems used in TES. LHS is widely used in engineering applications to conserve energy and reduce the dependence on oil. Moreover, it can be used to enhance the performance and reliability of energy systems, reduce green house emissions and fill the gap between supply and demand [8-11]. PCMs are an indispensable way of storing a large amount of latent heat during melting and releasing it during solidification [12].

The utilization of PCMs in active and passive solar heat storage in buildings has been attracting interest since 1940 [13]. The intensive search for TES systems, which are more efficient than SHS led to the investigation of the latent heat method. Early studies of LHS concentrated on the fusion-solidification of low cost and readily available salt hydrates. However, salt hydrates can undergo supercooling, segregation and melt incongruently (when the salt is not entirely soluble in its water of hydration at the melting point), which limit their usage as phase change materials. In spite of the considerable advantages, the development of reliable and practical storage systems utilizing salt hydrates and similar inorganic substances faced major hurdles. To avoid some of the drawbacks associated with inorganic PCMs, interest has been directed towards organic PCMs which have been studied for TES in buildings since 1980 [14]. Currently, the use of PCMs in building applications [15-16] is considered one of the hot topics in latent heat storage technology.

Different methods are used to integrate PCMs into building materials such as gypsum plaster (PL), concrete and gypsum wallboard to reduce the energy demand for heating and cooling. By incorporating PCMs into buildings, the indoor peak temperature can be reduced and the peak load for a heating and cooling system could be postponed by several hours and shifted into an off-peak period. Although the preparation and thermal properties have been extensively studied, the flammability of PCM-containing materials is a less
researched area. Fire safety is the most important issue nowadays thus, improving the flammability performance of PCMs is essential [17-20]. This thesis deals specifically with PL.

PL is cheap, simply and conveniently constructed, and can insulate against heat and sound. PL is commonly used in building applications specifically for decoration. A typical PL consists mainly of calcium sulphate di-hydrate (CaSO\(_4\) 2H\(_2\)O) and approximately 21% (by weight) chemically bound water of crystallization [21]. In addition, gypsum contains about 3% free water. When the PL is subjected to a temperature between 100 and 150 °C, depending on the heating rate, 75% of the chemically bound water is driven off and evaporates within the structure [22]. This process is known as dehydration and is an endothermic chemical reaction as shown in Eq 1. With further increase in the temperature, the remaining 25% of the chemically bound water is also removed. Hence, the second chemical reaction shown in Eq 2 is also endothermic, i.e. when the calcium sulphate hemihydrate losses the remaining water to form calcium sulphate anhydrite (CaSO\(_4\)).

\[
\text{CaSO}_4\text{2H}_2\text{O} \rightarrow \text{CaSO}_4\text{1/2H}_2\text{O(s)}+3/2\text{H}_2\text{O(g)} \quad (1)
\]

\[
\text{CaSO}_4\text{1/2H}_2\text{O} \rightarrow \text{CaSO}_4(s)+1/2\text{H}_2\text{O(g)} \quad (2)
\]

In a fire, PL is subjected to high temperature which in turn is enough to release and transfer the water through the board, absorbing energy and thus reducing the mean wall temperature. The dehydration process can thus positively improve the fire resistance of the building’s walls and thus increase the safe evacuation time for occupants. However, when a PCM is incorporated into building materials, the most significant concern is its flammability, particularly for organic PCMs. In a fire, the burning PCM can produce significant amounts of smoke, toxic gases [23] and flame which can be simply transferred from the point of origin to adjacent spaces [24-26]. Uncontrolled building fires can cause a great number of fatalities, injuries and economic loss. In 1944, a fire in Hartford Circus [27] caused the deaths of 168 people. A fire in 2004 occurred at a residential care home in Lanarkshire, Scotland and resulted 14 deaths with another four injured [28]. In 2006, 19 people were killed due to a fire in Felagio Shopping Mall in Qatar [29]. More recently, 71 people died in a fire at Grenfell tower in London [30].
Buildings have to meet the requirements of buildings regulations. In this sense the fire and smoke behaviour of building materials has to be tested to fulfil some of the requirements in order for them to be used in specific applications. In recent years, stringent flammability, safety standards and legislation have been imposed on building materials to help protect buildings from fire hazards [31]. For example, heat release rates and ignition times of combustible materials have to be taken into account in order to satisfy the building criteria [ASTM E119, ISO/TR 834 and BS 476]. These criteria relate mainly to life safety levels, fire exposure, structural performance, fire growth and spread [32]. Hence, in engineering practice, much attention has been paid to the provisions of fire-protection systems. The two main categories are (a) active and (b) passive fire protection. Active fire protection is of the installation of fire fighting systems (sprinklers, smoke control system, pressurization. etc) [31-37] to prevent fire spread. Passive fire protection can be provided within the structure itself such as by the incorporation of a flame retardant in a building material. PCMs if not treated with flame retardants when incorporated in building materials will become an additional fuel for the fire.

1.1 Research Aims and Objectives:

The main aim of this research is to develop fire safe and energy efficient construction materials, such as PL, incorporating PCMs. The objectives to fulfil this aim are:

1. To develop and characterise efficient thermal storage materials/systems by incorporating PCMs into PL.
2. To understand the mechanism of action of the PCMs without, or in combination with other additives in PL.
3. To investigate the fire and mechanical behaviours of existing and newly developed/modified PL materials.
4. To improve the flammability properties of modified PL using flame retardant carrier materials with/without flame retardants.
5. To develop a small scale method to characterize the thermal storage efficiency of PL containing PCMs and study the effect of flame retardants on thermal energy storage performance.
6. Use information gained in 1-5 to set up guidelines for use of different types, combinations and quantities of materials to be used in a typical room/building.

In this thesis PL has been chosen as the building material. The thermal, mechanical, morphology and flammability properties of PL containing PCMs with/without carrier
materials have been studied. Moreover, these properties have been investigated after adding flame retardant carrier materials with/without flame retardants to the prepared samples.

1.2 Structure of Thesis

Chapter 1 presents the background to thermal energy storage based on the latent heats of PCMs integrated in building materials. Moreover, the fire safety issues of modified building materials with PCMs are also discussed.

A general review on PCMs, including the classification of PCMs and the techniques of incorporating PCMs into building materials are discussed and compared in Chapter 2. The types of flame retardants and the flame retardants added to PCM to decrease its flammability are also introduced.

Chapter 3 includes the series of experiments, following the scientific methods to address the research question "is it possible to incorporate PCMs in building materials such as PL in order to improve the thermal performance and adding flame retardants to reduce the flammability of PCM"?

Chapter 4 investigates immersion and direct incorporation techniques used to integrate PCMs in PL. So as to study the effect of PCMs on PL, the thermal properties and stability are studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. The surface morphologies of samples prepared by direct incorporation are analysed using scanning electron microscopy (SEM). The mechanical properties of samples are evaluated in flexural and compression modes. To evaluate the flammability of these materials, the cone calorimetric technique is used. The thermal energy storage performance of a cube with its top board containing PCM is studied using a temperature controlled incubation chamber.

Chapter 5 describes the carrier materials used with PCMs in order to prevent their leakage. To evaluate the effect of these form-stable composite PCMs on PL, the thermal properties of form-stable composite PCMs, with/without PL, are studied using DSC. Also, thermal stability is studied by TGA. The dispersion of PCMs in carrier material particles has been investigated using SEM. A temperature controlled incubation chamber was used to evaluate the thermal energy storage performance of cube. Moreover, the mechanical and fire performance are discussed.
The form-stable composite PCM containing PL samples with optimum fire and mechanical properties from Chapter 5 have been selected in Chapter 6 and their thermal energy storage performances studied by making test rooms (cubes) with 5 sides of PL containing form-stable composite PCMs and measuring the indoor temperatures. A flame retardant form-stable composite PCM is prepared. The thermal, morphology, mechanical and flammability properties of PL with flame retardant form-stable composite PCM have been studied.

Chapter 7 presents the key findings of the research by discussing the outcomes of the study, and provides recommendations for the future work in this field.

1.3 References


CHAPTER TWO
LITERATURE REVIEW

2.1 Phase Change Materials (PCMs)

The first practical application of a PCM (sodium sulphate decahydrate) was reported by Telkes [1] in 1948, who created the first PCM heated solar house [2] by storing heat through circulating air using ducts. The next similar experiment was conducted by Gardenhire in 1953 but unfortunately due to the leakage, segregation and supercooling of the PCM used, their experiments failed [3]. Utilization of the thermal energy storage properties of PCMs attracted much interest after the fuel crisis in 1970 [4-6]; since then they have been considered as a key renewable technology through their ability to store latent heat at certain temperatures, referred to as melt enthalpy. During daytime, when the temperature increases, the solid-liquid phase change occurs to absorb heat from the environment while maintaining the temperature constant, the reaction being endothermic. At night, when the temperature falls below than the melting temperature, the liquid-solid phase change occurs to release the stored latent heat while the temperature of the material remains relatively constant, the reaction being exothermic.

There are a variety of PCMs whose melting temperatures fall within the range which can be used for low, medium and high temperature applications. PCMs of low melting temperatures close to human comfort range (17-28 °C) have been considered for building applications according to the American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE) [7]. Ideally PCMs to be used in thermal energy storage should have a large latent heat of transition, high specific heat and high thermal conductivity. The latent heat and specific heat must be high in order to store a significant amount of heat and avoid supercooling. Moreover, PCMs should have a small volume change on transition, a low vapour pressure, and a high density in order to ensure containment in minimal volume at operating temperatures. PCMs should also be non-corrosive, non-toxic and have low cost in order to encourage their usage.

2.2. Classification of PCMs

PCMs are generally classified into three different groups based on their composition: Organic, Inorganic and Eutectic materials [8] as shown in Figure 2.1.
Figure 2.1: Classification of PCMs [9]

Figure 2.2 represents the typical melting temperature range of each group. It can be noticed from this figure that the melting temperature of several types of paraffin and salt hydrate are in the range of human comfort temperature, which make them suitable to be used in building applications.

Figure 2.2: The melting enthalpy and melting temperature for different groups of PCMs [adapted from Ref 10]

### 2.2.1 Organic phase change materials

Organic PCMs are categorized as paraffin (PA) and non-paraffin compounds. The PA compound is formed by saturated hydrocarbon which corresponds to the chemical formula of \( \text{C}_n\text{H}_{2n+2} \). Paraffin wax is considered the most used PCM in this group [11]. Non-paraffinic compounds include fatty acids [12], esters, alcohols and glycols. The characteristics of organic PCMs include congruent melting, high latent heat of fusion, no supercooling, chemical and thermal stability, non-corrosivity and ability to be incorporated.
directly into building materials. On the other hand, flammability, lower thermal conductivity and lower enthalpy are the main defects of this group. Table 2.1 shows some examples of organic PCMs and Table 2.2 presents the commercially available PCMs.

### Table 2.1: List of organic PCMs [13]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting temperature (°C)</th>
<th>Latent heat of fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyl stearate</td>
<td>19</td>
<td>140</td>
</tr>
<tr>
<td>Paraffin C_{10-18}</td>
<td>20-22</td>
<td>152</td>
</tr>
<tr>
<td>Capric-Lauric acid</td>
<td>21</td>
<td>143</td>
</tr>
<tr>
<td>Dimethyl sabacate</td>
<td>21</td>
<td>120</td>
</tr>
<tr>
<td>Polyglycol E 600</td>
<td>22</td>
<td>127.2</td>
</tr>
<tr>
<td>Paraffin C_{13-24}</td>
<td>22-24</td>
<td>189</td>
</tr>
<tr>
<td>I-Dodecanol</td>
<td>26</td>
<td>200</td>
</tr>
<tr>
<td>34%Mistiric acid+66%Capric acid</td>
<td>24</td>
<td>147.7</td>
</tr>
<tr>
<td>Paraffin C18 (45-55%)</td>
<td>28</td>
<td>244</td>
</tr>
<tr>
<td>Vinyl stearate</td>
<td>27-29</td>
<td>122</td>
</tr>
<tr>
<td>Capric acid</td>
<td>32</td>
<td>152.7</td>
</tr>
</tbody>
</table>

### Table 2.2: Commercial PCMs available in the international market [13]

<table>
<thead>
<tr>
<th>PCM name</th>
<th>Type of Product</th>
<th>Melting temperature (°C)</th>
<th>Latent heat of fusion (J/g)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT 20</td>
<td>Paraffin</td>
<td>22</td>
<td>172</td>
<td>Rubitherm GM BH</td>
</tr>
<tr>
<td>Climsel C23</td>
<td>Salt hydrate</td>
<td>23</td>
<td>148</td>
<td>Climator</td>
</tr>
<tr>
<td>Climsel C24</td>
<td>Salt hydrate</td>
<td>24</td>
<td>216</td>
<td>Climator</td>
</tr>
<tr>
<td>RT 26</td>
<td>Paraffin</td>
<td>25</td>
<td>131</td>
<td>Rubitherm GM BH</td>
</tr>
<tr>
<td>RT 25</td>
<td>Paraffin</td>
<td>26</td>
<td>232</td>
<td>Rubitherm GM BH</td>
</tr>
<tr>
<td>STL 27</td>
<td>Salt hydrate</td>
<td>27</td>
<td>213</td>
<td>Mitsubishi chemical</td>
</tr>
<tr>
<td>S27</td>
<td>Salt hydrate</td>
<td>27</td>
<td>207</td>
<td>Cristopia</td>
</tr>
<tr>
<td>RT 30</td>
<td>Paraffin</td>
<td>28</td>
<td>206</td>
<td>Rubitherm GM BH</td>
</tr>
<tr>
<td>RT 27</td>
<td>Paraffin</td>
<td>28</td>
<td>179</td>
<td>Rubitherm GM BH</td>
</tr>
<tr>
<td>TH 29</td>
<td>Salt hydrate</td>
<td>29</td>
<td>188</td>
<td>TEAP</td>
</tr>
<tr>
<td>Climsel C32</td>
<td>Salt hydrate</td>
<td>32</td>
<td>212</td>
<td>Climator</td>
</tr>
<tr>
<td>RT32</td>
<td>Paraffin</td>
<td>31</td>
<td>130</td>
<td>Rubitherm GM BH</td>
</tr>
</tbody>
</table>
2.2.2 Inorganic phase change materials

Inorganic PCMs (see Table 2.3) such as calcium chloride hexahydrate, potassium fluoride tetrahydrate, manganese nitrate hexahydrate, calcium bromide hexahydrate and sodium thiosulphate pentahydrate have a phase transition close to human comfort temperature (~22 °C). Furthermore, they have good thermal conductivity and non-flammability. However, they suffer from decomposition, corrosiveness, segregation, supercooling and lack of thermal stability which can affect their thermal properties to some extent.

Table 2.3: List of salt hydrate PCMs [9]

<table>
<thead>
<tr>
<th>PCM material</th>
<th>Melting temperature (°C)</th>
<th>Latent heat of fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$H$_2$O$_4$.6H$_2$O</td>
<td>14</td>
<td>108</td>
</tr>
<tr>
<td>KF.4H$_2$O</td>
<td>18</td>
<td>330</td>
</tr>
<tr>
<td>K$_2$H$_2$O$_4$.4H$_2$O</td>
<td>18.5</td>
<td>231</td>
</tr>
<tr>
<td>LiBO$_2$.8H$_2$O</td>
<td>25.7</td>
<td>289</td>
</tr>
<tr>
<td>FeBr$_3$.6H$_2$O</td>
<td>27</td>
<td>105</td>
</tr>
<tr>
<td>CaCl$_2$.6H$_2$O</td>
<td>29-30</td>
<td>170-192</td>
</tr>
<tr>
<td>Na$_2$SO$_4$.10H$_2$O (Glauber’s salt)</td>
<td>32</td>
<td>251-254</td>
</tr>
</tbody>
</table>

2.2.3 Eutectics

Two or more components can be mixed to form a eutectic (EM), each component of which melts and freezes congruently forming a mixture of the component crystals during crystallization. This group can be further divided into three diverse groups: Organic-organic, organic-inorganic and inorganic-inorganic eutectics. The inorganic-inorganic eutectic PCMs group has sharper melting points and higher thermal storage densities per volume compared to organic compounds; exemplars are listed in Table 2.4.
Table 2.4: List of Inorganic eutectic mixtures [13]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting temperature (°C)</th>
<th>Latent heat of fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66.6% CaCl₂.6H₂O + 33.4% MgCl₂.6H₂O</td>
<td>25</td>
<td>127</td>
</tr>
<tr>
<td>48% CaCl₂+ 4.3% NaCl+ 0.4% KCl+ 47.3% H₂O</td>
<td>26.8</td>
<td>188</td>
</tr>
<tr>
<td>47% Ca(NO₃)₂.4H₂O+ 53% Mg(NO₃)₂.6H₂O</td>
<td>30</td>
<td>136</td>
</tr>
<tr>
<td>60% Na(CH₃COO).3H₂O+ 40% CO(NH₂)₃</td>
<td>30</td>
<td>200.5</td>
</tr>
</tbody>
</table>

2.3. Techniques of Incorporation PCMs into building Materials

There are four most promising techniques of PCMs incorporation: direct incorporation, immersion, encapsulation and form-stable composite PCMs.

2.3.1. Immersion technique

A porous construction material such as PL, gypsum wallboard and concrete block is dipped into hot melted PCM for a period of time, then removed and allowed to cool so that the PCM absorbed by means of capillary action remains in the pores of the materials [14-16]. Long-term thermal reliability, thermal properties and degradation in the chemical structure of 64 % capric acid (CA) / 36 % lauric acid (LA) and 73 % CA / 27 % myristic acid (MC) have been investigated by Karaipekli et al [17]. They showed that the PCMs had good thermal properties and long-term thermal reliability. The thermal stabilities of some fatty acids as PCMs such as: LA, palmitic acid (PAM), stearic acid (SA) and MC with melting temperature (40-63 °C) have been investigated by Sari and Kaygusuz [18], who also studied, the corrosion resistance of containment capsules such as: stainless steel, aluminum, carbon steel and copper for the fatty acids. Good thermal stability was found for MC and PAM, with copper and carbon steel being the most compatible containment materials. The impregnation of gypsum wallboard with an EM of 76.5 % CA and 23.5 % PAM for 1 hour has been studied by Karaipekli and Sari [19]. The Melting and freezing temperatures of CA-PAM were 21.85 and 22.15 °C, respectively and their latent heats of melting and freezing found to be 171.22 and 173.16 J/g, respectively.

Shilei et al [20, 21] mixed an EM of CA-LA with wallboard to form phase change wallboards (PCW), the results are shown in Table 2.5. They also studied the difference of stored thermal energy between PCW room and ordinary wallboard room at the same
climate conditions by noting the shifting of the energy consumption during day and night times. The obtained results during three continuous days in winter in the northeast of China showed the enhancing of the indoor thermal comfort, reducing the energy consumption and mitigating indoor temperature fluctuation. Medyan [22] impregnated the eutectic mixture of CA-LA acids as PCM in gypsum wallboard of thicknesses 6 and 12.5 mm. Gypsum wallboard samples were immersed in PCM for 1 hour at 60 °C. The results for 6 mm thick sample are given in Table 2.5. In 12.5 mm thick samples, latent heat was slightly decreased compared to 6 mm thick sample. It was also observed that the immersion process did not affect the physical properties of the gypsum wallboard.

Table 2.5: Thermal properties of EM mixture

<table>
<thead>
<tr>
<th>EM Compound</th>
<th>Melting Temp (°C)</th>
<th>Freezing Temp (°C)</th>
<th>Latent heat of melting (J/g)</th>
<th>Latent heat of freezing (J/g)</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.1%CA+34.9%LA</td>
<td>19.67 (19.10)</td>
<td>---</td>
<td>126.56 (35.23)</td>
<td>---</td>
<td>Shilei [20]</td>
</tr>
<tr>
<td>82%CA+18%LA</td>
<td>20.39 (18.49)</td>
<td>19.13 (18.58)</td>
<td>150.30 (39.12)</td>
<td>144.18 (36.69)</td>
<td>Shilei [21]</td>
</tr>
<tr>
<td>65%CA+35%LA 12.5 mm</td>
<td>17.48 (17.9)</td>
<td>---</td>
<td>133.08 (33.1)</td>
<td>---</td>
<td>Medyan [22]</td>
</tr>
<tr>
<td>6 mm</td>
<td>18.1</td>
<td></td>
<td>(36.8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Values in brackets are the thermal properties of PCW

Despite great advantages of this method to easily convert ordinary wallboard to PCM wallboard with low cost, the leakage of the liquid PCM to the surface of the gypsum wallboard is unavoidable. This can be clearly observed after the PCW experienced several heating-cooling cycles when the PCW heated particularly above the melting temperature of PCM used [23-25]. Therefore, the change in thermal properties of the PCM with increasing thermal cycling can be adversely affected.

### 2.3.2 Direct incorporation

Direct incorporation technique is considered as the most economical method since it involves limited additional equipment processes. Liquid and powdered PCM [16] are added to and mixed directly with building materials during production. The drawbacks of this method are the leakage of PCM used and reduction of the mechanical strength of construction materials significantly. To overcome these problems and utilize the material readily, the incorporation of a kind of shape-stabilized PCMs into building materials can be
achieved by blending PCMs with carrier materials. Therefore, it is indispensable to develop a novel route for incorporating PCM into construction materials, which is simple and low cost compared with encapsulation of PCM. In addition, it is able to enhance the thermal conductivity of PCM and prevent the leakage of PCM and can improve the consistency of organic PCM with building materials.

2.3.3 Form-stable composite PCMs

The incorporation of form-stable composite PCM into building materials can be achieved by blending PCM with carrier materials. The form-stable composite PCM has been used to confine the optimum maximum percentage of PCM without leakage. The form-stable composite can be formed by natural immersion or vacuum impregnation.

2.3.3.1 Nanoclay

Nanoclays (NC) are widely used in materials as fire retardants, and to decrease gas permeability and to increase the mechanical strength of the materials. Their high porosity has recently created a significant interest in their use in building applications for energy storage. Fang et al [26] prepared three PCM composites by blending PA (RT20), dodecanol and butyl stearate (BS) with an organically modified montmorillonite (MMT). PA(RT20)/MMT PCM composite was seen to be the best candidate for building applications, as this had suitable melting temperatures and latent heats of fusion, good compatibility with gypsum, high heat transfer efficiency and thermal energy storage performance.

2.3.3.2 Diatomaceous earth

Diatomaceous earth (DE) is formed from the skeletal remains of single celled plants which are called diatoms. It can be used as a carrier material for storing PCM because of its high porosity, absorptivity and inertness.

The thermal energy storage performance of cement-based composite (TESC) was evaluated by Xu and Li [27] by impregnation of PA-DE form-stable composite PCM into cement. 47.4 wt% of PA as thermal energy storage material was incorporated into DE. With the addition of 30 wt% of composite PCM, the thermal performance of the cement panel was significantly improved. However, the mechanical properties, i.e., the flexural
and compressive strengths were decreased compared with cement. The thermal energy storage properties of PA/calcined DE composite PCM have been studied by Sun et al [28]. The maximum mass fraction of PA that could be added in the composite was 61 wt %. DSC and thermal cycling results showed that calcined PA-DE composite had good thermal properties. 61.5 % of CA was mixed with 38.5 % of LA by Li et al [29] to form EM which was successfully impregnated into DE to form EM-DE composite PCM. Karaman et al [30] prepared polyethylene glycol/DE as composite PCM through vacuum impregnation technique. The maximum percentage of polyethylene glycol retained into the pores of DE was 50 wt%. The melting temperature and the latent heat determined by DSC were 27.7 °C and 87.09 J/g, respectively. After subjecting the composite PCM to 1000 melting and freezing cycles, the obtained results showed no significant changes in the thermal properties of the composite PCM, which indicated that this composite had thermal reliability. Furthermore, the composite PCM reduced the indoor temperature by 1.01 °C compared to a room without composite PCM.

2.3.3.3 Expanded Perlite

Perlite, an amorphous volcanic glass, has relatively high water content. When it is subjected to heat between 850-1115 °C, the volume of particles can be expanded up to 10-20 times their original volume to form expanded perlite (EP) due to the vaporization of water. Its high porosity and fire resistant properties have attracted researchers’ attention to use it for thermal energy storage and insulation.

Sari et al [31] impregnated 60 wt% of LA into EP using a vacuum impregnation technique. The thermal properties of this composite are shown in Table 2.6, which were retained after 1000 melting/freezing cycles. In order to enhance its thermal conductivity, 10 % of expanded graphite (EG) was mixed with composite PCM. Also, Sari and Karaipekli [32] prepared composite PCM of CA-EP and the Table 2.6 lists its melting temperature and latent heat of fusion tested by DSC. The thermal reliability after 5000 thermal cycles was observed to be varied by ±10%. Furthermore, the addition of 10% of EG into composite PCM successfully increased the thermal conductivity. In another study, Karaipekli and Sari [33] mixed CA and MC together to form a EM, 55 wt% of EM was successfully incorporated into EP without leakage by vacuum impregnation method. 10% EG has been added to increase the thermal conductivity of the CA-MC/EP composite PCM. Table 2.6 shows the thermal properties measured by DSC. According to a thermal cycling test, the results after 5000 thermal cycling showed that the composite PCM maintained its thermal
reliability. Moreover, fatty acid esters-based composite PCM formed from erythritol tetrapalmitate (ETP) and erythritol tetrastearate (ETS) into EP and DE have been fabricated by Sari and Karaipekli [34]. The maximum percentage of PCM confined by EP and DE through surface tension forces and capillary action was measured to be 62 and 57 wt%, respectively. The melting temperature was in the range of 19.64-30.15 °C and the latent heat of fusion was varied between 110.6 -119.19 J/g. Moreover, after 1000 thermal cycles, the composite PCM retained thermal stability. 5% of EG was also added to composite PCM to increase its thermal conductivity.

Karaiphekli et al [35] prepared form-stable PCMs by incorporating 55 wt% of PA into EP without seepage. The thermal properties of this composite were shown in Table 2.6. The thermal cycling test results indicated that the PA-EP composite PCM had good thermal reliability after 5000 thermal cycling. The maximum mass fraction of LA retained by EP without leakage was found to be 70 % by Jiesheng et al [36]. The DSC results are given in Table 2.6. SEM micrographs indicated that the LA was successfully absorbed in the pores and on the surface of EP. Thermal cycling test after 100 cycles showed that there were no obvious changes observed in the thermal properties of LA-EP composite PCM. Based on the test results, it was concluded that LA-EP composite PCM has great potential for thermal energy storage applications.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Temp (°C)</th>
<th>Freezing Temp (°C)</th>
<th>Latent heat of melting (J/g)</th>
<th>Latent heat of freezing (J/g)</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>60% LA+40% EP</td>
<td>44.13</td>
<td>---</td>
<td>93.36</td>
<td>---</td>
<td>Sari et al [31]</td>
</tr>
<tr>
<td>55% CA+45% EP</td>
<td>31.8</td>
<td>19.13</td>
<td>98.1</td>
<td>---</td>
<td>Sari and Karaipekli [32]</td>
</tr>
<tr>
<td>55%CA-MC+45% EP</td>
<td>21.70</td>
<td>20.7</td>
<td>85.40</td>
<td>89.75</td>
<td>Karaipekli and Sari [33]</td>
</tr>
<tr>
<td>55% PA +45% EP</td>
<td>42.27</td>
<td>40.79</td>
<td>87.4</td>
<td>90.25</td>
<td>Karaipekli et al [35]</td>
</tr>
<tr>
<td>70% LA+30% EP</td>
<td>43.2</td>
<td>105.58</td>
<td>---</td>
<td>---</td>
<td>Jiesheng et al [36]</td>
</tr>
<tr>
<td>65% SA-LA+35% EP</td>
<td>31</td>
<td>---</td>
<td>119</td>
<td>---</td>
<td>Peng et al [37]</td>
</tr>
<tr>
<td>60% PA+40% EP</td>
<td>27.56</td>
<td>---</td>
<td>80.9</td>
<td>---</td>
<td>Lu et al [38]</td>
</tr>
</tbody>
</table>

The thermal properties of stearic acid (SA)-LA/EP composite PCM have been evaluated by Peng et al [37]. The results showed that the maximum mass fraction of SA-LA confined in EP without seepage was 65 %. The thermal properties of composite were reported in Table 2.6. The thermal reliability after 100 thermal cycles measured by DSC did not show
significantly change in the phase transition temperature and latent heat. TGA results and thermal cycling test showed that the SA-LA/EP composite PCM was thermally stable and reliable. The mechanical properties test results of the SA-LA/EP composite PCM mixed with gypsum wallboard showed reduction in flexural strength. The thermal performance test of a formed wallboard room was done using an in-house heating setup, consisting of an insulation box and infrared lamp (275W). The obtained results confirmed that the SA-LA/EP wallboard has the ability to preserve heat and reduce the fluctuation of indoor temperature. Lu et al [38] successfully incorporated 60 % of PA into EP without leakage to form PA-EP composite PCM. DSC results were illustrated in Table 2.6. The TGA results showed that the EP improved the thermal stability of PA-EP composite PCM and it was more stable compared with PA. Thermal cycling results confirmed that this composite had thermal stability and reliability after 1000 and 2000 thermal cycles. SEM results revealed that the PA has been distributed uniformly in the porous EP. All results proved that the PA-EP composite PCM is convenient to be used in building applications for thermal energy storage. Zhang et al [39] mixed (LA-MC-PAM in the ratio 52.3, 32.5 and 15.2 wt%) with EP to fabricate a form-stable composite PCM of EM. The melting temperature of EM was 31.41 °C. The maximum mass fraction of EM confined into EP was found to be 94.7 wt%. The thermal cycling test results indicated the phase change temperature and latent heat were slightly changed compared to that before thermal cycling.

2.3.3.4 Expanded graphite

Sari and Karaipekli [40] successfully incorporated PAM into EG to form PAM-EG composite PCM. The thermal properties are shown in Table 2.7. The composite PCM was subjected to 3000 melting and freezing cycles, the results indicated that the observed changes in the thermal reliability were in the acceptable range. Besides, the thermal conductivity of the composite PCM was increased 2.5 times compared with pure PAM. These results confirmed that the EG was suitable to be applied for solar latent heat thermal energy applications.

The thermal properties of incorporating of polyethylene glycol into EG shown in Table 2.7 has been investigated by Wang et al [41]. The observed changes in thermal properties for composite PCM after 100 melting/freezing cycles were less than 2.5%. Li et al [42] investigated the mixture of PA-EG to form composite PCM. The thermal properties of PA-EG were presented in Table 2.7. 20% of composite PCM was mixed with cement to
fabricate the heat storage cement mortar (HSCM). The flexural and compressive strength of modified cement mortar decreased with increase in composite PCM content. To evaluate the heat storage effect of HSCM, a testing device was designed. The maximum indoor temperature difference at the centre of the cube was 2.2 °C during the heat storage and 1.5 °C during the heat release process.

Table 2.7: Thermal properties of form-stable composite PCM with EG

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Temp (°C)</th>
<th>Latent heat of melting (J/g)</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>80% PAM+20% EG</td>
<td>60.88</td>
<td>148.36</td>
<td>Sari and Karaipekli [40]</td>
</tr>
<tr>
<td>90% PG+10% EG</td>
<td>61.47</td>
<td>161.2</td>
<td>Wang et al [41]</td>
</tr>
<tr>
<td>85% PA+15% EG</td>
<td>28.55</td>
<td>183</td>
<td>Li et al [42]</td>
</tr>
</tbody>
</table>

Graphite powder and EG were incorporated into form stabilized PA/high density polyethylene (HDPE) to improve its thermal conductivity. Cheng et al [43] reported that the composite PCM with EG was much better than the composite PCM with graphite powder. The thermal conductivity was improved by addition of 4.6 wt% of EG more than four times compared with composite PCM without EG but the latent heat value was dropped by incorporating additives.

2.3.3.5 Other carrier materials

Fly ash (FA) consists of fine powder and has been used in concrete instead of Portland cement. FA has potential benefits such as it improves strength and segregation; reduces the cracks, bleeding and permeability of the materials. In addition, it can be integrated with PCMs to be applied in building materials to enhance the energy efficiency [44]. Wang et al [45] have studied the impregnation of 47 wt% of SA into silica fume (SF) using vacuum impregnation technique. The melting temperature and latent heat of fusion were found to be 58.8 °C and 82.53 J/g, respectively. Moreover, after 600 melting/freezing cycles, the results showed that the composite PCM had good thermal reliability. SEM images demonstrated that SA was held by SF through hydrogen bonding. 20% of CA-MC has been successfully incorporated into grinded vermiculite (VMT) by Karaipekli and Sari [46]. Thermal cycling testing indicated that the composite PCM had an excellent thermal and chemical reliability after 3000 melting/freezing cycles.
Memon et al [47] mixed n-octadecane as PCM with glass powder (GP) as a carrier material to form composite PCM. The maximum percentage of n-octadecane confined by GP was 8%. Thermal cycling and TGA results proved that the composite PCM was thermally reliable and stable. 33.3 wt% of n-octadecane was incorporated into molecular sieve 5A (alkali aluino silicate in the calcium form of type A crystal structure) by Chen et al [48] to form composite PCM. A form-stable composite PCM including LA and activated carbon have been investigated by Chen et al [49]. The maximum mass ratio of LA retained into activated carbon without seepage was determined to be 33.3 wt%. The thermal conductivity of LA-activated carbon was higher than that of the LA. The SEM results indicated that the PCM absorbed in the porous of the activated carbon was uniformly distributed by capillary and surface tension forces.

Li et al [50] investigated in impregnation of SA into the interlayer of the multilayer graphene oxide (GO). GO has been made from graphite powder by the chemical reaction with concentrated acids (85% H₃PO₄ and 98% H₂SO₄) and oxidant, KMnO₄. The thermal properties measured by DSC showed that the melting temperature was 33 °C and the latent heat was 55.7 J/g when the mass ratio of GO was 48 wt%. Moreover, it was noticed that when the mass ratio of SA increased in the SA-GO composite PCM, multiple phase change peaks appeared. Furthermore, Li et al [51] impregnated CA-PAM into attapulgite clay under vacuum. The optimum mass fraction of EM retained into attapulgite was 35 wt% of composite PCM. Mehrali et al [52] prepared a form-stable PCM of PA and GO sheets by the vacuum impregnation method. The thermal conductivity of PA-GO composite PCM was increased three times more than that of PA. In another work by Mehrali et al [53], the vacuum impregnation method was also used to fabricate PAM into graphene nanoplatelets (GNPS). The maximum mass fraction of PAM incorporation into GNPS was found to be 91.94% without leakage. Furthermore, the thermal conductivity of the PAM-GNPS composite PCM was improved 10 times more than that of PAM.

Yang et al prepared polyethylene glycol (PEG)/silica framework (SiO₂) composite PCM by the sol-gel method [54]. The sol-gel method may be described as the polycondensation reactions of a molecular precursor in a liquid phase to form a colloidal solution (sol) which is subsequently converted to an oxide network (gel). They studied the thermodynamic properties of the composites and the confinement effect of SiO₂ on the shape-stabilization crystallinity. It was noted that the confinement effect was greatly based on the molecular
weight of PEG. The performance of PEG/SiO$_2$ composite PCM fabricated by the sol-gel method has also been studied by Tang et al [55] and Zhang et al [56].

Karaipekli and Sari [57] incorporated fatty acid esters (erythritol tetrapalmitate and erythritol tetrastearate) as PCMs into gypsum and cement through a vacuum impregnation technique. The maximum percentage of esters confined by gypsum and cement were measured to be 22 wt% and 18 wt%, respectively. Moreover, thermal cycle testing indicated that the composite PCM was reliable after 1000 melting/freezing cycles. The incorporation of lauryl alcohol (LAC) into kaolin (KO) using a vacuum impregnation technique was studied by Memon et al [58]. The maximum percentage of LAC confined in KO was 24 wt%. SEM images of the composite PCM showed that the porous structure of KO was covered by LAC because of the effect of capillary and surface tension forces. Thermal cycling test and TGA results indicated that the composite PCM was thermally reliable and stable. The thermal performance test was also investigated on a small scale, the indoor thermal temperature using form-stable composite PCM panels was reduced by 4 °C compared with cement panels without composite PCM.

Ground granulated blast furnace (GGBS) as a carrier material was used to incorporate dodecyl alcohol (DA) as PCM through vacuum impregnation technique by Memon et al [59]. The maximum mass fraction of DA confined in GGBS without leakage was measured to be 11 wt%. Inaba and Tu [60] mixed 74 wt% of PA with HDPE as a carrier material to form the form-stable PCM. Furthermore, to reduce the expulsion of the PA from the composite PCM during the repeated melting/freezing cycles, a small amount of a viscosity resin of ethylen-α olein was added to the mixture. SEM showed that PA was dispersed uniformly in HDPE and also no leakage of the PA was noticed from the composite PCM. In order to have a high strength of the form-stable PCM with a small amount of HDPE, six kinds of HDPE as a carrier materials and refined and semi-refined PA as thermal energy storage were selected by Hong and Xin [61]. The obtained results demonstrated that composite PCM with high strength performed well when the percentage of HDPE was 25-30 wt%. It was noted that the product was easy to prepare and had appropriate latent heat. Xiao et al [62] mixed 80 wt% of PA with styrene-butadiene-styrene copolymer (SBS) as a carrier material to form composite PCM. The thermal conductivity of composite PCM was enhanced by incorporation of 3 % EG into composite PA-SBS.
2.3.4 Encapsulation of PCMs

Encapsulation of PCMs has attracted significant attention in order to prevent the leakage of the PCMs from the construction materials during their cycled phase change transitions, to control volume changes during the phase transition and to provide opportunities to fabricate advanced PCMs with higher heat transfer [63]. These particles contain core materials as PCMs surrounded by shell material or coating. The shell material must be compatible with construction materials. The encapsulation techniques can be classified as:

2.3.4.1 Macroencapsulation

PCMs can be encapsulated in any type of container such as spheres, panels and tubes. Chromium–nickel and aluminum are commonly used shell materials [64]. The size of these containers is usually larger than 1cm. These large structures (see Figure 2.3) are incorporated into construction materials. The drawbacks of this method are: the macrocapsules have to be protected against destruction or perforation, and these are more difficult to integrate into the construction materials, which may make these systems more expensive. Moreover, its poor thermal conductivity and tendency to solidify/melt at the edges, leads to a slower energy uptake and release which may prevent the system from discharging the stored heat completely overnight.

![Figure 2.3: Examples of products containing macroencapsulated phase change materials](image)

Figure 2.3: Examples of products containing macroencapsulated phase change materials

Lift to right: soaked foam covered with foil, filled polymer bags with transparent or aluminium compound foil and aluminium panel made by Rubitherm [65].

2.3.4.2 Microencapsulation

Microencapsulation is the process of enclosing solids or droplets of liquids or gases in a polymeric or inorganic shell to maintain their shape and prevent leakage during the phase change process. The characteristics of this method are thermal reliability, shell mechanical
strength and penetration abilities. The diameter for these particles may vary from 1 to 1000 μm. The shell materials generally used for the protection of PCM from destruction are: urea-formaldehyde (UF) resin [66], melamine-formaldehyde (MF) resin, and polyurethanes (PU) [67]. Coacervation (the interaction of two polymers whose macromolecules bear opposite charges), suspension (suspension of the water immiscible reaction mixture as droplets in the aqueous continuous phase), emulsion (the monomer is emulsified in the polymerization medium by the aid of a surfactant and the initiator as an aqueous solution is added) [68] are considered different techniques to prepare microcapsules with a polymer sheath and a PCM core. Microencapsulation has been shown to be the most promising method of encapsulation for integration of PCMs in construction materials because it reduces the risk of PCMs leaking from the material in their liquid state. On the other hand, microencapsulation leads to a lower latent heat storage capacity per unit volume and more weight than the pure PCM due to the presence of additional encapsulating material. These may also affect the mechanical strength of the building materials.

Kuznik and Virgone [69] investigated the thermal performance of 60 wt% of microencapsulated PA within a copolymer as composite material incorporated into full scale test room of wallboard. Three different external climates were tested namely a summer day, a mid season day and a winter day in order to compare the results obtained between regular wallboard and composite wallboard. The results showed that the air temperature in the room with PCM was reduced compared with regular wallboards. In another study, 60 % microencapsulated PA wax within a copolymer, Dupont Energain as a commercial PCM product has been investigated by Sunliang et al [70]. The results showed that this acts as an efficient energy storage material.

### 2.3.4.3 Nanoencapsulation

Nanoencapsulation is a process of enclosing nano-sized particles within solid or liquid state. The size of the particles is below 1μm. Recently, nanocapsules have received considerable attention for thermal energy storage systems because of their high surface area to volume ratio compared to microcapsules. Higher heat transfer because of encapsulation is expected to overcome the low thermal conductivity problem of PCM. Furthermore, nano particles can be easily incorporated into construction materials, also they offer good protection for PCMs against external environmental and the shell material should not be damaged during the incorporation of PCM. PCMs such as paraffins, wax (n-hexadecane, n-octadecane, n-docosane, n-nonadecane) and fatty acids can be used as core
material. Also, the shell material can be SiO$_2$, urea-formaldehyde [71], styrene (St), methyl-methacrylate (MMA) and polymethyl methacrylate (PMMA) [72].

Nanoencapsulated, microencapsulated and macroencapsulated PCMs within building materials suffer from high cost and the protection of PCM against destruction during mixing PCM capsules with building materials. Despite the ability of shell materials to prevent PCM leakage and interaction between the PCMs and the core material, the sophisticated processes required for encapsulation of PCMs is considered one of the drawbacks for their commercial exploitation.

2.4 Major Applications of PCMs in Buildings

2.4.1 PCM enhanced wallboards

Gypsum wallboard and PL are considered one of the most common building materials. The large thermal mass of their walls can be used to store heat during day time and release it during night particularly in moderate climates. Furthermore, the integration of PCM into gypsum wallboard and PL can enhance their energy storage capacity. Gypsum wallboard and PL are chosen for PCM incorporation because of the following reasons.

1. They are widely used construction materials
2. PCM is held by them under capillary and surface tension forces
3. They have a larger heat exchange area and smaller heat exchange depth
4. Heat can be changed at faces, core faces and combinations thereof

Furthermore, the wallboards [73-75] are cheap and widely used in various applications making them very suitable for PCM impregnation. PCMs incorporated into gypsum wallboard and ceiling board have enabled enhancement the thermal energy storage capacity of buildings. The performance of gypsum wallboards incorporated with organic PCMs has been studied by Hawes et al [76]. Immersion technique was used to impregnate 25-30 wt% of PCM in gypsum wallboards. Compared with ordinary wallboard, the phase change wallboard (PCW) had 4 °C increase in temperature and hence, thermal energy performance, flexural strength was in the required range, good compatibility with wall papers and paints and good fire resistance were also found. Moreover, the increased weight by PCM absorbed into gypsum wallboard was 22 wt% which was still in the range of accepted weight by the industry.
Scalat et al [77] also impregnated 25.2% of PCM (50% butyl stearate (BS) and 48% butyl palmitate (Emerest 2326)) into gypsum wallboard using an immersion technique. The full scale testing room (2.29 x 2.27 x 2.45 m) was fabricated with gypsum wallboards. The results obtained from experiments demonstrated that the PCW was a good candidate for thermal energy storage applications. The thermal energy performance of gypsum wallboard impregnated with 26 wt% of CA-LA was experimentally investigated by Shilei et al [21] in winter in China. The thermal performance of the rooms with and without PCM were tested for three continuous days. A 2040 W electric heat membrane was installed in the ceiling to heat the rooms up. According to the test results, the maximum temperature fluctuation in the PCW was 1.15 °C less than that of ordinary wall room. It was concluded that, the PCM can reduce the indoor thermal temperature fluctuations.

The thermal properties of the PCW subjected to the variation of room temperature during daytime have been evaluated by Neeper [78]. The parameters which played substantial role in storing energy during a daily cycle were a) the melting temperature of the PCM b) the temperature range over which melt occurred c) the latent heat of fusion per unit area of wallboard. Moreover, the PCM incorporated in interior partitions and exterior walls of the buildings were also investigated.

The experimental and numerical simulation study on the full scale test room of PCW (2.82 x 2.22 x 2.24 m) has been investigated by Athienitis [79]. 25% of BS was incorporated into gypsum wallboard. The results obtained from PCW demonstrated that the maximum temperature can be decreased by 4 °C during daytime and the heating load can be reduced at night. Oliver [80] studied the thermal performance of gypsum wallboards which contained 45 wt% of microencapsulated PA. To study the influence of the boundary conditions on the energy exchange, several parameters such as air temperature, velocity, thickness, and location of board were taken into account. Moreover, some of the construction materials (gypsum wallboard, sandwich panel made with aluminum sheets with insulator core, brick wall and thermal brick wall) were tested. According to the test results, the stored thermal energy in PCW with thickness of 1.5 cm was 5 times higher than that in an ordinary wallboard. To improve the thermal inertia of light building envelope, Ahmad et al [81] incorporated a PCM of polyethylene glycol 600 (PEG 600) within vacuum insulation panels (VIPs). Two test cells were fabricated and each one consisted of five opaque faces insulated with VIPs and one glazed face. According to the test results,
the thermal efficiency of the PCM has been clearly noticed in summer with a reduction in cell temperature. In winter, the negative indoor efficiency was prevented by PCM.

Microencapsulated PCM (Rubitherm RT27) incorporated into gypsum blocks (10 x 6 x 3 cm) with concentrations 4.7 wt% and 7.5 wt% was evaluated by Borreguero et al [82]. The thermal performance of gypsum blocks with PCM compared with gypsum blocks without PCM showed that the gypsum blocks containing a higher amount of PCM had low and high external temperatures for heating and cooling processes, respectively. Furthermore, it was noticed that the time needed to reach the steady state was increased by incorporation of PCM microcapsules into the wall. Sari et al [83] incorporated CA-SA into gypsum wallboard to form the PCW. The thermal performance test conducted on a small test room showed a decrease in the indoor room temperature by 1.3 °C. Microencapsulated PCM incorporated into lightweight buildings has been studied by Schossig et al [84]. The thermal performance of gypsum wallboard with 40 wt% of PCM at thickness 6 mm and gypsum wallboard with 20 wt% of PCM at thickness 15 mm were evaluated, tested and compared with a reference room. The results showed that microencapsulated PCM was effective to increase the comfort of lightweight buildings and reducing the cooling demands. Schossig et al concluded that the microencapsulated PCM has the merits of good heat transfer, easy application and no need to protect it against destruction.

2.4.2 PCMs in Concrete

PCMs can be encapsulated and impregnated in porous concrete [85-86,64] which can substantially enhance the thermal storage capacity of a building [87-89]. The incorporation of different percentages of microencapsulated PCM (1, 3, 5%) on the material properties of concrete was studied by Hunger et al [86]. The results showed that the thermal performance of concrete was improved to save energy by 12 % (with 5% PCM) as a result of increasing the heat capacity. Furthermore, the highest reduction in compressive strength was 69 % at 5 % PCM used. This reduction was due to:

1. Damage of microcapsules during mixing resulting in the leakage of PA and subsequent interference with the surrounding matrix.

2. Significant disparity between the intrinsic strength of the micro-capsules and the concrete constituents.
Olaya et al [90] stated that the stored thermal energy could be improved by 300% when using PCMs and also the temperature fluctuations in buildings can be significantly decreased. Kissock and Limas [91] mixed 10 % of PA into concrete and simulated the diurnal load reduction achievable using the PCM concrete. The results indicated that the peak diurnal cooling and heating loads transmitted through the building envelope components have been reduced by 19 % and the annual load was reduced by 13 % more than that of traditional concrete mass. The PCM concrete containing 5% microencapsulated PA wax prepared by Cabeza et al [63] was shown to improve the thermal inertia of the prepared boxes. In comparison with the standard concrete walls, the surface temperature of the PCM concrete took 2 h longer and the surface temperature of walls remained up to 3 °C lower. The increasing PCM levels into cementitious materials can adversely affect their mechanical properties [92] and delayed the time taken to reach the peak temperature during the heating cycle and reduced it during cooling [93-94]. The PCMs also changed the curing conditions of the concrete. Zhang et al [95] incorporated a PCM of BS in porous aggregates of expanded shale aggregates, expanded clay and normal clay using a vacuum impregnation technique. The maximum absorption of PCM by porous aggregates was found to be 68 wt%. They found that the porous aggregates and PCMs are chemically stable and they have huge thermal energy storage densities [96]. The thermal performance of n-octadecane/EG composite PCM mixed with cement mortar has been evaluated by Zhang et al [97]. The percentage of the composite PCM was varied from 0.5 to 2.5 wt%. This test indicated that the composite strength decreased with the increase of n-octadecane / EG composite in cement mortar. However, the indoor centre temperature measured in the small test room (100 x 100 x 100 mm) made of n-octadecane/EG composite PCM was reduced. This decrease was much higher with the increase in the percentage of n-octadecane / EG composite PCM in the cement mortar.

The thermal behaviour of prepared cubes with dimension of 2 x 2 x 3 m (Figure 2.4) during 2005 and 2006 in Spain [63] were evaluated by Castellón et al [98]. All cube sides were made of concrete containing 5wt% microencapsulated PCM (Micronal), which had a melting temperature of 26 °C and latent heat of fusion 100 J/g. The thermal energy performance showed that the PCM used reduced the temperature difference up to 4 °C during summer compared to reference cube. The following cases were set up as:

Case 1: (free cooling), the windows were opened at night and closed during the day time.

Case 2: the located windows in the south wall were opened for the whole day.
Case 3: the windows were closed for the whole day.

According to the results, the best option was the free cooling in order to get more stored energy.

Figure 2.4: Image of Experimental House, Spain [63]

2.5 Fire performance

Organic PCMs incorporated in building materials such as concrete, gypsum wallboards and PL if not flame retarded, can burn readily and produce considerable amount of toxic gases and dense smoke during burning [99-102]. Fire and dense smoke makes it difficult for occupants to escape through exit routes easily and for fire fighters to enter the building. Usually PCMs are directly incorporated into gypsum wallboard [103]. Some researchers have tried encapsulating PCMs inside a composite building block [104-105], which PCMs are contained within the block hence, flammability is less. Another method is to encapsulate PCM in polymers as shape stabilized to be used in building structure. However, both the PCM and polymers significantly increase the fire hazard and need to be cured by fire retardant [106].

The most important thing to take into account while using PCMs and flame retardants is the additional cost. Hence, Farid et al [107-108] studied the additional cost from using PCMs and they found the energy stored compensated the extra cost from using PCM, however, cheaper carrier materials and flame retardants should be used [106]. Flame retardant additives are usually used to provide a reasonable level of fire safety and increasing evacuation time to reduce the probability of injury, death, explosions, property damage [109] and prevention against fire spread to neighbouring properties. These flame retardants can be classified as:

1. Flame quenchers like halogenated alkanes [110].
2. Inorganic flame retardants, such as aluminum hydroxide and magnesium hydroxide [111]. These materials decompose by endothermic reactions and hence, act as absorber for heat from the surrounding polymer, thus reducing its temperature below the decomposition temperature. They also release water, which helps in cooling down the polymer.

3. Intumescent fire retardants (IFR) [107,112]. These materials include EG, ammonium polyphosphate (APP), pentaerythritol (PER) and melamine (MA). This type creates a voluminous char layer to prevent the underlying material from further exposure to the ignition source.

2.5.1 Flame retardancy of polymer encapsulated PCM

Zhang et al [113] prepared the flame retardant form-stable PCMs (FSPCM) of PA/HDPE/IFR (APP+PER+MA)/iron(powder) keeping a PA/HDPE/IFR ratio 3:1:1. Iron content ranged between 0-10 phr and HDPE was used to encapsulate PA. The SEM images illustrated that PA dispersed into HDPE and iron was dispersed in the FSPCM. It was observed that the fire retardancy was improved by adding iron powder to the PA/HDPE/IFR formulation. The cone calorimeter results indicated that the increase of the amount of iron significantly decreased the peak heat release rate (PHRR). The study indicated that iron could improve the thermal stability of PA/HDPE/IFR particularly when increasing the mass of iron and helped the composition prepared to form a more efficient char layer to protect the materials from further decomposition. The latent heats of the FSPCMs measured by DSC were in the range of (79.9-68.7 J/g) and these were still close to those of pure PA and HDPE after taking the theoretical latent heat into account. This was because there was no chemical reaction between the PA and HDPE in the FSPCMs. Moreover, with the increase in the amount of iron, the latent heat of fusion decreased.

Flame retardant form-stable PCMs made of PA, HDPE, EG and IFR (APP, PER, and MA) have been investigated by Zhang et al [114-115]. HDPE and IFR were dried firstly. Secondly, the blends were premixed in a high-speed blender, and then extruded by a twin-screw extruder. After being dried, the flame retardant shape-stabilized PCM was obtained. The SEM results showed that the PA and EG were uniformly dispersed in the HDPE structure. The latent heat values measured by DSC indicated that the melting temperature was still the same as pure PA (51 °C) and the latent heat values of prepared samples were lower than the theoretical values. The cone calorimeter test of the composites at a heat flux of 35 kW/m² showed that the PHRR was significantly decreased with the addition of flame
retardant. The reason was the forming of intumescent char layers in the case of IFR. When EG was used, the surface of material was covered by an intumescent char layer. Thus, the strength and stability of this char during heating could be increased.

Cai et al [106] prepared the form-stable PCM of PA and HDPE with flame retardants using twin-screw extruder. The flame retardants used were PER, melamine phosphate (MPP), melamine cyanurate (MCA), 1,2-(pentabromophenyl) (BPBE), antimony trioxide (AO) and decabromo diphenyl ethane (TDE). The morphology study by SEM showed that the flame retardants had no notable effect on the PCM morphology. The latent heat measured by DSC did not show change after adding flame retardants. That means the thermal properties of PA-HDPE (around 52 KJ/kg) were still almost the same after adding flame retardants. The addition of flame retardants particularly MPP+PER reduced PHRR compared to that of PA-HDPE by about 56 %. TGA results revealed that the decomposition temperature increased and the char residue has been increased.

Form-stable phase change nanocomposites materials (PCNM) based on organophilic montmorillonite (OMT), HDPE/ethylene-vinyl acetate (EVA) alloy, PA and IFR using the twin-screw extruder technique were also studied by Cai et al [116]. The SEM images showed that the HDPE-EVA alloy/OMT nanocomposites worked as the carrier material. Moreover, PA was uniformly dispersed in the formed structure. The latent heat results indicated that the IFR additives did not have much effect on the latent heat of the form-stable PCNM. In addition, the latent heat values of the form-stable PCNM were improved using a lower amount of HDPE and EVA. TGA results revealed that the flame retardant form-stable PCNM produced a large amount of char residue at 800 °C which contributed to improve the thermal degradation performance.

Other flame retardants MPP and PER were mixed with PA, HDPE and OMT using a twin screw extruder technique by Cai et al [117]. SEM results showed that the PA dispersed well in HDPE. With the addition of flame retardants, the PHRR was much reduced compared to the HDPE-PA hybrid. This reduction in PHRR was about 66 % using OMT+MPP+PER. On adding OMT, the fire performance was improved, the reason may be that the OMT reacted with MPP to form an aluminophosphate and ceramic which played an important role to increase the efficiency of the intumescent char shield. The TGA results showed that the char residue of the form-stable PCM increased with IFR. The
latent heat measured by DSC indicated that the form-stable PCM did not have much change with the addition of IFR and OMT.

In another study [118], they mixed 75 wt% of PA with HDPE/EVA. Moreover, OMT was mixed with different proportions of HDPE/EVA using a twin-screw extruder. The TGA analysis showed that the incorporation of the OMT into PA/HDPE-EVA composite contributed to an increase in the thermal stability. DSC results demonstrated that the PA had two phase change peaks, the first one at 42 °C, and the second one at 58 °C. Moreover, the PA peak still existed in the form-stable composite PCM. In terms of latent heat, the latent heat of PA in the form-stable composite PCM was decreased with the increase of the OMT percentage. The cone calorimeter results indicated that the PHRR was remarkably decreased with the increase of OMT amount.

The flame retardant system containing microencapsulated red phosphorous (MRR) and magnesium hydroxide (MH) was selected by Cai et al [119] to mix with PA, HDPE, EVA and a desired amount of OMT to form the flame retardant form-stable PCM. Again a twin screw extruder was used to prepare this sample aforementioned. The morphology of sample indicated that the HDPE-EVA/OMT nanocomposites was noticed as a carrier material and the PA dispersed in the formed composition. The TGA results showed that the flame retardant used produced a great amount of char residue. The transition temperature of the prepared samples measured by DSC was almost the same as for PA. However, the latent heat of fusion in the mixture of PA+HDPE+EVA reduced more than others because the high amount of HDPE added made the net structure more compact. Thus, the molecular heat movement of the PA was confined in the form-stable composite PCM. The latent heat of flame retardant form-stable PCM was higher due to the lower HDPE content. The cone calorimeter results measured at 35 kW/m² exhibited that the PHRR was decreased from 533 kW/m² to 176 kW/m² using 20% MH, 5% MRR and 3% OMT. OMT is able to form a more compact and homogenous charred residue, contributing to enhanced flame retardant properties.

The form-stable composite PCM containing 60 wt% of PA with HDPE prepared using the twin-screw extruder technique was investigated by Cai et al [120]. The flame retardants EG and APP were added. The SEM images showed that the PA was dispersed in the structure of HDPE and also the particles of the EG and APP were distributed well in the form-stable composite PCM. The DSC analysis showed that the PA had two phase change
peaks, the main and minor peaks were around 55 °C and 37 °C, respectively. In terms of latent heat, the results illustrated that the latent heat of PA in the form-stable composite with flame retardant had been slightly decreased compared to that of PA. The TGA results demonstrated that the thermal stability was improved with addition of the flame retardants. Cone calorimetry test showed that the heat release rate (HRR) of form-stable composite PCM with flame retardants was greatly decreased compared to that of form-stable composite PCM particularly when using 4 %wt of EG+21wt% of APP.

Flame retardants were used to decrease the flammability of form-stable PA(RT21)/HDPE composite PCM by Sittisart and Farid [121]. Different flame retardants such as APP, MMT, PER and EG were tested. The form-stable RT21/HDPE contained 60 % of PA was mixed with different proportions of flame retardants. The TGA results showed that the thermal stability was improved by adding flame retardant to the PCM composite. The thermal properties measured by DSC indicated that the latent heat of form-stable PA/HDEP was slightly decreased from 136.3 J/g to 125.3 J/g for form-stable PA/HDPE with 20 wt% (APP+PER) and 5 wt% MMT, and 127.8 J/g for form-stable PA/HDPE with (10 wt% APP+10 wt% EG). The flammability test using the cone calorimeter demonstrated that the impregnation of flame retardants into PCM reduced its flammability.

2.5.2 Flammability and flame retardancy of construction materials containing PCMs

Haurie et al [111] showed that the gypsum samples containing > 20 % of PA produced flame when subjected to a heat source in both the cone calorimeter and dripping tests. This indicated that the PA increased the fire risk of the gypsum. To reduce the flammability of samples the flame retardants aluminum hydroxide and hydromagnesite were used. The fire behavior of a cement mortar prepared with PCM composite material of GR27 granulated material was also studied by Haurie et al [122]. The dripping test showed the addition of PCM caused flaming in the mortar when exposed to a heat source. Smoke release testing indicated that the addition of paraffin induced the release of smoke during subjecting to high temperatures. In another study [123], they mixed different percentages of microencapsulated PA into single layer mortars of cement. With microcapsulated PA, the mechanical properties, thermal conductivity and diffusivity were decreased. From the dripping test, the presence of PA worsened the fire behavior of the mortar.
2.6 Conclusion

Considerable research over the years has focused on the importance of stored latent heat by incorporating PCMs into building materials in order to save energy, enhance heat transfer and increase the thermal mass in buildings. To achieve these aims, some studies have been directed at developing encapsulation methods: at macro, micro and nano levels. But the drawbacks of this method are its cost and complicated processing. Therefore, many studies have employed a cheaper, simpler and less complicated method i.e. the preparation of form-stable composite PCMs. As indicated in the literature review above, researchers studied the thermal properties of PCMs added to the carrier materials, usually measured by DSC, and then analysed their thermal performance. But they did not study all types of carrier materials that could be used to incorporate various PCMs in building materials. Moreover, they did not take into account the flammability of PCMs. Organic PCMs incorporated in building materials are highly flammable, there is thus a fire risk related to PCM-containing PL. Therefore, to meet building fire requirements, the addition of flame retardant to PCM PL is necessary. As a consequence it is important to understand the fire and smoke behavior of phase change materials in building applications with and without flame retardants.

Research on flame retardants incorporated into PCM wallboards has not been much reported in the literature and needs further study to understand the effect of use of flame retardant materials on the thermal properties and the thermal energy storage performance of PCMs in building materials applications. Such a study is the focus of the work reported in this thesis. If flame retardants are added to PCMs, the percentage of PCM is consequently reduced. Therefore, the stored thermal energy will also be reduced. An alternative strategy is to develop a fire resistant coating for PCM particles to delay the time to ignition and reduce the spread of flame. However, the use of a coating has some drawbacks such as reducing the heat transfer as a result of insulating the PCM. One possible solution is to use a flame retardant additive like expanded graphite to improve the fire performance and also the thermal conductivity of the PCM.

2.7 References


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[10] Cui, R."Effect of selected phase change materials concentration and manufacturing process on the properties of plaster mixture systems". MSc Thesis. 2011, Clemson University. USA.


[58] Memon, S.A.; Yiu Lo, T.; Shi, X.; Barbhuiya, S.; Cui, H. "Preparation, characterization and thermal properties of lauryl alcohol/Kaolin as novel form-


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[107] Farid, M.M. "Energy storage for efficient use in domestic and industrial applications". International conference on renewable energy: generation and applications. (ICREGA 2010), March 8–10, UAE.


as a shape stabilized phase change thermal energy storage material”. Thermochim Acta. 2006, 451:44–51.


CHAPTER THREE

EXPERIMENTAL

This chapter discusses the materials and experimental methodologies used for enhancing the thermal energy storage efficiency of building materials by using phase change materials. The building material chosen for this study was plasterboard (PL); phase change materials selected were paraffin (PA), eutectic mixture (EM) of capric acid (CA) and lauric acid (LA), and butyl stearate (BS). For phase change materials, carrier materials have also been used. These include nanoclay (NC), diatomaceous earth (DE), expanded perlite (EP), fly ash (FA) and brick dust (BD). Flame retardants used were ammonium polyphosphate (APP), tris(tribromoneopentyl)phosphate (FR370), expanded graphite (EG) and resorcinol bis(diphenyl phosphate) (RDP). Immersion, direct incorporation and form-stable PCM composite with/without flame retardant formation techniques have been used to integrate phase change materials into plasterboard.

3.1 Materials

3.1.1 Plasterboard

Gypsum powder was sourced from British Gypsum, British Gypsum Thistle Multi Finish and used as received. The general composition provided by the manufacturer is that it mainly contains calcium sulphate hemihydrates [1]. Other constituents such as clay, limestone (calcium carbonate) and minor amounts of quartz and hydrated lime are also present.

3.1.2 Chemicals to improve the porosity of PL

Conplast, air retaining admixture (AE383) was sourced from Fosroc UK [2]. Conplast AE383 is a colourless solution which instantly disperses in water. It is a chloride-free, air-entraining admixture based on synthetic surfactant materials.

3.1.3 Phase change materials

- Paraffin: N-octadecane (Paraffin, PA), 99% with melting temperature range of
26-29 °C and latent heat of 250 J/g was sourced from Sigma-Aldrich [3].

- Eutectic Mixture: Dodecanoic acid (Lauric acid, LA), 98%, with melting temperature of 43-45 °C [4] and latent heat of 160 J/g and decanoic acid (Capric acid, CA), 99% with melting temperature of 29-33°C [5] and latent heat of 138 J/g were sourced from Alfa Aesar. The eutectic mixture (EM) was prepared by mixing 70 wt% of CA and 30 wt% of LA.
- Butyl stearate (BS) with melting temperature of 17-22 °C and latent heat of 113 J/g was sourced from Sigma-Aldrich [6].

3.1.4 Carrier materials

- Commercial organic modifier of nanoclay (NC), 20A, with particle size of 0.2 mm was supplied by BYK additives and instruments UK [7]. The organic modifier NC consists of dimethyl, dihydrogenatedtallow and quaternary ammonium salt.
- Diatomaceous earth (DE) with particle size of 0.2 mm was supplied by Diaguard Natural Protector UK [8]. The components of DE are 80-90% silica, 2-4 alumina and 0.5-2% iron oxide.
- Expanded Perlite (EP) with particle size of 0.8 mm was supplied by Lorbex UK [9]. EP consists of 2-5% bond water, silica, calcium oxide and magnesium oxide.
- Fly ash (FA) with particle size of < 20 μm was supplied by Fibretech UK [10]. FA consists of silica, alumina and iron oxide.
- Brick dust (BD) with particle size of 0.2 mm was supplied by Cornish Lime UK [11]. BD consists of clay-bearing soil, sand and lime.
- Expandable graphite (Aflammit PCI 599) was supplied by Thor, Germany [12]. EG consists of powder-like black flakes.

3.1.5 Flame retardants

- Ammonium polyphosphate (APP), C60 (Budenheim) having an average diameter of 7μm was supplied by Budenheim.
- Tris(tribromoneopentyl) phosphate (FR370) was sourced from ICL-IP [13].
- Resorcinol bis(diphenyl phosphate) (RDP) Fyrolflex RDP flame retardant was supplied by Chemtura [14].
3.2 Sample preparation

3.2.1 Plasterboard

Plasterboard (PL) was prepared by mixing gypsum powder with water in 2.5:1 ratio with a handheld electric mixer until a uniform blend was achieved as shown in Figure 3.1(a). Then, the prepared slurry was poured in a wooden mould of dimensions 100 mm x 100 mm x 10 mm and the mould was placed at room temperature for 14 days to dry (see Figure 3.1(b)).

![Figure 3.1: Photographs of (a) blend of gypsum powder and water, and (b) plasterboard formed after drying process.](a) (b)

For obtaining optimized processing conditions, liquid conplast was mixed with gypsum powder and water in the ratios 0.125:2.5:0.875 and 0.075:2.5:0.925, using two different mixing times, 5 and 10 min. Then, the above mentioned procedure was followed to prepare PL samples of 12 mm thicknesses using conplast.

3.2.2 Incorporation of PCMs by the immersion technique

The immersion method involves immersing the PL into a bath filled with hot melted PCM for a certain time, while the temperature of PCM is maintained just above its melting point. PCM is absorbed into porous material by capillary action to form phase change wallboard (PL_PCM) as shown in Figure 3.2. The PL is then removed from liquid PCM and allowed to cool. These samples are called PL_PCM throughout this thesis. Three following methods were used to optimise the percentage of PCM absorbed by PL.
3.2.2.1 Immersion of as prepared samples

To characterise the depth of PCM impregnated into PL, the immersion method was used firstly on the as prepared samples. LA as a PCM was selected to determine the required immersion time to get optimum impregnation. The temperature of the immersed sample in a bath filled with constant volume of LA was maintained at 50 °C and the immersion time was varied between 0.5- 6 h. The conditions used are given in Table 3.1, all samples were weighed before and after immersion to establish the percentage of LA absorbed into PL. The penetration was examined using an optical microscope (handheld digital microscope (Celestron)) in order to evaluate the distribution of LA absorbed into PL. The cross section area was obtained by cutting the sample at its middle with the Plasplugs electrical cutter. Images were captured at 20 x - 200 x magnifications and are shown in Figure 3.3. From these images penetration depth was calculated by image analysis software.

Table 3.1: LA absorbed into the PL

<table>
<thead>
<tr>
<th>Sample</th>
<th>Immersion time (h)</th>
<th>PCM absorbed (%)</th>
<th>Thickness (mm)</th>
<th>Penetration depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>8.7</td>
<td>12.3</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>10.9</td>
<td>12.7</td>
<td>6.2</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>8.6</td>
<td>12.9</td>
<td>4.2</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>7.5</td>
<td>12.2</td>
<td>3.5</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>8.5</td>
<td>13</td>
<td>3.5</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>9.8</td>
<td>12.7</td>
<td>5.9</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>9.6</td>
<td>12.9</td>
<td>5.3</td>
</tr>
</tbody>
</table>
Figure 3.3: Optical microscopic images of cross-sections of PL samples after immersion in PCMs

It can be observed from Table 3.1 and Figure 3.3 that the LA did not penetrate thoroughly into the samples. Moreover, some cracks and small holes were formed in the PL during its preparation, which resulted in more absorption of LA. The optimum time of immersion selected was 1 h, when the PCM absorbed was 10.9 %, and the depth of LA penetrated was 6.2 mm, which were the highest values compared to others.

3.2.2.2 Effect of adding Conplast

Since the LA was not uniformly absorbed within PL by the above method, the chemical material Conplast was added into the mixture of PL and water during PL formation to enhance its porosity by entrapping air and improve the cohesion between particles. Samples were prepared by adding 3% and 5% of Conplast in PL and using mixing times of 5 and 10 min. The percentage of PCM absorbed was compared with PL without additives. All samples were weighed before and after immersion to determine the percentage of LA absorbed into the modified PL, the results are given in Table 3.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mixing Time (min)</th>
<th>Conplast percentage (%)</th>
<th>PCM absorbed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0</td>
<td>5.3</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>3</td>
<td>8.6</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>5</td>
<td>12.1</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>0</td>
<td>4.8</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>3</td>
<td>8.2</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>5</td>
<td>9.6</td>
</tr>
</tbody>
</table>
It can be seen from Table 3.2 and Figure 3.4 that by adding Conplast the percentage of PCM increased which further increased with the increase of Conplast percentage. On the other hand, the increase of mixing time from 5 min to 10 min adversely affected the percentage absorption. Although with Conplast the porosity increased, hence absorption increased, the LA did not penetrate uniformly in the samples. To overcome this problem, a vacuum impregnation method was used to increase the percentage of PCM absorbed and achieve total penetration through PL by removing their air-bubbles formed.

3.2.2.3 Vacuum impregnation method

PL (prepared without Conplast) was firstly placed in a vacuum oven for 10 min at 80 °C. Then, PL was immersed in a certain amount of PCM, which was placed in the vacuum oven at 50 °C (above the melting temperature of PCM) at the vacuum internal pressure 65 kPa. The immersion time was varied between 15 to 60 min then the sample was taken out to dry. All samples were weighed before and after immersion to establish the percentage of PCM absorbed. The obtained results from the vacuum impregnation method as depicted in Table 3.3 show that the amount of PCM absorbed into PL was much more than that of previous methods of immersion. The possible reason could be that all the air has been removed with vacuum, creating pores, which are then filled with PCM. It can be also observed from Figure 3.5 that the PCM thoroughly penetrated into the samples. Table 3.3 demonstrates the percentage of PCMs of PA, EM and BS absorbed in PL at various immersion times ranging from 15 to 60 min. Leakage of PCM was visually observed in the samples which were immersed at 45 min and 60 min. Whereas, the optimum immersion time without leakage was determined to be 30 min due to at this time the PCM absorbed was higher compared to that of 15 min. Moreover, Figure 3.5 shows the penetration of PCM into samples, which indicates that the samples had complete penetration when the immersion time was 30 min.
### Table 3.3: PCM absorbed into PL at different immersion time using vacuum oven

<table>
<thead>
<tr>
<th>Sample</th>
<th>Immersion time (min)</th>
<th>% PA</th>
<th>% EM</th>
<th>% BS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>12.6</td>
<td>5.95</td>
<td>8.8</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>17.3</td>
<td>17.1</td>
<td>14.6</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>16.3</td>
<td>20.2</td>
<td>15.8</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>18.3</td>
<td>20</td>
<td>17.5</td>
</tr>
</tbody>
</table>

Figure 3.5: Images of PCM penetrated into PL at 30 min (a) PA, (b) EM and (c) BS

#### 3.2.3 Incorporation of PCMs by the direct incorporation technique (PL+PCM)

For the direct incorporation method, 10% of liquid PCM was taken as optimum and then added to gypsum powder and mixed directly with it before making the slurry and then water was added. The prepared slurry was poured in a wooden mould of dimensions 100 mm x 100 mm x 10 mm and the mould was placed at room temperature for 14 days to dry.

#### 3.2.4 Form-stable PCM composite preparation

The form-stable PCMs composites were prepared by adsorbing PCM into the carrier materials and then the carrier materials containing the PCM were incorporated into gypsum powder. The carrier materials used for different PCMs include nanoclay (NC), diatomaceous earth (DE), expanded Perlite (EP), fly ash (FA) and brick dust (BD). For each blended structure, the leakage test was applied by heating the blends at least 10 °C above the melting temperature of PCM in order to visually observe if there is a leakage. The blends where leakage was observed were discarded and the most suitable composites of PCM-carrier materials were selected for further study. The blend/composite preparation for each PCM is discussed below.
3.2.4.1 Paraffin

PA, NC, DE, EP, FA, BD were used as the raw materials. Different mass fractions of PA (30, 40, 50, 60, 70, 80% w/w) were mixed with all carrier materials at room temperature. PA was melted at 40 °C for 30 min in an oven and then immediately mixed with carrier materials. The optimum mass fraction of PA without leakage was found to be 60%, 60%, 60%, 40% and 20% in each of the blends of PA-NC, PA-DE, PA-EP, PA-FA and PA-BD respectively as shown in Figure 3.6. In order to obtain fine particles of composites, blends were placed into freezer for 20 min, after cooling, the blends were ground by mill.

![Digital images of form-stable composite of (a) 60%PA-40%NC (b) 60%PA-40%DE (c) 60%PA-40%EP (d) 40%PA-60%FA and (e) 20% PA-60%BD](image)

Figure 3.6: Digital images of form-stable composite of (a) 60%PA-40%NC (b) 60%PA-40%DE (c) 60%PA-40%EP (d) 40%PA-60%FA and (e) 20% PA-60%BD

3.2.4.2 Eutectic mixture

EM was melted at 40 °C for 30 min in an oven and then different mass fractions of EM (30, 40, 50, 60, 70, 80% w/w) were immediately mixed with EP and BD at room temperature. The optimum mass fractions of EM retained in the EP and BD without leakage were found to be 60% and 20% respectively as shown in Figure 3.7.
The blends of EM-NC, EM-DE and EM-FA did not produce useful composites. All samples containing different proportions of carrier materials were sticky at room temperature due to the EM in these blends coming out as shown in Figure 3.8. Hence, NC, DE and FA were unsuitable to be used as carrier materials for EM.

3.2.4.3 Butyl stearate

Different mass fractions of BS (30, 40, 50, 60, 70, 80% w/w) after melting at 40 °C for 30 min in an oven were promptly mixed with all carrier materials at room temperature. The optimum mass fraction of BS contained in the EP and BD particles without leakage was observed to be 60% and 20% respectively as shown in Figures 3.9.
It can be clearly noticed from Figure 3.10 that the blends were sticky after mixing different proportions of the BS with NC, DE and FA at room temperature due to the leakage of BS. Thus, NC, DE and FA were inappropriate for use as carrier materials for BS.

![Digital images of form-stable composite of (a) 50%BS-50%NC and (b) 50%BS-50%DE and (c) 20% BS-80%FA](image)

Figure 3.10: Digital images of form-stable composite of (a) 50%BS-50%NC and (b) 50%BS-50%DE and (c) 20% BS-80%FA

### 3.3 Flame-retarded PL-PCM composites

#### 3.3.1 Flame retardants used in direct incorporation and form-stable composite methods

Two samples with 5 and 10% of flame retardant, APP were prepared by first mixing APP with gypsum powder and then 10% of BS was added, followed by water. APP powder did not homogeneously mix with gypsum powder and BS. Hence, APP was not used in the further work. An another flame retardant, FR 370 was tried. 10 wt% and 20 wt% FR370 powder with respect to BS were added in the gypsum powder using the same procedure as for APP, but unfortunately the FR370 powder migrated to the surface of the sample as shown in Figure 3.11. To overcome this problem, 10 and 20% of FR370 were added to PA to form-stable PA-FA and then the mixtures of PL+PA-FA FR370 were prepared. The particles FR370 did not mix within the composite, indicating the non-homogeneity of the powder flame retardant with PA. The flammability test was however, done on this sample as will be discussed in the Section 3.4.5. Hence, FR370 was not used in the further work.

![Digital image of Flame retardant FR370 powder mixed with PL and BS](image)

Figure 3.11: Digital image of Flame retardant FR370 powder mixed with PL and BS
3.3.2 Flame-retardant form-stable composite PCM

Expanded graphite (EG) was used both as a carrier material and a flame retardant. The expandable graphite (see Figure 3.12(a)) was first dried in an oven at 80 °C for 12h and then heated up at 600 °C for 10 min [16] to form expanded graphite (see Figure 3.12(b)).

![Digital images of (a) expandable graphite and (b) expanded graphite](image)

PA and BS were separately melted at temperature of 40 °C for 30 min in an oven and then different mass fractions of them were immediately mixed with EG at room temperature. The mixture was prepared by adsorbing the melted PCM into the pores of EG. The leakage test was also applied, and the suitable amount of PA and BS mixed with EG without leakage has been observed to be 80 wt% for both of them (see Figure 3.13).

![Digital images of (a) PA-EG and (b) BS-EG](image)

20 wt% of flame retardant RDP with respect to PCM was firstly added to the sample PA-FA (selected based on results in Chapter 5). RDP did not mix very well and some lumps between FA and RDP were observed. Hence, this sample was discarded.

To add RDP to PA-EG and BS-EG, firstly RDP was mixed with PA or BS. RDP was homogenously mixed with BS, but did not mix well with PA. The mixtures were stirred vigorously with a spatula, then were kept in oven for 12 h at 50 °C so that EG can absorb molten PCM. After cooling to room temperature the mixtures were stirred again. The process was repeated many times until uniform mixtures were obtained. These mixtures
were then added to EG to form PA-EG-RDP and BS-EG-RDP, respectively. The images are shown in Figure 3.14.

![Digital images of (a) PA-EG and (b) BS-EG with flame retardant RDP](image)

Figure 3.14: Digital images of (a) PA-EG and (b) BS-EG with flame retardant RDP

12.5 % of PCM-EG with or without RDP was firstly mixed with 87.5% of PL and then the water was added. The uniform mixtures were obtained using a hand held electric mixer. The prepared mixtures were poured into wooden moulds of dimension of 100 mm x 100 mm x 10 mm for 14 days at room temperature to dry.

### 3.4 Testing and characterization

#### 3.4.1 Thermal characterization

Thermal properties of 1-3 specimens of PCMs, PL, carrier materials, PCM-carrier materials, PL+PCM, PL_PCM, PL+PCM-carrier materials and PL+PCM-carrier materials with/without flame retardant have been studied using Differential Scanning Calorimetry (DSC) [16-17]. The DSC Q2000-1673 thermal analysis has been performed on 5-10 mg samples in the temperature ranges 0-60 °C, 0-50 °C or 0-40 °C with a heating rate of 3 °C /min and 2 °C /min under a constant stream of nitrogen at atmospheric pressure. To measure the melting and freezing temperature of PCM, the tangent line is drawn at the point of greatest slope of the leading edge of the peak. Whereas, the latent heat of fusion is calculated as the area under the peak curve by numerical integration. Moreover, melting and solidification peak temperatures have been defined as the temperature of the points, which are located furthest from the base line. In this research, the thermal properties such as: melting temperature, latent heat of melting temperature, freezing temperature, latent heat of freezing temperature and specific heat were measured by DSC.
3.4.2 Thermal stability characterizations

Thermal stability of PCMs, PL, carrier materials, PCM-carrier materials, PL+PCM, PL_PCM, and PL+PCM-carrier materials with/without flame retardant were performed using thermogravimetric analysis using SDT 2960 Simultaneous (DTA-TGA) (TA instrument). The sample weight was between 10 and 20 mg. One specimen from each sample was heated from room temperature to 850 °C with a constant heating rate of 10 °C/min under air atmosphere with 100 ml/min flow rate. To produce the mass loss curves of the samples, the masses of the samples were recorded as a function of the temperature. The results obtained from the mass loss curves were analysed in order to determine the onset temperature of decomposition and the percent of mass residue at various temperatures.

3.4.3 Scanning electron microscopy (SEM)

To study the morphology of samples, scanning electron microscopy (SEM) was used. The cross sectional area of samples of PL, carrier materials, PCM-carrier materials, PL+PCM and PL+PCM-carrier materials with/without flame retardant prepared were mounted on aluminum stubs using SEM conductive adhesive tape. The small piece of sample mounted on the stub was then placed inside the chamber of Polaron Range SC7620 Sputter Coater in order to obtain a uniform gold coating by exposing for 45 s of plasma exposition. The coated samples were tested with the Hitachi S3400-N scanning electron microscope using accelerating voltages of 5 kV and 6 kV.

3.4.4 Mechanical Testing

The mechanical properties of the PL, PL+PCM, PL_PCM and PL+PCM-carrier materials with/without flame retardant samples were evaluated in two different modes; flexural and compression.

3.4.4.1 Flexural test (three-points bending)

Flexural properties of samples were investigated using a three point bending test according to the standard procedure specified in BS EN 13279- 1-2008 [18] and BS EN 12390-5-2009 [19]. The Instron 3369 Universal tester was unsuitable to measure the flexural
properties of PL because the PL has a very brittle nature. Hence, an alternative setup as shown in Figure 3.15 was used. Three replicated specimens of the size of 130 mm x 36 mm x 10 mm were tested for each sample. Two steel bars were cut and mounted on the flat table by clamps. The specimens were placed on the two parallel supports with rounded tips of a radius of 4 mm which were positioned on the two steel bars. A hanger was used to set up the steel rod at the middle of specimen to carry the weights. In addition, to measure the deflection of specimen, a rounded tip indicator of a strain gauge with a precision of (0.01 mm/mm) was used. Loading was applied by adding weights gradually until failure (when the specimen could not carry any more load and broke). The load and deflection values of the tested specimens were recorded, from which the load-deflection curves were plotted. The flexural strength $\sigma_f$ and modulus of elasticity $E_l$ can be calculated using the following equations.

$$\sigma_f = \frac{My}{I}, \quad I = \frac{bh^3}{12}, \quad E_l = \frac{FL^3}{48EI}$$

$\sigma_f$: is the stress in the outer surface at the middle point, (MPa)

$M$: is the moment applied at the middle of the specimen, (N.M)

$Y$: is the distance from the centre of specimen to outer surface, (m)

$I$: is the polar moment of inertia of rectangular cross sectional area, (mm$^4$)

$b$: is the width of the test beam, (mm)

$h$: is the depth of the test beam, (mm)

$E_l$: is the modulus of elasticity, (GPa)

$F$: is the load applied at given point on the load deflection curve, (N)

$L$: is the length of support span, (mm)

$\delta$: is the deformation of specimen, (mm)
3.4.4.2 Compression Test

The compression test was performed using a methodology based on BSEN1052-1:1999. An Instron 3369 Universal tester machine as shown in Figure 3.16 was used. Three replicated specimens of the size of 50 mm x 50 mm x 10 mm were tested for each sample. Each specimen was mounted on the lower jaw of machine using steel plate 200 mm x 200 mm x 20 mm and then the load of 150 kg (upper jaw) was applied. The compression strength (stress) and strain values were calculated, from which the stress-strain curves were plotted. The compression strength \( \sigma_c \), strain \( \varepsilon \) and modulus of elasticity \( E_c \) can be calculated using the following equations:

\[
\sigma_c = \frac{F}{A}, \quad \varepsilon = \frac{L}{L_0}, \quad E_c = \frac{\sigma}{\varepsilon}
\]

\( \sigma_c \): is the stress in the outer surface at the middle point, (MPa)

\( F \): is the load applied at given point on the load deflection curve, (N)

\( A \): is the cross sectional area of specimen, (m\(^2\))

\( \varepsilon \): is the strain rate, (mm/mm)

\( L \): is the original length of the specimen, (mm)

\( L_0 \): is the length of the specimen after deformation, (mm)

\( E_c \): is the compression modulus of elasticity, (GPa)
3.4.5 Flammability testing

Cone calorimetric experiments were carried out according to the procedures explained in the ISO 5660-1 standard using a Fire Testing Technology cone calorimeter with slight modifications to the sample holder and methodology. Parameters obtained include time-to-ignition (TTI), flame out time (FOT), heat release rate (HRR, kW/m²), peak of heat release rate (PHRR, kW/m²), total heat release (THR, MJ/m²), effective heat of combustion (EHC, MJ/kg) and mass loss (%).

Three specimens of each composition (sample) with dimensions of 75 mm x 75 mm x 10 mm were tested instead of using the standard dimensions of 100 mm x 100 mm x 10 mm [20] due to the limitations in the quantity of materials available. In previous work in our laboratory, the comparison of the results from samples of reduced size with standard 100 mm x 100 mm specimens have been explained in detail [21]. The cone calorimeter was used in two orientations, horizontal and vertical. In horizontal orientation, standard sample holder was used as in ISO 5660 with the 75 mm x 75 mm specimens wrapped in the usual way and then placed in the sample holder (75 mm x 75 mm x 75 mm). The height was adjusted to 25 mm from front face of sample to the cold cone heater face.

In vertical orientation [22], the tested samples (75 mm x 75 mm x 10 mm) were mounted as shown in Figure 3.17. A special sample holder as shown in Figure 3.18 was built "in house" from 1.5 mm mild steel; 25 mm side right angle pieces were cut and folded to the required length and depth and then welded up. At the rear face of the sample holder, a central space was designed in order to measure the temperature. The sample holder was
provided with an internal backing board of 6 mm thick calcium silicate (Duratic) immediately followed by a layer of calcium silicate wool on the backing board. Three holes for the thermocouples were drilled with diameter of 1 mm through marking a board with a vertical centre line according to the position of the sample determined. The distances between holes were 10 mm above and 10 mm below the central hole of the backing board. The unexposed surface of the specimen was wrapped with aluminium foil with thickness (100 μm). A mineral insulated thermocouple type k (310 stainless steel sheath) was set up by pushing it through the holes on the backing board and calcium silicate wool to contact with the sample wrap. Moreover, the wires were used to mount the sample and thermocouples in order to get accurate measurements. In each test of three specimens, the temperature change at the unexposed side was automatically recorded using a data logger. A mild steel shutter was constructed with calcium silicate card insulation on the side facing the cone heater in order to reduce the pre-heating of the sample.

Two types of ignition source, spark and pilot ignition were used and samples tested under different conditions. In this experiment, the spark ignition was set up as usual for horizontal orientation. In vertical orientation, the spark ignition source was situated 13 mm from the surface of specimen. The surface of the specimen was kept 25 mm from the cone heater. For pilot ignition, a simple diffusion butane flame of 50 mm length was provided from a 3.2 mm outside diameter stainless steel tube burner arrangement; the pilot flame was held in position using a retort stand on an adjacent table such that the flame was 10 mm from the sample surface with the flame extending from the edge of the sample to slightly beyond the mid-point, 10 mm below the horizontal centre line because a high irradiance was applied to the sample.

The exhaust duct of the cone calorimeter was positioned so as to ensure a 24 L/s flow rate to extract the volatiles generated from the tested samples and then feeding into an oxygen analyser to measure the amount of oxygen consumed during combustion. The principle of the cone calorimetry is based on the theory that most fuels generate approximately 13.1 MJ of heat release per 1 kg of oxygen consumed [23]. Cone calorimeter software (ConeCalc, Fire Testing Technology) has been used to convert the measured amount of oxygen consumed during the combustion of the tested samples to the amount of heat energy released from the samples.
To understand the effect of orientation and the source of ignition on the cone parameters, testing was performed on a standard flammable material, for which wood was chosen. The wood samples were tested at heat flux of 50 kW/m². This test was performed in horizontal and vertical orientations with spark igniter and pilot flame till ignition. All results in terms of TTI, PHRR, THR and mass loss (%) during the test are presented in Table 3.4.

**Effect of orientation, horizontal versus vertical:** In Figure 3.19(a), the effect of orientation, while the spark igniter was on until ignition on the cone parameters can be seen. It can be noticed that in vertical orientation the PHRR and THR were slightly higher than in the horizontal orientation, the difference though is still within the error range of the cone tests. Moreover, the mass loss rate was almost the same as shown in Figure 3.19(b).

**Effect of ignition source, spark versus pilot ignition:** The effect of ignition sources on samples is shown in Figure 3.19 as well. With pilot ignition it is difficult to judge when the
ignition has occurred. It should be noted that the heat release observed due to the pilot flame was compensated in the heat release observed by the cone. As can be seen from results, with pilot ignition there was earlier ignition than with the spark ignition, PHRR was also increased, but not significantly. THR was greatly increased. Mass loss rate is also not much affected.

![Figure 3.19: a) HRR and b) mass loss versus time curves for wood on cone exposure at 50 kW/m² heat flux, vertical spark versus pilot flame until ignition](image)

**Table 3.4: Cone calorimetric results from wood at 50 kW/m² external heat flux under different orientations and ignition scenarios**

<table>
<thead>
<tr>
<th>Testing condition</th>
<th>TTI (s)</th>
<th>PHRR1 (kW/m²)</th>
<th>PHRR2 (kW/m²)</th>
<th>THR (MJ/m²)</th>
<th>Mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hor, Spark Ign_Std</td>
<td>20±0.7</td>
<td>174±3</td>
<td>159±4</td>
<td>81.3±1</td>
<td>80±0.3</td>
</tr>
<tr>
<td>Vert, Spark Ign_Std</td>
<td>21±2</td>
<td>186±3</td>
<td>161±3</td>
<td>84.4±2</td>
<td>80±2</td>
</tr>
<tr>
<td>Hor, Pilot flame_till ign</td>
<td>8±0.4</td>
<td>174±2</td>
<td>174±1.4</td>
<td>110±5</td>
<td>79±0.4</td>
</tr>
<tr>
<td>Vert, Pilot flame_till ign</td>
<td>8</td>
<td>181±3</td>
<td>173±4</td>
<td>112±4</td>
<td>78.8</td>
</tr>
</tbody>
</table>

From these results it can be concluded that in these samples, which are flammable, there is not much effect of the orientation on their flammability properties. In order to be more sure about the effects of orientation and ignition source on the flammability properties of PL samples before going further to the real samples, rough samples of PL and PL containing EM (PL_EM, PL+EM) were studied. They were tested at 50 and 70 kW/m² heat flux. No ignition was observed at 50 kW/m², whereas at 70 kW/m² ignition occurred in EM containing samples. Limitations of the cone heater prevented testing above this heat flux. The control sample of PL did not ignite under any condition. A number of tests were
performed on one set of samples (gypsum containing EM) with a spark igniter on until ignition, spark igniter on all the time, and pilot flame on all the time. From these tests, one condition was selected and used for the rest of samples as described in later chapters.

**Effect of orientation, horizontal versus vertical:** It is clearly noticed from Figure 3.20(a) and Table 3.5 that the PHRR and THR in vertical orientation were higher than those in horizontal orientation. There is not a significant effect on the mass loss rate as seen from Figure 3.20(b).

**Effect of ignition source, spark versus pilot ignition:** Figure 3.21 illustrates also the effect of ignition sources on vertically oriented samples. The pilot flame was left on all the time and to compare with spark ignition, the latter was on all the time as well. The results indicate that the samples tested using pilot ignition ignited earlier than those tested using spark ignition. Also, the PHRR and THR of samples tested by pilot flame were much higher. Mass loss rate is also slightly increased. These results are in agreement with the results from the wood samples.

**Effect of igniter: on until ignition or all the time:** There was not much effect of the igniter being on all the time or just until ignition in both PL which did not ignite and direct incorporated samples as can be seen from results in Table 3.5. In the immersion method, there was variation in the concentration of EM in different samples due to each specimen being individually immersed in the bath of melted EM, hence there was variation in the cone parameters as well.

From these results it can be concluded that in these samples, which are not very flammable, there is not much effect of the orientation, type of igniter and whether it is on all the time or not. Hence, the fire behaviours of the real samples of PL, PL+PCM, PL_PCM and PL+PCM-carrier materials were evaluated later using vertical cone calorimeter tests at a heat flux of 70 kW/m² with the spark igniter on all the time, corresponding to a fully developed fire.
Figure 3.20: a) HRR and b) mass loss versus time curves for PL without/with EM on cone exposure at 70 kW/m² heat flux, horizontal versus vertical orientation with spark ignition till ignition

Figure 3.21: a) HRR and b) mass loss versus time curves for PL without/with EM on cone exposure at 70 kW/m² heat flux, vertical spark ignition versus pilot flame ignition all the time
Table 3.5: Cone calorimetric results of PL without/with EM at 70 kW/m² external heat flux under different orientations and ignition scenarios

<table>
<thead>
<tr>
<th>Sample</th>
<th>Testing condition</th>
<th>TTI (s)</th>
<th>PHRR (kW/m²)</th>
<th>THR (MJ/m²)</th>
<th>Mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>Hor, Spark Ign_Std</td>
<td>-</td>
<td>-</td>
<td>2.7</td>
<td>19.5</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_Std</td>
<td>-</td>
<td>-</td>
<td>9.8</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_all test</td>
<td>-</td>
<td>-</td>
<td>2.1</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>Vert, Pilot flame all test</td>
<td>-</td>
<td>-</td>
<td>11.3</td>
<td>18.6</td>
</tr>
<tr>
<td>PL+EM</td>
<td>Hor, Spark Ign_Std</td>
<td>47</td>
<td>54.3</td>
<td>26.2</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_Std</td>
<td>40</td>
<td>65.4</td>
<td>31.3</td>
<td>24.4</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_all test</td>
<td>390</td>
<td>74.2</td>
<td>28.2</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>Vert, Pilot flame all test</td>
<td>45</td>
<td>83.3</td>
<td>33.3</td>
<td>26.3</td>
</tr>
<tr>
<td>PL_EM</td>
<td>Hor, Spark Ign_Std</td>
<td>305</td>
<td>65.7</td>
<td>13.6</td>
<td>22.9</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_Std</td>
<td>47</td>
<td>98.5</td>
<td>40.2</td>
<td>22.9</td>
</tr>
<tr>
<td></td>
<td>Vert, Spark Ign_all test</td>
<td>245</td>
<td>67.7</td>
<td>16.2</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td>Vert, Pilot flame all test</td>
<td>47</td>
<td>105.5</td>
<td>45.8</td>
<td>24.9</td>
</tr>
</tbody>
</table>

Flame retardants: The flammability results for PL+PA-FA-FR370 with 10 and 20% FR370 showed that both samples ignited at the same time with similar peak heat release rates, other parameters were almost similar as shown in Figure 3.22 and Table 3.6. As explained before the particles of powder FR370 did not mix homogenously with PA-FA and separated in the mixture. Hence, to decrease the flammability and to get homogenous mixture other flame-retardant carrier material EG and flame retardant RDP will be selected in further studies (Chapter 6).

(a) (b)

Figure 3.22: Cone calorimetric results of PL with flame-retardant FR370 form-stable composites PA at 70 kW/m²: (a) HRR and (b) mass loss curves as a function of time
Table 3.6: Cone calorimetric results of PL with flame retardant FR370 form-stable PA composites at 70 kW/m² external heat flux

<table>
<thead>
<tr>
<th>Samples</th>
<th>TTI (s)</th>
<th>FO (s)</th>
<th>Mass loss (%)</th>
<th>Peak PHRR (kW/m²)</th>
<th>T_PHR (s)</th>
<th>THRR (MJ/m²)</th>
<th>EHC (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+PA-FA+20% FR370</td>
<td>18±1.4</td>
<td>500±12</td>
<td>32.4±1</td>
<td>178±5.7</td>
<td>62.5±3.5</td>
<td>58±3</td>
<td>8.7±1.4</td>
</tr>
<tr>
<td>PL+PA-FA+10% FR370</td>
<td>20±1.4</td>
<td>573±12</td>
<td>32±0.6</td>
<td>174±7</td>
<td>62.5±3.5</td>
<td>62.5±2</td>
<td>7.5±1</td>
</tr>
</tbody>
</table>

3.4.6 Thermal energy storage performance

To assess the impact of integrating PCMs into PL, the Binder temperature test chamber (Model KB 23, Binder) cooled incubator was used to subject the prepared samples to realistic thermal conditions and to compare the temperature difference between samples. The temperature ranges were from -5 °C to 100 °C with microprocessor heating and refrigerating systems and adjustable fan speed. The purpose of this experiment was to determine how quickly the heat can be stored and released to improve the indoor thermal temperature. A small test room of PL with dimension of 100 mm x 100 mm x 100 mm and thickness 10 mm was prepared using 6 pieces of PL as shown in Figure 3.23. 4 k-type (±0.004) thermocouples were placed at different locations: at the bottom of top board (T1), middle of cube (T2) and at the centre of wall (T3) and linked to a data acquisition (see Figure 3.24). The thermocouples were connected into the data logger (Pico (TC-08) to record the temperatures of the test room at each second interval.

The thermal energy storage performance was evaluated in heating and cooling modes. Due to the limitation in the quantity of materials available, firstly only the top board of the cube was the one containing PCMs and the temperatures measured at the bottom of top board (T1) with/without PCM were studied. The samples tested as the top board of the cube containing PCMs included control PL, PL+PCM, PL_PCM and PL+PCM-carrier materials with/without flame retardants. The cube was placed in the temperature test chamber. The chamber was switched on for 1 h before testing in order to set up the temperature inside the chamber and test room to be at room temperature 20 °C to ensure that a steady-state condition was performed. In heating mode, the samples were heated from ~ 20 °C (room temperature) to 50 °C for 55 min with a heating rate of 0.54 °C/min and the temperature was kept at 50 °C for 25 min. In cooling mode, the samples were cooled from 50 to 6 °C for 95 min with a cooling rate of 0.46 °C/min and the temperature was kept at 6 °C for 25 min.
The temperature and time were recorded for 200 min, from these results the time-temperature curves were plotted.

For the selected samples with optimum energy storage and flammability properties, five sides of cube were of PCM containing PL samples as will be discussed in details in Chapter 6. For this setup the temperature inside the room with thermocouple T2 (indoor temperature) was the focus of the study. Before the test, the indoor temperature was setup ~ 5 °C for 2 hours by decreasing the chamber’s temperature. Hence, the experiment started from steady-state conditions. The samples were heated up from ~ 5 to 50 °C for 83 min and the temperature was maintained at 50 °C for 42 min and cooled down from 50 to 5 °C for 120 min with the same heating and cooling rate before. There are two reasons for selecting this temperature range:

1. These temperatures cover the range sufficient for the PCMs to enable both melting and freezing phases to occur.
2. These temperatures represent the range of temperatures either in the hot and cold areas around the world. So that, the realistic thermal conditions are taken into account in this experiment.

The temperature and time were recorded for and the time-temperature curves plotted and analyzed.

Figure 3.23: Small test room to evaluate the thermal energy performance
Figure 3.24: a) Binder temperature test chamber and b) test setup showing small test room with attached thermocouples and data logger

3.5 References


[14] Resorcinol bis(diphenyl phosphate) (RDP), Fyrolflex (RDP), Chemtura, Safety Data Sheet.


CHAPTER FOUR

Plasterboard Impregnated with Phase Change Materials

This chapter investigates the effect of incorporating phase change materials (PCMs) namely paraffin (PA), eutectic mixture (EM) and butyl stearate (BS) into plasterboard (PL). PCMs have been incorporated in PL by two methods, direct incorporation and immersion. The samples prepared by direct incorporation method are called PL+PA, PL+EM and PL+BS and the samples prepared by immersion method are PL_PA, PL_EM and PL_BS. In order to study the effect of PCM on PL, the thermal properties were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The surface morphologies of samples prepared by direct incorporation method were analysed using scanning electron microscopy (SEM). The mechanical properties of these samples and of PL with Conplast were evaluated in flexural and compression modes. To evaluate the flammability of these materials, the cone calorimetric technique was used. The thermal energy storage performance of a cube formed from PL was studied using a temperature controlled incubation chamber (Figure. 3.24).

4.1 Criteria for selection of PCMs

Heat storage and release can be achieved over a wide range of temperatures, the selection criteria of PCMs [1-2] are based on following criteria:

a) Thermodynamic considerations – transition temperature, latent heat of fusion and heat transfer properties
b) Physical properties – density, appearance and volumetric change
c) Kinetic consideration – avoidance of crystallization and supercooling
d) Consideration of stability and compatibility
e) Consideration of flammability and toxicity
f) Cost considerations

On the basis at the above criteria, from the literature studies and the results of previous work, the selected PCMs in this research were PA, EM and BS. These PCMs have a good latent heat of fusion in the range of 17-28 °C, to satisfy the human comfort temperature range under different conditions. The thermal properties of PA, EM and BS measured by DSC are presented in Figure 4.1. The derived data of onset melting temperature, onset freezing temperature and latent heat of melting and freezing from these curves are given in
Table 4.1. The melting and freezing temperatures of PCMs measured by DSC were in the range of temperatures mentioned in their material safety data sheet. It can be observed from Figure 4.1(a) and Table 4.1 that the melting and freezing temperatures of PA are 27.7 °C and 27.1 °C, respectively, which are in the thermal comfort temperature range. Whereas, the latent heats of melting and of freezing are 243 J/g and 250 J/g respectively, which suggest that the PA has the largest latent heat compared to others, which can be utilised for thermal energy storage applications.

Figure 4.1: DSC curves of (a) PA, (b) EM, and (c) BS and at 3 °C /min scanning rate

The EM tested in this work is a mixture of decanoic (capric) acid (CA) and dodecanoic (lauric) acid (LA) [3-4]. Figure 4.2 shows the DSC curves of CA and LA. The melting temperature and the latent heat of melting of CA and LA are 30.3 °C and 42.2 °C, 138.3 J/g and 159.6 J/g respectively, both of which are enough for their use for thermal energy
storage. It can be noticed from Figure 4.1(b) that the melting temperature of LA was decreased by the addition of CA to LA. In this experiment, CA and LA were mixed in 70:30 wt% proportions.

![Figure 4.1(b) showing the effect of CA on LA's melting temperature](image)

Figure 4.1(b) and Table 4.1 show that the melting and freezing temperatures of EM are 18.5 °C and 18.7 °C respectively, which is a good temperature for indoor environments. The latent heats of melting and of freezing are 153 J/g and 151 J/g, respectively. However, the latent heat of EM is much less than that of PA.

![Figure 4.2: DSC curves of (a) CA and (b) LA recorded at 2 °C/min scanning rate](image)

Table 4.1: Thermal Properties of PA, EM and BS by DSC

<table>
<thead>
<tr>
<th>PCM</th>
<th>Melting temperature (°C)</th>
<th>Freezing temperature (°C)</th>
<th>Latent heat of melting (J/g)</th>
<th>Latent heat of freezing (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>27.7 ± 0.07 (31.7)*</td>
<td>27.1 ± 0.07 (23.8)*</td>
<td>243 ± 5</td>
<td>250 ± 7</td>
</tr>
<tr>
<td>EM</td>
<td>18.5 ± 0.2 (23.6)*</td>
<td>18.7 ± 0.3 (14)*</td>
<td>153 ± 2</td>
<td>151 ± 3</td>
</tr>
<tr>
<td>BS</td>
<td>17.6 ± 0.07 (24.6)*</td>
<td>20.9 ± 0.2 (14)*</td>
<td>113 ± 1</td>
<td>112 ± 0.4</td>
</tr>
</tbody>
</table>

* = Temperatures at the end of the peak, representing the completion of the phase change

It can be seen from Figure 4.1(c) that there are three peaks, representing three phase changes during heating or cooling processes for BS. During the heating process, the first and second peaks of phase change occurred at around 7.5 °C and 10.3 °C respectively which represents the glass transition temperature of BS (solid-solid BS). This is attributed to the change of its crystalline structure from one lattice configuration to another. The third main peak of phase change was noticed at around 21.7 °C which represents the solid-liquid
phase change. During the cooling process, the first mean peak which represents the liquid-
solid phase change appeared at 18.9 °C, whereas, the second and third small peaks occurred at around 9.3 °C and 6.4 °C respectively which represent the glass transition
temperature. The values of melting temperature, freezing temperature, and latent heats of
melting and freezing were determined to be 17.6 °C and 20.9 °C, 113 J/g and 112 J/g
respectively (see Table 4.1). These results demonstrate that the phase transition
temperature of BS is in the thermal comfort temperature range. Moreover, the latent heat is
significantly smaller compared to those of the PA and EM. In terms of latent heats, PCMs
can be ranked as:

PA > EM > BS

4.2 Physical and morphological properties of plasterboard containing PCMs

4.2.1 Samples prepared by direct incorporation method

Samples prepared as discussed in Section 3.2.3 (Chapter 3), are listed in Table 4.2. As can
be seen from the results, the densities of samples containing 10% of PCM were higher than
of the control sample, PL.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PCM added (%)</th>
<th>Sample thickness (mm)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>----</td>
<td>10</td>
<td>1.64</td>
</tr>
<tr>
<td>PL+PA</td>
<td>10</td>
<td>10</td>
<td>1.8</td>
</tr>
<tr>
<td>PL+EM</td>
<td>10</td>
<td>10</td>
<td>1.8</td>
</tr>
<tr>
<td>PL+BS</td>
<td>10</td>
<td>10</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The surface morphologies of PL+PA, PL+EM and PL+BS have been investigated by SEM
and are shown in Figure 4.3. Figure 4.3(a) represents the microstructure of PL. With the
addition of PCM, the particles of PL seem to be uniformly coated by PA and BS. Also, a
homogenous distribution of these PCMs in gypsum powder can be observed in Figure
4.3(b and d). In the case of PL+EM, Figure 4.3(c) shows that the particles of EM did not
disperse uniformly in gypsum powder and the morphology was almost the same as of PL.
4.2.2 Samples prepared by immersion method

In the immersion method, the amount of PCM absorbed is dependent on the porosity of the material. Three specimens of PL samples were immersed separately into baths filled with hot melted PA, EM and BS for 30 min using the vacuum impregnation method (see Section 3.2.2) while the temperature of PA, EM and BS was maintained at 50 °C in an oven. An image of one sample is shown in Figure 4.4. It can be observed from Table 4.3 that all samples absorbed ~20-22\% of PCM except PL_PA, with only ~18\% absorption. Moreover, there is a variation in the concentration of PCM absorbed within different specimens owing to each specimen being separately immersed in PCM. The densities of PL samples immersed in PCMs increased as a result of the PCM absorbed as seen from values given in Table 4.3. 

![Image of sample prepared by immersion method](image)

Table 4.3: Composition of PL prepared by immersion technique

<table>
<thead>
<tr>
<th>Sample</th>
<th>PCM absorbed (%)</th>
<th>Sample thickness (mm)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>----</td>
<td>10</td>
<td>1.64</td>
</tr>
<tr>
<td>PL_PA</td>
<td>18±0.8</td>
<td>10</td>
<td>1.94±0.01</td>
</tr>
<tr>
<td>PL_EM</td>
<td>20.7±1.6</td>
<td>10</td>
<td>1.98±0.02</td>
</tr>
<tr>
<td>PL_BS</td>
<td>20.9±1.4</td>
<td>10</td>
<td>1.98±0.01</td>
</tr>
</tbody>
</table>
4.3 Thermal characteristics of PCMs in plasterboard

4.3.1 Samples prepared by direct incorporation method

The DSC curves of PL+PA, PL+EM and PL+BS are presented in Figure 4.5. The derived data from these curves and the calculated latent heat of PCM based on the mass fraction of PCM in these samples are reported in Table 4.4. Figure 4.5(a) and Table 4.4 show that the onset of melting and freezing temperatures of PA in the sample of PL+PA are measured to be 27.6 °C and 27.3 °C, respectively, which are almost the same as those of pure PA (see Table 4.1). The measured latent heats of melting and of freezing are 10 J/g and 9.3 J/g, respectively. From these, the calculated latent heats of melting and freezing for the PA alone, taking into account the percentage of PA added, can be seen to have been reduced to 99.7 J/g and 93.1 J/g, respectively, compared to 243 J/g and 250 J/g for pure PA. Figure 4.5(b) and Table 4.4 illustrate that the onset of melting temperature of EM in the mixture of PL+EM is 17.5 °C and its latent heat has been reduced to be 4.9 J/g compared to that of pure EM (see Table 4.1) with calculated latent heat for just the EM component of 48.9 J/g. On the other hand, the results during cooling were 17.7 °C and 5.4 J/g as freezing temperature and latent heat respectively, which indicate that the EM in the sample PL+EM had low thermal properties. This could be due to poor dispersion and aggregation of EM into PL as seen from the SEM image in Fig. 4.3 (c). In the case of PL+BS as shown in Figure 4.5(c) and Table 4.4, the onset melting and freezing temperatures of the BS are 18.6 °C and 21 °C respectively, which is same as obtained for pure BS (see Table 4.1). The latent heats of melting and of freezing were significantly decreased compared to pure BS to be 6.4 J/g and 6.5 J/g with calculated latent heat for just the BS component of 63.9 J/g and 65.3 J/g, respectively. These results indicate that the latent heats of fusion obtained for different PCMs when incorporated within PL are in the order:

\[ \text{PA} > \text{BS} > \text{EM} \]

This can be more clearly seen from Figure 4.6 where the highest specific heat capacity values were found in the order of, PA > BS > EM, corresponding to their latent heat. The latent heats of PCMs by direct incorporation are less than that of pure PCMs due to the separated and scattered molecules of PCMs during mixing with PL. When they are in small units, not enough material is available to melt with considerable latent heat. The values are higher for PA which suggests that during dispersion, molecules of PA might have aggregated, whereas EM, which shows best dispersion in SEM images (Fig.4.3(c)), shows
the least latent heat of melting or freezing. The latent heats of PA and BS after incorporation in PL are still acceptable to be applied for thermal energy storage in building materials [5-7].

Figure 4.5: DSC curves of (a) PL+PA (b) PL+EM and (c) PL+BS at 3 °C/min scanning rate
Table 4.4: Thermal Properties of PCMs incorporated into PL by DSC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melting temp (°C)</th>
<th>Freezing temp (°C)</th>
<th>Measured latent heat of melting (J/g)</th>
<th>Measured latent heat of freezing (J/g)</th>
<th>*Derived latent heat of melting of PCM (J/g)</th>
<th>*Derived latent heat of freezing of PCM (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+PA</td>
<td>27.6±0.3 (31.3)</td>
<td>27.3±0.1 (23.5)</td>
<td>10±1.5</td>
<td>9.3±1</td>
<td>99.7</td>
<td>93.1</td>
</tr>
<tr>
<td>PL+EM</td>
<td>17.5±0.4 (22.5)</td>
<td>17.7±2 (8.6)</td>
<td>4.9</td>
<td>5.4</td>
<td>48.9</td>
<td>54</td>
</tr>
<tr>
<td>PL+BS</td>
<td>18.6±0.2 (23)</td>
<td>21±0.3 (17.1)</td>
<td>6.4±0.5</td>
<td>6.5±0.5</td>
<td>63.9</td>
<td>65.3</td>
</tr>
</tbody>
</table>

- Average of two replicate results
- Values in italics and brackets are the temperatures at the end of the peak, representing the completion of the phase change
- * = Calculated based on mass fraction of PCM in PL

Figure 4.6: DSC curves showing specific heats vs. temperature of control sample (PL) compared to those of PL+PA, PL+EM and PL+BS

4.3.2 Samples prepared by Immersion method

The DSC results of PL_PA, PL_EM and PL_BS are presented in Figure 4.7 and the derived data are given in Table 4.5. Figure 4.7(a and c) and Table 4.5 showed that the onset melting and freezing temperatures of PA and BS in the mixtures of PL_PA and PL_BS were similar to those of pure PA and BS and those produced by direct incorporation method. The glass transition temperature in the sample PL_BS was similar to that observed in pure BS. EM in the sample PL_EM exhibits a phase transition temperature the same as that of pure EM (see Table 4.1) and EM in the sample PL+EM. The latent heats of PCM in immersion method are shown in Table 4.5. Although the latent heats of PA and EM are greatly reduced compared to those of pure PA and EM, they are higher than those obtained with the direct incorporation method, which are due to higher percentages of PA and EM in these samples, i.e., 18 and 20.9%, respectively. Also, both
PA and EM molecules were absorbed in the interstices of PL, hence exist as a distinct phase to melt compared to small molecules which get separated in the direct incorporation method, however the effectiveness will depend on the pore sizes as small sized PCMs will easily penetrate through the interstices. This can be seen particularly for EM, which showed much higher latent heat compared to those in direct incorporation method.

On the contrary, the latent heat of PCM in the sample PL_BS by the immersion method was less than that of pure BS and the direct incorporation method (see Table 4.1 and 4.4), which could be due to the non-uniformity of the sample by the immersion method. These results illustrate that the highest latent heat of fusion obtained in this method is in the order of:

$$PA > EM \approx BS$$

It should however, be noted that in immersion method the PCM absorption might not be uniform throughout the sample thickness and hence, these values may vary depending on where the test sample has been taken from.
Figure 4.7: DSC curves of (a) PL_PA (b) PL_EM and (c) PL_BS at 3 °C/min scanning rate

Table 4.5: Thermal properties of PCMs immersed in PL by DSC

<table>
<thead>
<tr>
<th>PCM</th>
<th>Melting temp (°C)</th>
<th>Freezing temp (°C)</th>
<th>Latent heat of melting (J/g)</th>
<th>Latent heat of freezing (J/g)</th>
<th>*Derived Latent heat of melting (J/g)</th>
<th>*Derived Latent heat of melting (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL_PA</td>
<td>27.7±0.2 (30.5)</td>
<td>27.3±0.05 (25)</td>
<td>27.5±0.5</td>
<td>27.6±0.4</td>
<td>152.8</td>
<td>153.3</td>
</tr>
<tr>
<td>PL_EM</td>
<td>18±0.4 (22.3±0.3)</td>
<td>17.7±0.4 (14.2)</td>
<td>13.1±2</td>
<td>10.5±2</td>
<td>63.4</td>
<td>50.7</td>
</tr>
<tr>
<td>PL_BS</td>
<td>18.6±0.1 (22.5)</td>
<td>21.2±1 (16)</td>
<td>12.2±2</td>
<td>12±2</td>
<td>58.4</td>
<td>57.4</td>
</tr>
</tbody>
</table>

- Average of two replicate results
- Values in italics and brackets are the temperatures at the end of the peak, representing the completion of the phase change
* Derived = Calculated based on mass fraction of PCM in PL

The specific heat values of samples in the course of solid-liquid phase change were in an agreement with the measured latent heats of melting as shown in Figure 4.8. The specific heat values can be ranked as:

PA > EM > BS
4.4 Thermal stability of PCMs in plasterboard

4.4.1 PCMs

The thermal stabilities of PA, EM and BS were investigated using thermogravimetric analysis (TGA) by heating from room temperature to 850 °C at 10 °C/min heating rate under a air atmosphere (100 ml/min). The TGA and differential temperature analysis (DTA) curves of PCMs are presented in Figure 4.9. The analyses of all results are reported in Table 4.6. It can be observed from Figure 4.9(a) that all PCMs used had a single step of mass loss, and their onset of volatilization temperatures were 100, 100 and 150 °C for PA, EM and BS, respectively. This means the PCMs were stable up to these temperatures. Afterwards, the PCMs started losing weight and were completely volatilised by 230, 210 and 270 °C, respectively. PA and EM started losing their mass at lower temperature than did BS. From DTA curves in Figure 4.9(b), it can be seen that PA had two types of thermal transitions, an endothermic DTA peak at 190 °C, representing the volatilization of PA, and an exothermic DTA peak at 230 °C, because of oxidation. In the case of EM, the endothermic DTA peak was physically observed at 206 °C, indicating its volatilization. On the contrary, BS had exothermic DTA peaks at 268 °C, representing its thermal oxidation.
Figure 4.9: TGA (a), DTA (b) curves of PCMs from room temperature to 850 °C in air

Table 4.6: TGA and DTA results of PCMs

<table>
<thead>
<tr>
<th>Samples</th>
<th>TGA</th>
<th>DTA Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp Range (°C)</td>
<td>Mass Loss (%)</td>
</tr>
<tr>
<td>PA</td>
<td>100-230</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>0</td>
</tr>
<tr>
<td>EM</td>
<td>100-210</td>
<td>100</td>
</tr>
<tr>
<td>BS</td>
<td>150-270</td>
<td>100</td>
</tr>
</tbody>
</table>

4.4.2 Samples prepared by direct incorporation method

The TGA and differential temperature analysis (DTA) curves of samples prepared by the direct incorporation method are presented in Figure 4.10. The derived data from these curves are reported in Table 4.7. It can be seen from Figure 4.10 and Table 4.7 that the control sample of PL lost 16% of its mass between 106 to 180 °C, which was accompanied by the endothermic peak at 156 °C, representing the first dehydration reaction of PL as result of desorption of water (0.75*21%=15.75%) as also reported in literature [8-9]. This was followed by second mass loss between 650-740 °C, indicating 3.7% of mass loss which is due to the decomposition of calcium carbonate and magnesium carbonate content of gypsum boards [10-12], leaving 80.3% residue of PL at 750 °C.

With the addition of PA, there were two steps of thermal decomposition in PL+PA similar to PL. The first step occurred between 100 to 220 °C with mass loss of 20%, accompanied by the endothermic DTA peak at 156 °C similar to PL, representing desorption of water and volatilization of PA. Whereas, the second step was observed between 710 to 750 °C
with mass loss of 3.7%, assigned to the second step of thermal decomposition of control PL, indicating endothermic DTA peak at 730 °C, giving 76.3% residue at the end. The sample of PL+EM showed three mass loss stages, the first step is between 100 and 185 °C close to PL+PA with mass loss of 18.7%. The second step of mass loss was observed between 280-360 °C with mass loss of 4%. The second mass loss was accompanied by the exothermic DTA peak at 340 °C, indicating the possible oxidation EM. Whereas, the third step of thermal decomposition was observed in the range of 710-740 °C similar to PL+PA, producing 74.1% residue at 750 °C.

As seen in Figure 4.10, PL+BS had three mass loss steps. The first step was noted in the range of 100-170 °C similar to PL+PA and PL+EM with mass loss of 14.4%. This was followed by the second mass loss between 170-245 °C indicating 5.5% of its mass was lost in the PL+BS, this mass loss corresponded mainly to the volatilization of BS. The third mass loss step of PL+BS happened in the range of 670-720 °C, losing 5.2% of its mass, accompanied by the endothermic DTA peak at 700 °C, which was in agreement with control PL (decarbonation of calcium carbonate).

![Figure 4.10: TGA (a), DTA (b) curves of control (PL) and samples prepared by direct incorporation method from room temperature to 850 °C in air](image-url)
Table 4.7: TGA and DTA results of samples prepared by direct incorporation method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp Range (°C)</th>
<th>Mass Loss (%)</th>
<th>Residue (%)</th>
<th>Residue 750 °C (%)</th>
<th>Max Temp (°C)</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>106-180</td>
<td>16</td>
<td>80.3</td>
<td>80.3</td>
<td>156</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>650-740</td>
<td>3.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PL+PA</td>
<td>100-220</td>
<td>20</td>
<td>76.3</td>
<td>76.3</td>
<td>156</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>710-750</td>
<td>3.7</td>
<td></td>
<td></td>
<td>730</td>
<td>Endo</td>
</tr>
<tr>
<td>PL+EM</td>
<td>100-185</td>
<td>18.7</td>
<td>74.2</td>
<td>74.1</td>
<td>156</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>280-360</td>
<td>4</td>
<td></td>
<td></td>
<td>340</td>
<td>Exo</td>
</tr>
<tr>
<td></td>
<td>710-740</td>
<td>3.1</td>
<td></td>
<td></td>
<td>730</td>
<td>Endo</td>
</tr>
<tr>
<td>PL+BS</td>
<td>100-170</td>
<td>14.4</td>
<td>74.9</td>
<td>74.8</td>
<td>156</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>170-245</td>
<td>5.5</td>
<td></td>
<td></td>
<td>241</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>670-720</td>
<td>5.2</td>
<td></td>
<td></td>
<td>700</td>
<td>Endo</td>
</tr>
</tbody>
</table>

PL+BS left 74.8% residue at 750 °C, which was almost similar to that observed in PL+EM. This was attributed to the amount of the PCM used in these mixtures was the same. It can be also clearly noticed that the TGA results of direct incorporation method were corresponding to that of control PL and the additional mass loss was due to the PCM added. All samples had almost the same residue except the sample PL+PA, which had difference of around 2%, which could be due to the non-uniformity of PA absorbed and the experimental errors.

4.4.3 Samples prepared by Immersion method

The TGA and differential temperature analysis (DTA) curves of PL immersed in PCMs as shown in Figure 4.11 and Table 4.8 are similar to those of samples with additives as discussed above.

Figure 4.11: TGA (a), DTA (b) curves of control (PL) and PCMs immersed into PL from room temperature to 850 °C in air
Table 4.8: TGA and DTA results of samples prepared by immersion method

<table>
<thead>
<tr>
<th>Samples</th>
<th>TGA</th>
<th>DTA Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp Range</td>
<td>Mass Loss (%)</td>
</tr>
<tr>
<td>PL</td>
<td>106-180</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>650-740</td>
<td>3.7</td>
</tr>
<tr>
<td>PL_PA</td>
<td>100-180</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>680-730</td>
<td>6</td>
</tr>
<tr>
<td>PL_EM</td>
<td>100-185</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>280-360</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>710-730</td>
<td>2.7</td>
</tr>
<tr>
<td>PL_BS</td>
<td>100-170</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>170-245</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>670-720</td>
<td>5</td>
</tr>
</tbody>
</table>

The temperatures of mass loss stages in TGA and corresponding DTA peaks in the samples PL_PA, PL_EM and PL_BS were similar to those observed in the samples prepared by the direct incorporation method and the slight differences between them are probably due to the non-uniformity of PCM absorbed in the former. Compared to control sample of PL, the additional mass loss in PL_PCM was due to the decomposition of the PCM.

4.5 Mechanical performance of plasterboard containing PCMs

To study the effect of PCMs on the mechanical performance of PL, samples of PL prepared without/with Conplast and PL containing PCMs were tested in flexural and compression modes.

4.5.1 Effect of conplast on the mechanical properties of plasterboard

As discussed in Section 3.2.2.2 (Chapter 3) Conplast was added to some PL samples during their production in order to increase their porosity. This section compares the results of samples without/with Conplast and the effect of mixing time in order to get optimal conditions. The stress-strain curves from flexural test in Figure 4.12(a) show a linear relationship with R-squared (percentage variable variation) values between 0.82 and 0.88 (Table 4.9). None of the samples could withstand the applied stress of more than 4 MPa and broke at the centre.
Figure 4.12: Strain-stress curves from a) Three-point bending test and b) Compression test for PL with different proportion of conplast at mixing times of 5 and 10 min

The results in Table 4.9 show that the stress-at-failure and modulus of PL without Conplast at mixing times of 5 and 10 min were similar, i.e., 4 MPa and 2.5 GPa. These properties were maintained on addition of 3% Conplast at mixing times of 5 and 10 min, only stress-at-failure was decreased on mixing for 10 min. On increasing the percentage of Conplast to 5%, the stress-at-failure was reduced, which may be due to the reason that the coherence between PL particles was decreased as a result of entrained additional air.

The strain-stress results of the compression test are demonstrated in Figure 4.12(b) and compression properties are presented in Table 4.9. The mixing time of 5 or 10 minutes had little effect on the modulus of elasticity of PL (81.4-81.7 GPa), though the crushing strength slightly increased from 11.9 to 14.0 MPa. The term ‘crushing strength’ has the same meaning as ‘compressive strength’, [13] but is preferred for construction materials such as plaster and concrete, which do not compress but crumble on application of the load. The reduction of crushing strength and modulus of elasticity was clearly observed on addition of Conplast, decreasing further on increasing Conplast to 5%. On increasing the mixing time to 10 minutes, the crushing strength decreased further, though the modulus of elasticity was not much affected. % reduction in flexural and crushing strengths and moduli are given in Table 4.9 to further emphasise this point that the mechanical properties are reduced by adding Conplast, the reduction is greater with increasing Conplast concentration and increasing mixing time. The reduction can be explained that when Conplast is added and mixing is vigorous, additional entrapped air weakens the bonds between PL particles. Because no big differences have been observed in the mechanical
properties of PL prepared at 5 and 10 min, the PL prepared at 5 min was selected as a control sample in this research.

Table 4.9: Mechanical properties of control PL and PL at thickness 12 mm with different concentration of Conplast

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mixing time (min)</th>
<th>Flexural properties</th>
<th>Compression properties</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stress-at-failure (MPa)</td>
<td>Modulus (GPa)</td>
<td>R²</td>
<td>Crushing Strength (MPa)</td>
</tr>
<tr>
<td>PL</td>
<td>5</td>
<td>3.9±0.1</td>
<td>2.5±0.5</td>
<td>0.88</td>
<td>11.9±0.4</td>
</tr>
<tr>
<td>PL-3% conplast</td>
<td>5</td>
<td>4±0.1</td>
<td>2.8±0.2</td>
<td>0.86</td>
<td>10.3±0.4</td>
</tr>
<tr>
<td>PL-5% conplast</td>
<td>5</td>
<td>2.5±0.1</td>
<td>2.4±0.3</td>
<td>0.82</td>
<td>4.8±0.6</td>
</tr>
<tr>
<td>PL</td>
<td>10</td>
<td>4±1.2</td>
<td>2±0.3</td>
<td>0.88</td>
<td>14.0±0.3</td>
</tr>
<tr>
<td>PL-3% conplast</td>
<td>10</td>
<td>3±0.2</td>
<td>2.3±0.3</td>
<td>0.82</td>
<td>8.8±0.5</td>
</tr>
<tr>
<td>PL-5% conplast</td>
<td>10</td>
<td>2.4±0.1</td>
<td>1.9±0.3</td>
<td>0.86</td>
<td>6.2±0.4</td>
</tr>
</tbody>
</table>

- Average of three replicate results
- Values between brackets are the % reduction in mechanical properties of modified samples compared to control sample (PL)

4.5.2 Samples prepared by the direct incorporation method

Flexural and compression properties of PL, PL+PA, PL+EM and PL+BS are shown in Figure 4.13 and analysed results are reported in Table 4.10. The trends observed in stress-strain curves (Figure 4.13(a)) are more linear than in the previous section, shown by R-squared values between 0.95 and 0.99 (Table 4.10), indicating that the addition of PCMs does not affect the uniformity of the samples. The flexural and crushing strength measured for the control sample (PL) of thickness 10 mm, prepared at a mixing time of 5 min were 3.2 MPa and 38.4 MPa, respectively, which are slightly less than in the previous section. Since these samples were individually prepared in the lab, slight variations are expected. As can be seen from results in Table 4.10, the addition of PCMs in PL has a little effect on the modulus of elasticity, the values for PL, PL+PA and PL+BS were almost similar taking standard deviation into consideration for three replicated specimens. The modulus of PL+EM though was considerably reduced. The flexural strength of all samples containing PCMs decreased compared to PL (Table 4.10). The flexural strength was found to be 3.1 MPa, 1.6 MPa and 2.9 MPa for the samples PL+PA, PL+EM and PL+BS, respectively. The highest reduction (50%) was observed for PL+EM, indicating weak interaction
between PL and EM. Whereas, reductions were only 3.1% and 9.4% for the samples PL+PA and PL+BS, respectively. These reductions can be explained due to the reduction in coherence between PL particles due to the PCM presence.

In the compression mode, the crushing strength of samples is generally reduced [14] as a result of PCM addition similar to that observed in the flexural mode. The highest reduction was also noticed in PL+EM (51.8%) compared to PL and the reductions were 44% and 37.2% for the samples PL+PA and PL+BS, respectively as shown in Table 4.10. It was also observed that the lowest moduli of elasticity were observed for the samples of PL+PA and PL+EM compared to PL. The reduction in PL+BS was less than those of PL+PA and PL+EM.

Figure 4.13: Stress-strain curves from a) Three-point bending test and b) Compression test for PL and PL+PCM samples prepared by the direct incorporation method.

Table 4.10: Mechanical properties of PL and PL+PCM samples prepared by direct incorporation method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural properties</th>
<th>Compression properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stress-at-failure (MPa)</td>
<td>Modulus (GPa)</td>
</tr>
<tr>
<td>PL</td>
<td>3.2±0.03</td>
<td>2.8±0.3</td>
</tr>
<tr>
<td>PL+PA</td>
<td>3.1±0.03 (−3.1%)</td>
<td>2.6±0.12</td>
</tr>
<tr>
<td>PL+EM</td>
<td>1.6±0.2 (−50%)</td>
<td>1.6±0.3</td>
</tr>
<tr>
<td>PL+BS</td>
<td>2.9±0.06 (−9.4%)</td>
<td>2.4±0.3</td>
</tr>
</tbody>
</table>

- Average of three replicate results
- Values between brackets are the % reduction in mechanical properties of PL+PCM compared to control sample (PL)
4.5.3 Samples prepared by the Immersion method

The mechanical properties in flexural and compression modes of PL immersed in PCMs are presented in Figure 4.14 and the results summarized in Table 4.11. Linear trends were also observed similar to samples from the direct incorporation method as shown in Figure 4.14(a) with R-squared values of 0.91-0.99. It can be observed that the presence of PCMs increased the modulus of elasticity of PL from 2.8 to ~3.5 GPa. PCMs also increased the flexural strength of immersed samples compared to PL except for the sample PL_EM. The increase in flexural strength was 4.7 MPa, 3.6 MPa and 3 MPa for PL_PA, PL_BS and PL_EM, respectively, i.e., PA and BS helped in increasing the strength by 46.9% and 12.5% respectively (Table 4.11), whereas, EM reduced it by 6.3%. The immersion method shows better results for mechanical properties, even with the higher PCM concentration than by the direct incorporation method, which can be explained on the basis that in the immersion method PCM fills the pores of the PL and hence, does not affect the structure of the PL, whereas in the direct incorporation method they are distributed in the PL and hence affect the structure formation. The slight reduction in flexural strength by EM may be due to the reason that the ionic EM tends penetrate further into smaller pores, hence weakening the structure.

On the contrary, the results from the compression test in Table 4.11 demonstrate that the modulus and crushing strength of immersed samples were significantly decreased compared to PL. PL_BS had the highest value compared to other immersed samples. The highest reduction of 54.4% was in PL_EM. At the same time for PL_PA and PL_BS, the reductions in crushing strength were 29.2% and 10.7%, respectively. The modulus of elasticity decreased in PL_EM by 41% and PL_PA by 23.2% compared to PL. As can be seen from Tables 4.10 and 4.11, the compression properties of these samples are much higher than respective flexural properties, which could be explained by the fact that when a load is applied, the sample deforms, but the sample becomes more compact.
Figure 4.14: Strain-stress curves from a) Three-point bending test and b) Compression test for PL and PL_PCM samples prepared by immersion method

Table 4.11: Mechanical properties of control PL and PL_PCM prepared by immersion method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural properties</th>
<th>Compression properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stress at failure (MPa)</td>
<td>Modulus at failure (GPa)</td>
</tr>
<tr>
<td>PL</td>
<td>3.2±0.06</td>
<td>2.8±0.3</td>
</tr>
<tr>
<td>PL_PA</td>
<td>4.7±0.3</td>
<td>3.6±0.2</td>
</tr>
<tr>
<td></td>
<td>(+46.9%)</td>
<td>(-29.2%)</td>
</tr>
<tr>
<td>PL_EM</td>
<td>3±0.08</td>
<td>3.7±0.5</td>
</tr>
<tr>
<td></td>
<td>(-6.3%)</td>
<td>(-54.4%)</td>
</tr>
<tr>
<td>PL_BS</td>
<td>3.6±0.07</td>
<td>3.2±0.2</td>
</tr>
<tr>
<td></td>
<td>(+12.5%)</td>
<td>(-10.7%)</td>
</tr>
</tbody>
</table>

- Average of three replicate results
- Values between brackets are the % increasing and reduction in mechanical properties of PL_PCM compared to PL

4.6 Fire performance of plasterboard containing PCMs

Three specimens of each sample were tested using a cone calorimeter in vertical orientation as discussed in Section 3.4.5 (Chapter 3), in one specimen three thermocouples were inserted on the back surface of the sample. Details of the setup are given in Section 3.4.5.

4.6.1 Samples prepared by the direct incorporation method

The curves of heat release rate (HRR) and mass loss as a function of time of samples prepared by direct incorporation method are graphically presented in Figure 4.15. The derived parameters from these curves; time to ignition (TTI), flame-out time (FOT), total mass loss, peak heat release rate (PHRR), total heat release rate (THR) and effective heat
of combustion (EHC) are given in Table 4.12. It can be seen from the results that the control sample (PL) did not ignite and hence produced negligible THR and EHC values, i.e., 0.5 kW/m$^2$ and 0.2 MJ/kg, respectively. Also, it can be observed from the results in Figure 4.15(a) that for all samples containing PCMs, there were two peaks of heat release rate (PHRR) due to ignition. The first peak could be attributed to the release of PCM on or near the surface and the second peak to the delayed release of PCM. This two peak behaviour has also been seen by other researchers [15-16]. The PL+PA sample ignited at 13 s, produced the highest PHRR, the first peak of 88 kW/m$^2$ at 60 s and the second peak of 116 kW/m$^2$ at 160 s, with mass loss 22.3%, and produced the highest THR and EHC values, 45 MJ/m$^2$ and 7.9 MJ/kg, respectively.

Among all the PCMs, similar to PA, the BS containing sample ignited at 23 s. EM containing samples had a slightly higher TTI value of 43 s. Both of them had two peaks of heat release of similar intensities. The THR values of EM and BS were similar ~34 MJ/m$^2$ and lower than that of the PA containing sample. These results illustrated that PL+PA was much more flammable than the other PCMs, shown by having the higher PHRR, THR and EHC values, and the shortest ignition time. PL+EM was less flammable than PL+BS, shown by it having the lowest PHRR and longest TTI.

All of samples had almost the same mass loss rate after taking the standard deviation into account and their mass losses were higher than that of control PL (16.5%) because of the PCMs presence. It can also be noticed from these results that the mass loss measured using the cone calorimeter was close to that measured by TGA particularly for the sample of PL+BS (see Table 4.7) even though these samples were heated quickly by cone. The slight difference between them could be attributed to the heating rate of 10 °C/min starting from room temperature in TGA test and the sensitivity of the TGA balance. Hence, the volatilization of samples using TGA was slightly higher than that of cone calorimeter. It can be noticed from the images of cone exposed samples in Figure 4.16 that PL showed minimal external damage and no significant cracks have been observed. However, the cracks, external surface damage and colour change can be noticed on the both sides of samples containing PCMs, which have been caused by the release and burning of the PCMs.
Figure 4.15: Cone calorimetric results of control (PL) and samples prepared by direct incorporation method at 70 kW/m\(^2\): (a) HRR and (b) mass loss curves as a function of time

Table 4.12: Cone calorimetric results of PL without/with PCM as direct incorporation method at 70 kW/m\(^2\) external heat flux

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI (s)</th>
<th>FO (s)</th>
<th>Mass loss (%)</th>
<th>Peak1 PHRR (kW/m(^2))</th>
<th>(T_{\text{PHRR}}) (s)</th>
<th>Peak2 PHRR (kW/m(^2))</th>
<th>(T_{\text{PHRR}}) (s)</th>
<th>THR (MJ/m(^2))</th>
<th>EHC (MJ/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>----</td>
<td>----</td>
<td>16.5±0.23</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.5±0.5</td>
<td>0.2±0.1</td>
</tr>
<tr>
<td>PL+PA</td>
<td>13±1</td>
<td>565±1</td>
<td>22.3±1.6</td>
<td>88±9</td>
<td>60±7</td>
<td>116±11</td>
<td>160±14</td>
<td>45±4.6</td>
<td>7.9±0.5</td>
</tr>
<tr>
<td>PL+EM</td>
<td>43±1</td>
<td>679±2</td>
<td>23.4±0.9</td>
<td>69±7</td>
<td>70±7</td>
<td>89±10</td>
<td>455±7</td>
<td>34±4</td>
<td>6.5±0.4</td>
</tr>
<tr>
<td>PL+BS</td>
<td>23±4</td>
<td>547±3</td>
<td>25.3±1.8</td>
<td>70±6</td>
<td>52±53</td>
<td>111±9</td>
<td>397±74</td>
<td>34±0.04</td>
<td>3.5±1.1</td>
</tr>
</tbody>
</table>
Figure 4.16: Images of (a) PL, (b) PL+PA, (c) PL+EM and (d) PL+BS, (after cone test (70 kW/m$^2$))

The temperature change measured at the unexposed surface to cone heater using three thermocouples as a function of time are presented in Figure 4.17. These thermocouples were placed on the back surface of the board, one in the middle and the other two at a distance of 10 mm on each side. The time taken to reach the temperatures 140 °C, 300 °C and the maximum during the duration of a test are given in Table 4.13. The rationale to select these temperatures is based on the standards ASTM E119 and BS 476-20:1987 [17-18] for fire tests of building materials, where in a test the average temperature at unexposed surface of the sample during the fire test should not exceed 140 °C. The temperature 300 °C was chosen because above this temperature some building materials such as concrete lose ~30-50% mechanical strength [19-22]. From the maximum temperature reached and time to reach the maximum temperature, the combustion behaviour of a PCM can be established.

As shown in Figure 4.17 for PL, which did not burn, the back surface temperature increased to 100 °C within 80 s and then remained steady until 290 s, after started rising slowly, reaching 150 °C in 570 s, after which it started increasing sharply. The first two steps correspond to the first dehydration reaction of the PL, after which due to loss of water content in the samples, cracks are created within the sample. Hence, the insulative effect of the air was lost and the temperature started rising to reach the maximum temperature of 358 °C at 1200 s. The thermal conductivity of PL is related mainly to its porosity and pore size [23-27], the greater the porosity and pore size are, the smaller thermal conductivity is. The thermal conductivity of PL is constant (0.25 W/m.k) at room temperature [28], but increases slightly with temperature during loss of water, as also observed by other researchers [29-30]. All samples containing PCMs ignited, and burned, hence, the temperatures measured on the reverse side were also higher than that of PL and the times taken to reach predetermined temperatures were shorter. The time measured to reach 140 °C was in the order of:
PL+PA<PL+BS<PL+EM

Whereas to reach 300 °C, PL+PA and PL+BS, took the same time, 480 s and PL+EM took longer, 738 s. These results indicate that the heat transfer rate using PA between both surfaces was the highest because of the higher flammability of PA. The slow temperature rise in PL+EM sample could be because EM was very well dispersed in PL, the separated molecules of micelles EM during mixing with PL, as explained in SEM and DSC results, may be too scattered to burn together with high intensity, hence the lowest heat transfer rate. The maximum temperatures measured at the unexposed surface were ranked as:

PL+BS>PL+PA>PL+EM

From these results, EM can be seen to be the best in terms of lowest flammability and heat transfer, when incorporated within PL.

![Temperature versus time curves of the reverse surfaces of PL without/with PCMs prepared by direct incorporation method on cone exposure at 70 kW/m² heat flux in vertical orientation](image)

Figure 4.17: Temperature versus time curves of the reverse surfaces of PL without/with PCMs prepared by direct incorporation method on cone exposure at 70 kW/m² heat flux in vertical orientation

Table 4.13: Temperature changes measured at unexposed surface of PL without/with PCMs prepared by direct incorporation method to cone heater

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time to reach 140 °C (s)</th>
<th>Time to reach 300 °C (s)</th>
<th>Time to reach Max (s)</th>
<th>Maximum temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>540</td>
<td>875</td>
<td>1200</td>
<td>358</td>
</tr>
<tr>
<td>PL+PA</td>
<td>266</td>
<td>480</td>
<td>1180</td>
<td>418</td>
</tr>
<tr>
<td>PL+EM</td>
<td>385</td>
<td>738</td>
<td>1200</td>
<td>397</td>
</tr>
<tr>
<td>PL+BS</td>
<td>310</td>
<td>480</td>
<td>831</td>
<td>459</td>
</tr>
</tbody>
</table>
4.6.2 Samples prepared by the immersion method

The cone calorimetric results of the samples prepared by immersion are presented in Figure 4.18 and Table 4.14. Compared to the results of control PL which did not ignite, all immersed samples had one major peak of HRR as shown in Figure 4.18(a), which was attributed to the prompt release of PCM absorbed on the surface of materials. PL_PA ignited at 21 s, and a very high PHRR of 539 kW/m² was generated, producing 133.5 MJ/m² of THR and losing 29.3% mass. High EHC (15.1 MJ/kg) of this sample reflects the high flammability of PA. PL_EM had the shortest TTI, 4 s, and burned with PHRR of 448 kW/m² and a mass loss of 32.3%. However, its lowest THR (102 MJ/m²) and EHC (10.1 MJ/kg) values among all samples indicate its better fire performance as also seen from samples prepared by the direct incorporation method. Whereas, PL_BS ignited earlier than PL_PA at 13 s with a burning time less than those observed for PL_PA and PL_EM. PL_BS burned with the lowest PHRR of 375 kW/m² compared to other immersion samples with mass loss similar to PL_EM, this was due to the flaming drips and once they had dropped away, they kept burning outside. The samples prepared by the immersion method had more total mass loss compared to the control PL and also those prepared by the direct incorporation method. This is due to higher concentrations of PCMs absorbed in these samples.

After the flammability test, PL showed minimal external damage and no significant cracks were observed as shown in Figure 4.19, whereas, all PL_PCMs exhibited considerable cracks on the surface. This external surface damage was higher than those of samples prepared by the direct incorporation method.

![Figure 4.18: Cone calorimetric results of PL and PL_PCMs samples at 70 kW/m²: (a) HRR and (b) mass loss curves as a function of time](image-url)
Table 4.14: Cone calorimetric results of PL and PL immersed in PCMs at 70 kW/m$^2$ external heat flux

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI (s)</th>
<th>FOT (s)</th>
<th>Mass loss (%)</th>
<th>PHRR (kW/m$^2$)</th>
<th>THR (MJ/m$^2$)</th>
<th>EHC (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>----</td>
<td>----</td>
<td>16.5±0.23</td>
<td>----</td>
<td>0.5±0.5</td>
<td>0.2±0.1</td>
</tr>
<tr>
<td>PL_PA</td>
<td>21±1</td>
<td>648±1</td>
<td>29.3±0.7</td>
<td>539±70</td>
<td>133.5±9</td>
<td>15.1±1</td>
</tr>
<tr>
<td>PL_EM</td>
<td>4±1</td>
<td>683±2</td>
<td>32.3±0.6</td>
<td>448±28</td>
<td>102±10</td>
<td>10.1±0.6</td>
</tr>
<tr>
<td>PL_BS</td>
<td>13±1</td>
<td>635±1</td>
<td>32±1</td>
<td>375±15</td>
<td>109.2±8</td>
<td>12.2±0.5</td>
</tr>
</tbody>
</table>

Figure 4.19: Images of PL and PL immersed in PCMs after cone test (70 kW/m$^2$): (a) PL, (b) PL_PA, (c) PL_EM and (d) PL_BS

The temperature changes of the unexposed surface of sample as a function of time during the test for 20 min are illustrated in Figure 4.20. Table 4.15 shows the times measured and the maximum temperatures as explained in the previous section. Due to ignition and burning, the temperature rose rapidly particularly from 32 s onwards. Trends in the rises of temperature in the various types of samples are reflections of respective heat release rate versus time curves. The time taken to reach 140 and 300 °C and the maximum temperature at unexposed surface are higher than for samples prepared by the direct incorporation method because of burning on the surface was higher and when the absorbed PCMs were burnt, cracks were created, reducing the thermal conductivity of the PL.

While PL_PA and PL_BS samples took almost the same time to reach the temperatures of 140 and 300 °C, PL_EM took longer. After dehydration and release/burning of PCM, PL_BS had the maximum temperature during test, 470 °C at 1017 s then PL_PA. The
longest taken time to reach the maximum temperature and the lowest temperature rise was found in PL_EM, similar to the results for samples prepared by the direct incorporation method.

Figure 4.20: Temperature versus time curves of the reverse surfaces of PL and PL_PCM samples on cone exposure at 70 kW/m² heat flux in vertical orientation

Table 4.15: Temperature changes measured at unexposed surface of PL without/with PCMs prepared by immersion method to cone heater

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time to reach 140 °C (s)</th>
<th>Time to reach 300 °C (s)</th>
<th>Time to reach Max °C (s)</th>
<th>Maximum temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>540</td>
<td>875</td>
<td>1200</td>
<td>358</td>
</tr>
<tr>
<td>PL_PA</td>
<td>365</td>
<td>560</td>
<td>1150</td>
<td>420</td>
</tr>
<tr>
<td>PL_EM</td>
<td>429</td>
<td>775</td>
<td>1200</td>
<td>408</td>
</tr>
<tr>
<td>PL_BS</td>
<td>361</td>
<td>548</td>
<td>1017</td>
<td>470</td>
</tr>
</tbody>
</table>

From these results, it can be concluded that the samples prepared by the direct incorporation method had better fire performances than those prepared by the immersion method, shown by the lower PHRR, THRR, mass loss and EHC as shown in Figures 4.21-4.23. The reason is that the amount of PCM in the immersion method is higher and also the concentration of PCM on the surface of the sample is greater [16].
4.7 Thermal energy performance of PCMs in plasterboard

To determine how quickly the heat can be stored and released from the PCM containing PL, a cube of dimension 100 mm x 100 mm x 100 mm was constructed using six pieces of PL, the top board of which was the one containing PCMs. Thermocouples were used to
measure the temperatures in heating and cooling modes as discussed in Section 3.4.6 (Chapter 3). Figures 4.24 and 4.25 illustrate temperatures measured at the bottom of the top board (containing PCMs) of the cube as a function of time, while the cube was heated inside the binder temperature test chamber from 20 °C to 50 °C, kept at 50 °C for 25 min and then cooled to 6 °C for samples without and with PCMs by direct incorporation (Figure 4.24) and immersion methods (Figure 4.25). During the heating cycle, the samples in each method had almost the same rise of temperature except the sample prepared containing PA, which showed a slower temperature rise, especially during the 25-37 °C range, which is due to the high latent heat of the melting process. Other PCMs had melting point < 20 °C, hence this effect is not observed. All PCM containing samples had slightly lower maximum temperature (peak temperature) reached during the test. The differences in the peak temperatures between PCM containing samples and PL are given in Table 4.16, where it can be seen that the values for samples prepared by the direct incorporation method were in the order of:

\[
\text{PL+PA} = \text{PL+BS} > \text{PL+EM}
\]

In the immersion method, the differences between peak temperatures of immersed samples and PL were higher than those prepared by the direct incorporation method except for PL_EM, where values were similar. These results confirm also that the immersed samples had more stored heat than additive samples, due to higher PCM contents in the former. These results are in agreement with the DSC results in terms of measured latent heat. The highest stored heat was observed for the PA in the sample of PL_PA, hence, it had the lowest peak temperature compared to PL, which is in agreement with its thermal properties measured by DSC. The highest peak temperature was found in PL_EM similar to direct incorporation method which indicated this sample did not absorb much heat, corresponding to their low latent heat measured using DSC. However, the PCM used reduced the fluctuation temperature by decreasing the peak temperature, the difference in peak temperature compared to PL as shown in Table 4.16 was in the order of:

\[
\text{PL_PA} > \text{PL_BS} > \text{PL_EM}
\]

In cooling cycles, the derived data from Figures 4.24 and 4.25 is presented in Table 4.17. This table contains the time taken to decrease the temperature from set points, specific to each PCM. The temperature range was selected 4 °C below the freezing point of a PCM. The quantity of heat, release of which is delayed during the freezing of the PCM in arbitrary units has been calculated by integrating the areas under the temperature-time
curves between chosen points either side of the freezing point of PCM (set-points given in Table 4.17) and subtracting the area under the temperature-time curve for the reference material, PL between the same set-points. The values are given in Table 4.17. These curves showed similar onset of freezing temperatures to DSC tests when the material changes its phase from liquid to solid to release the absorbed heat. PCM containing samples took more time than PL to release the stored heat [31]. The delayed heat release values show that the PA containing sample has a higher value compared to other samples, which was also seen by DSC results. Moreover, this delayed heat release in immersed samples was much higher than direct incorporated samples.

The PCM immersed samples took a longer time than that of PL and additive samples to decrease the temperature. Consequently, the releasing of absorbed heat from immersed samples was much slower than other samples because the PCMs could delay the heat transfer rate from outer surface to inner surface [32-35] as a result of decrease in thermal conductivity. PL’s thermal conductivity range of 0.25 W/m.k at room temperature [30] and PCMs have poor thermal conductivity (0.1-0.3 W/m.k) [36-37], which could decrease heat transfer and may contribute to low temperature changes. Moreover, the greater the amount of PCM absorbed, the higher amount of energy stored and released, similar to that seen in the DSC results.

![Figure 4.24: Comparison of temperatures measured at the bottom of top board of cube as a function of time between control sample PL and PL+PCM](image)

Figure 4.24: Comparison of temperatures measured at the bottom of top board of cube as a function of time between control sample PL and PL+PCM
Figure 4.25: Comparison of temperatures measured at the bottom of top board of cube as a function of time between control sample PL and PL_PCM

Table 4.16: The peak temperature reduction of the direct incorporation and immersed samples compared to PL

<table>
<thead>
<tr>
<th>Sample</th>
<th>PL+PA</th>
<th>PL_PA</th>
<th>PL+EM</th>
<th>PL_EM</th>
<th>PL+BS</th>
<th>PL_BS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak reduction (°C)</td>
<td>0.6</td>
<td>2.7</td>
<td>0.2</td>
<td>0.2</td>
<td>0.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 4.17: The time interval and delayed heat release at which the surface temperature of PCM plaster reached the determined set points during cooling cycle

<table>
<thead>
<tr>
<th>Set points</th>
<th>28-24 °C</th>
<th>18-14 °C</th>
<th>21-17 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>PL</td>
<td>PL+PA</td>
<td>PL_PA</td>
</tr>
<tr>
<td>Time (s)</td>
<td>396</td>
<td>840</td>
<td>1260</td>
</tr>
<tr>
<td>Delayed heat release (AU)</td>
<td>---</td>
<td>2782</td>
<td>9826</td>
</tr>
</tbody>
</table>

These results indicate that these PCMs are an effective way of storing energy to be applied in building materials. The immersion method is much better than direct incorporation method in terms of reducing the peak temperature and releasing the stored energy, since the immersion method leads to the incorporation of more PCM.

4.8 Conclusion

In this chapter, two techniques are used to integrate PCMs into PL: immersion and direct incorporation. The SEM results indicated good dispersion of PCMs. The DSC results indicated that among the PCMs used, PA has the highest latent heat. The latent heats of
melting and freezing of PCMs were reduced in PCM containing PL samples. The TGA results revealed that the PCMs are thermally stable up to 100 °C. The mechanical properties of PL are reduced more when PCMs are incorporated by the direct incorporation method than by the immersion method. Cone calorimeter testing indicates that the addition of PCM makes the PL (which does not itself ignite) flammable. The immersion samples show more severe fire performance than direct incorporation samples because the % PCMs absorbed is higher and also the concentration of PCM on the surface of the sample is more. All PCMs however, showed good thermal energy storage performance, the best being PA.

4.9 References


Bastami, M.; Chaboki-Khiabani, A.; Baghbadrani, M.; Kordi, M. "Performance of high strength concretes at elevated temperatures". Scientia Iranica. 2011, 18, 5, 1028–1036.


CHAPTER FIVE

Phase Change Materials Incorporation in Carrier Materials

In Chapter 4 PCMs were added to PL by addition or immersion methods. Both of these have limitations such as non-uniform dispersion and chances of leakage, in particular with the immersion method. To overcome these problems, carrier materials for PCMs were used to prepare form-stable PCM composites, which were then incorporated into PL. The PCMs of PA, EM and BS were mixed with the porous carrier materials namely nanoclay (NC), diatomaceous earth (DE), expanded perlite (EP), fly ash (FA) and brick dust (BD). The absorption of PCMs in carrier materials was studied by scanning electron microscopy. The selected form-stable PCMs composites were named as PA-NC, PA-DE, PA-EP, PA-FA, PA-BD, EM-EP, EM-BD, BS-EP and BS-BD. These composite PCMs were incorporated then into PL to form samples: PL+PA-NC, PL+PA-DE, PL+PA-EP, PL+PA-FA, PL+PA-BD, PL+EM-EP, PL+EM-BD, PL+BS-EP and PL+BS-BD. The thermal, flammability and mechanical performances of these samples are discussed in this chapter.

5.1 Form-stable PCMs composites and incorporation in plasterboards: physical and morphological properties

Each PCM was mixed with a carrier material, the maximum mass fractions of PA, EM and BS that could retain in the carrier materials was observed by a leakage test and latent heats of melting / freezing. The visual leakage test was applied by heating the blends at least 10 °C above the melting temperature of PCM to observe if there was any leakage.

5.1.1 Paraffin composites

Liquid PA was mixed with NC, DE, EP, FA and BD at room temperature. The optimum mass fraction of PA without leakage was observed to be 60, 60, 60, 40 and 20% in the blends PA-NC, PA-DE, PA-EP, PA-FA and PA-BD respectively (Section 3.2.4.1 (Chapter 3)) as shown in Table 5.1, similar attempts were made by other researchers to mix PA with NC [1], DE [2-4] and EP [5-6]. The SEM images of NC, DE, EP, FA, BD, PA-NC, PA-DE, PA-EP, PA-FA and PA-BD are shown in Figure 5.1. Figure 5.1(a) shows the microstructure of NC particles, which is similar to that observed of control sample (powder PL) (Figure 4.3(a)), please note that the NC was used as received, not dispersed in a
solvent to make a nanocomposite, hence these are micro sized clay particles. From Figure 5.1(b) it can be seen that NC particles were thoroughly covered with PA as a result of capillary action. The particles of NC were clearly shrunken after absorption compared to that of NC before absorption. Figure 5.1(d) indicated that the DE particles are smaller in size than NC particles. It can be also seen from Figure 5.1(e) that the PA was uniformly absorbed in the layer structure of DE because its porosity, reported in literature is in the range 35-65% [7]. Smaller particles of DE will provide larger surface area and hence better absorption.

Figure 5.1: SEM images of (a) NC, (b) PA-NC, (c) PL+PA-NC, (d) DE, (e) PA-DE, (f) PL+PA-DE, (g) EP, (h) PA-EP, (i) PL+PA-EP, (j) FA, (k) PA-FA, (l) PL+PA-FA, (m) BD, (n) PA-BD and (o) PL+PA-BD
Figure 5.1(g) demonstrated that the EP had a highly porous structure (88-94%) [8-9] which contributed to better absorption of molten PA without leakage as can be also seen from Figure 5.1(h) that the EP particles were covered by PA. Figure 5.1(j) demonstrated that the FA which had porosity less than EP (45-55%) [10] had spherical particles of < 20\(\mu\)m diameters. With the addition of PA, the FA particles were completely coated by PA as shown in Figure 5.1(k). It can be seen from Figure 5.1(m) that BD has a very compact structure of low porosity (26%) [11]. Figure 5.1(n) showed that PA was not absorbed within BD and some of PA particles were seen at the surface of BD particles. Therefore, this segregation between particles could be attributed to the low porosity and permeability of BD to absorb PA. PA particles were solidified at the surface of BD as the melting temperature of PA was around 27 °C, i.e. above room temperature.

All of these form-stable PCMs composites were incorporated in PL, the concentration of each was adjusted to maintain 10% of PA in the PL. Compositions of all samples are shown in Table 5.1, 16.7 wt% of PA-NC, 16.7 wt% of PA-DE, 16.7 wt% of PA-EP were mixed with PL and water in the ratio of 0.41:2.09:1 to form the samples of PL+PA-NC, PL+PA-DE, PL+PA-EP, respectively. 25 wt% of PA-FA and 50 wt% of PA-BD were also mixed with plaster and water in the ratio of 0.62:1.88:1 and 1.25:1.25:1 respectively to form the samples of PL+PA-FA and PL+PA-BD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PA (wt%)</th>
<th>PA Composite (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-NC</td>
<td>60</td>
<td>16.7</td>
</tr>
<tr>
<td>PA-DE</td>
<td>60</td>
<td>16.7</td>
</tr>
<tr>
<td>PA-EP</td>
<td>60</td>
<td>16.7</td>
</tr>
<tr>
<td>PA-FA</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>PA-BD</td>
<td>20</td>
<td>50</td>
</tr>
</tbody>
</table>

The SEM images of the PL+PA-NC, PL+PA-DE, PL+PA-EP, PL+PA-FA and PL+PA-BD are shown in Figure 5.1 (c,f,I,l and o), which demonstrates that the form-stable PCMs composites were uniformly dispersed in PL.

5.1.2 Eutectic mixture composites

The carrier materials NC, DE and FA could not hold EM and the EM leaked out as discussed in Section 3.2.4.2 (Chapter 3). The optimum mass percentages of EM retained in
the EP and BD without leakage were found to be 60% and 20% respectively as shown in Table 5.2, similar to what has been reported previously by Sari and Karaiskeli [12] for CA, Sari et al for LA [13] and Jiesheng et al for LA [14]. The SEM images of EM-EP and EM-BD shown in Figure 5.2 (a,c) illustrate that EM was uniformly dispersed in both EP and BD. 10% of EM in the form-stable composite of 16.7 wt% of EM-EP and 50 wt% of EM-BD was mixed with PL and water in the ratio of 0.41:2.09:1 and 1.25:1.25:1 respectively to form the samples of PL+EM-EP and PL+EM-BD (Table 5.2).

The SEM images of PL+EM-EP and PL+EM-BD are presented in Figure 5.2. It can be observed from Figure 5.2(b) that the composite EM-EP was dispersed uniformly in PL. However, some of EM leaked out of PL during mixing with EM-BD, which was visually noted. The reason was attributed to the low porosity of BD which did not have enough surface area to contain EM.

Table 5.2: Optimum mass fraction of EM retained in carrier materials and percentage of form-stable EM composite incorporated into PL

<table>
<thead>
<tr>
<th>Sample</th>
<th>EM (wt%)</th>
<th>EM Composite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EM-EP</td>
<td>60</td>
<td>16.7</td>
</tr>
<tr>
<td>EM-BD</td>
<td>20</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 5.2: SEM images (a) EM-EP, (b) PL+EM-EP, (c) EM-BD and (d) PL+EM-BD
5.1.3 Butyl stearate composites

The blends of BS-NC, BS-DE and BS-FA were sticky due to the leakage of BS as explained in Section 3.2.4.3 (Chapter 3). The optimum mass percentages of BS contained in the EP and BD without leakage were observed to be 60% and 20% respectively (see Table 5.3). The SEM images of BS-EP and BS-BD are shown in Figure 5.3, where it can be observed that the particles of EP are completely covered by BS because of the high porosity of EP as explained before whereas the low porosity of BD led to leaking out of some BS. In order to maintain 10% of BS in PL, 16.7 wt% of BS-EP and 50 wt% of BS-BD were mixed with PL and water in the mass ratios of 0.41:2.09:1 and 1.25:1.25:1 respectively to form the samples PL+BS-EP and PL+BS-BD respectively (Table 5.3). It can be observed from Figure 5.3(b) that the composite of BS-EP was rather appropriate with PL and also composites were uniformly dispersed in PL. On the other hand, Figure 5.3(d) exhibited that BS leaked out of the BS-BD particles in the PL.

Table 5.3: Optimum mass fraction of BS retained in carrier materials and percentage of form-stable BS composite incorporated into PL

<table>
<thead>
<tr>
<th>Sample</th>
<th>BS (wt%)</th>
<th>BS Composite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS-EP</td>
<td>60</td>
<td>16.7</td>
</tr>
<tr>
<td>BS-BD</td>
<td>20</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 5.3: SEM images of (a) BS-EP, (b) PL+BS-EP, (c) BS-BD and (d) PL+BS-BD
5.2 Thermal characterization of form-stable PCMs composites

5.2.1 Form-stable paraffin composites

The DSC results for PA, PA-NC, PL+PA-NC, PA-DE, PL+PA-DE, PA-EP, PL+PA-EP, PL-FA, PL+PA-FA, PA-BD and PL+PA-BD are presented in Figure 5.4. As discussed in the previous chapter, the endothermic transitions during the heating process represent melting while exothermic transitions during cooling represent freezing. The derived data of onset of melting temperature from the endothermic peaks, onset of freezing temperature from the exothermic peaks and latent heats of melting and of freezing from areas under the peaks are summarized in Table 5.4.

The results showed that the onset of melting temperatures of PA-NC, PA-DE, PA-EP, PA-FA, and PA-BD composites were measured to be 27.5, 27.7, 27.9, 28.3 and 27.4 °C, respectively. Whereas, the onset of freezing temperatures were found to be 27.1, 27.3, 27.5, 27.5 and 27.3 °C, respectively. Both of the melting and freezing temperatures of PA in the composites were almost similar to that of pure PA and were in the range of human comfort temperature. Moreover, it can be also indicated from the Figures and Table 5.4 below that the latent heats of melting of PA in the composites were measured to be 143.5, 145.8, 143.9, 97.8 and 48.7 J/g, respectively, while the latent heats of freezing were 140.7, 153.6, 150.4, 97.9 and 48.9 J/g, respectively. The calculated latent heat of PA in the composites based on the mass fraction of PA was almost similar to that of measured latent heat values by DSC as shown in Table 5.4. The slight difference between them could be due to the different PA batches used in different samples. These results indicated that the measured latent heat of PA in the composites by DSC was in agreement with the optimum mass fraction of PA mixed with carrier materials.

In terms of the thermal properties of PA in the composites PL+PA-NC, PL+PA-DE, PL+PA-EP, PL+PA-FA and PL+PA-BD, the melting and freezing temperatures are similar to those of pure PA and PA-carrier material composites. Furthermore, the derived latent heats of melting and of freezing are reduced compared to that of pure PA, the extent of reduction though depends on the carrier material used. For sample PL+PA in Chapter 4 the derived heats of melting and freezing were observed to be 99.7 and 93.1 J/g, respectively. Here while the values are less than PL+PA-NC, much higher values are obtained for PL+PA-DE and PL+PA-EP as depicted in Table 5.4. The samples can be ranked as:
PL+PA-DE > PL+PA-EP > PL+PA-FA > PL+PA-BD > PL+PA-NC

These results indicate that DE and EP, while they absorb PA, allow sufficient aggregation of PA molecules to act as efficient PCMs, due to the high porosity of EP and DE as explained in Section 5.1.1. This porosity is lower in FA, BD and NC which led to decreases in the latent heat values due to some PA absorbed in these carrier materials leaking out into PL during mixing particularly during use of NC particles.
Figure 5.4: DSC curve of the (a) PA-NC, (b) PL+PA-NC, (c) PA-DE, (d) PL+PA-DE, (e) PA-EP, (f) PL+PA-EP, (g) PA-FA, (h) PL+PA-FA, (i) PA-BD and (j) PL+PA-BD
Table 5.4: Thermal Properties of PA by DSC

<table>
<thead>
<tr>
<th>PCM</th>
<th>PA (%)</th>
<th>Melting temp (°C)</th>
<th>Freezing temp (°C)</th>
<th>Latent heat of melting (J/g)</th>
<th>Latent heat of freezing (J/g)</th>
<th>*Derived latent heat of melting (J/g)</th>
<th>*Derived latent heat of freezing (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>100</td>
<td>27.7</td>
<td>27.1</td>
<td>243</td>
<td>250</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PA-NC</td>
<td>60</td>
<td>27.5±0.1 (33.7)</td>
<td>27.1±0.04 (21.8)</td>
<td>143.5±2</td>
<td>140.7±3</td>
<td>239.2</td>
<td>234.5</td>
</tr>
<tr>
<td>PL+PA-NC</td>
<td>10</td>
<td>27.4±0.15 (30.5)</td>
<td>27.2±0.1 (21)</td>
<td>12.9±0.3</td>
<td>12.8±0.2</td>
<td>129.3</td>
<td>128.4</td>
</tr>
<tr>
<td>PA-DE</td>
<td>60</td>
<td>27.7±0.3 (33.6)</td>
<td>27.3±0.1 (22)</td>
<td>145.8±3</td>
<td>153.6±1</td>
<td>243</td>
<td>256</td>
</tr>
<tr>
<td>PL+PA-DE</td>
<td>10</td>
<td>27.6±0.1 (31.2)</td>
<td>27.3±0.1 (22)</td>
<td>22.1±1</td>
<td>22.3±1</td>
<td>221</td>
<td>222.5</td>
</tr>
<tr>
<td>PA-EP</td>
<td>60</td>
<td>27.9±0.2 (33.2)</td>
<td>27.5±0.2 (22.9)</td>
<td>143.9±3</td>
<td>150.4±1</td>
<td>240</td>
<td>250</td>
</tr>
<tr>
<td>PL+PA-EP</td>
<td>10</td>
<td>27±0.2 (31)</td>
<td>27.2±0.1 (23)</td>
<td>21.3±2</td>
<td>21.8±2</td>
<td>212.7</td>
<td>217.6</td>
</tr>
<tr>
<td>PA-FA</td>
<td>40</td>
<td>28.3±0.2 (31.4)</td>
<td>27.5±0.1 (23)</td>
<td>97.8±3</td>
<td>97.9±2</td>
<td>245</td>
<td>245</td>
</tr>
<tr>
<td>PL+PA-FA</td>
<td>10</td>
<td>27.6±0.2 (31.3)</td>
<td>27.4±0.2 (23)</td>
<td>17.7±1</td>
<td>17.9±2</td>
<td>176.6</td>
<td>179.3</td>
</tr>
<tr>
<td>PA-BD</td>
<td>20</td>
<td>27.4±1 (31.7)</td>
<td>27.3±2 (23.7)</td>
<td>48.7±1</td>
<td>48.9±1</td>
<td>244</td>
<td>244</td>
</tr>
<tr>
<td>PL+PA-BD</td>
<td>10</td>
<td>27.6±0.2 (30.5)</td>
<td>27.4±0.2 (23)</td>
<td>17.1±0.5</td>
<td>15.7±1</td>
<td>171</td>
<td>157</td>
</tr>
</tbody>
</table>

- Average of two replicate results

Values in italics and brackets are melting and freezing temperatures measured when PCM completely changes its phase at the end of the peak.

* = Calculated based on mass fraction of PCM in PL

The specific heat values of PA with carrier materials shown in Figure 5.5 were in agreement with latent heat values during phase transitions from solid to liquid and decreased compared to pure PA due to the maximum content of PA in the composites being equal to or less than 60%. These values were decreased much during PL+PA-carrier materials and the carrier materials used did not show any ability to store heat.
Figure 5.5: DSC curves showing specific heats vs. temperature of PA, carrier materials, PA-carrier materials and PL+PA- carrier material composite (all figures are in the same order)

5.2.2 Form-stable eutectic mixture composites

As can be seen from Figure 5.6 and Table 5.5, the onset of melting and freezing temperatures, and derived latent heats of melting and of freezing of EM in the EM-EP composite were similar to those of EM alone. However, in the PL+EM-EP, the melting temperate was recorded at 16.8 °C and the derived latent heats of melting and freezing were considerably reduced due to some leakage of EM from the EP and its dispersion in
PL. In the EM-BD, while the melting point was unchanged, the latent heats of melting and freezing were reduced compared to EM alone. Whereas, the melting temperature of EM in PL+EM-BD was decreased to $15.2 \, ^\circ\text{C}$ and the freezing temperatures was the same as for pure EM but the derived latent heats of melting and freezing were drastically reduced to $15.8 \, \text{J/g}$ and $0.7 \, \text{J/g}$, respectively.

These results show that EM is absorbed thoroughly in porous EP as also seen from SEM image of EM-EP (Figure 5.2 (a)), and to a slightly lesser extent in BD (see Figure 5.2 (b)), but when these are dispersed in PL, EM disperses uniformly largely as individual molecules and its melting/freezing capability as a material is lost.

![DSC curves of the (a) EM-EP, (b) PL+EM-EP, (c) EM-BD and (d) PL+EM-BD composites](image)

Figure 5.6: DSC curves of the (a) EM-EP, (b) PL+EM-EP, (c) EM-BD and (d) PL+EM-BD composites
Table 5.5: Thermal Properties of EM by DSC

<table>
<thead>
<tr>
<th>PCM</th>
<th>EM</th>
<th>Melting temp (%)</th>
<th>Melting temp (°C)</th>
<th>Freezing temp (°C)</th>
<th>Latent heat of melting (J/g)</th>
<th>Latent heat of freezing (J/g)</th>
<th>*Derived latent heat of melting (J/g)</th>
<th>*Derived latent heat of freezing (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EM</td>
<td>100</td>
<td>18.5</td>
<td>18.7</td>
<td>152.5</td>
<td>151.5</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>EM-EP</td>
<td>60</td>
<td>18.9±0.1</td>
<td>18.8±0.2</td>
<td>90.7±2</td>
<td>91.5±2</td>
<td>151.1</td>
<td>152.5</td>
<td></td>
</tr>
<tr>
<td>PL+EM-EP</td>
<td>10</td>
<td>16.8±0.3</td>
<td>22±1</td>
<td>2.9±0.2</td>
<td>2.3±0.2</td>
<td>29.4</td>
<td>23.3</td>
<td></td>
</tr>
<tr>
<td>EM-BD</td>
<td>20</td>
<td>18.9±2</td>
<td>18.9±0.2</td>
<td>27.6±1</td>
<td>28±2</td>
<td>137.7</td>
<td>139.9</td>
<td></td>
</tr>
<tr>
<td>PL+EM-BD</td>
<td>10</td>
<td>15.2±1</td>
<td>18.5±2</td>
<td>1.6±0.4</td>
<td>0.07</td>
<td>15.8</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

- Average of two replicate results
- Values in italics and brackets are melting and freezing temperatures measured when PCM completely change its phase at the end of the peak

*= Calculated based on mass fraction of PCM in PL

The specific heat curves of samples during heating process shown in Figure 5.7 correspond with their latent heats.

![DSC curves showing specific heats vs. temperature](image)

Figure 5.7: DSC curves showing specific heats vs. temperature of (a) EM, EP, EM-EP and PL+EM-EP and (b) EM, BD, EM-BD and PL+EM-BD composites (all figures are in the same order)

5.2.3 Form-stable butyl stearate composites

It can be clearly seen from Figure 5.8 and Table 5.6 that the BS in all composites had
several peaks during heating and cooling processes. The first small peak occurred around 7.5 °C during heating process and the second small peak was observed at around 10.3 °C during cooling process, representing the glass transition temperature of BS (solid-solid BS). However, the main peak illustrates the phase change of solid-liquid and vice versa, corresponding to the absorption and releasing of latent heat. The onset melting temperature, onset freezing temperature, latent heats of melting and freezing for both BS-EP and BS-BD were very similar to those of BS. When these were incorporated in PL, the melting and freezing temperatures remained unchanged, but the latent heats of melting and freezing were reduced, the reductions however, were not as drastic as seen in some other composites. Moreover, contrary to other composites, BD containing composites (PL+BS-BD) showed similar results to EP containing composites (PL+BS-EP), which indicates that absorption of BS in the composites leads to sufficient aggregation of BS to allow normal melting/freezing to occur, this effect can be seen from SEM images in Figures 5.3(c) and 5.3(d).
Table 5.6: Thermal Properties of butyl Stearate by DSC

<table>
<thead>
<tr>
<th>PCM</th>
<th>BS</th>
<th>Melting temp (%)</th>
<th>Melting temp (°C)</th>
<th>Freezing temp (°C)</th>
<th>Latent heat of melting (J/g)</th>
<th>Latent heat of freezing (J/g)</th>
<th>*Derived latent heat of melting (J/g)</th>
<th>*Derived latent heat of freezing (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS</td>
<td>100</td>
<td>17.6</td>
<td>20.9</td>
<td></td>
<td>113.2</td>
<td>112.2</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>BS-EP</td>
<td>60</td>
<td>18.3±0.1 (24)</td>
<td>21±0.2 (15)</td>
<td></td>
<td>68.8±1</td>
<td>69.2±1</td>
<td>114.6</td>
<td>115.3</td>
</tr>
<tr>
<td>PL+BS-EP</td>
<td>10</td>
<td>18.9±0.2 (22.9)</td>
<td>21.2±0.2 (17.8)</td>
<td></td>
<td>8.6±2</td>
<td>8.9±1</td>
<td>85.8</td>
<td>88.8</td>
</tr>
<tr>
<td>BS-BD</td>
<td>20</td>
<td>18.3±0.1 (22.8)</td>
<td>21.1±0.1 (16)</td>
<td></td>
<td>23.1±1</td>
<td>23±1</td>
<td>115.4</td>
<td>114.8</td>
</tr>
<tr>
<td>PL+BS-BD</td>
<td>10</td>
<td>18.6±0.2 (22.7)</td>
<td>21.2±0.1 (17.5)</td>
<td></td>
<td>9.6±0.3</td>
<td>10±0.3</td>
<td>96.2</td>
<td>99.6</td>
</tr>
</tbody>
</table>

- Average of two replicate results

Values in italics and brackets are melting and freezing temperatures measured when PCM completely change its phase at the end of the peak

*= Calculated based on mass fraction of PCM in PL

Figure 5.9 shows specific heat and shows that BS-EP was a little higher than BS-BD due to EP porosity is higher but PL+BS-BD was higher than PL+BS-EP, corresponding to latent heat results. In comparison with EM, the latent and specific heat values of BS were lower, which reduced latent heat of BS-EP and BS-BD compared to those of EM-EP and EM-BD. On the contrary, the latent and specific heats of BS in the PL+BS-EP and PL+BS-BD were higher than those observed in PL+EM-EP and PL+EM-BD because of the weak interaction.
between EM and PL. The latent heat value of PA was higher than those of EM and BS which clearly remained unchanged after mixing these PCMs with EP and were in the order of:

\[
\]

With the addition of PL, the latent heat values were greatly reduced

\[
\]

Figure 5.9: DSC curves showing specific heats vs. temperature of (a) BS, EP, BS-EP and PL+BS-EP composite and (b) BS, BD, BS-BD and PL+BS-BD composite (all figures are in the same order)
5.3 Thermal stability of form-stable PCM composite in Plaster

The thermal stabilities of the carrier materials, form-stable PCMs composites and form-stable PCMs composites incorporated into PL have been investigated using thermogravimetric (TGA) and differential temperature analysis (DTA) in air. The TGA and DTA curves are presented in Figures 5.10-5.35 and analysed results are given in Tables 5.7-5.12.

5.3.1 Carrier materials

The TGA and DTA analysis of the NC, DE, EP, FA and BD are presented in Figure 5.10 and Table 5.7. It can be observed from results that NC had two stages of mass loss, the major first stage occurred between 230 to 370 °C with mass loss of 22.2%. This was accompanied by the exothermic DTA peak at 360 °C, representing the decomposition of the organic modifier (dimethyl, dihydrogenated tallow, quaternary ammonium salt) used for NC. The second mass loss was observed between 370 to 710 °C, losing 16.1% of its mass with exothermic DTA peak at 642 °C, producing 61.7% residue at 750 °C. This was mainly attributed to the dehydroxylation of the clay layers [15].

DE, formed from silica, alumina and iron oxide, which do not burn, lost 7.8% of its mass during the first stage of mass loss between 70 to 260 °C giving an endothermic DTA peak at 174 °C. The second stage of mass loss was observed in the range of 260-720 °C, losing 2.4% of its mass, giving 89.8% residue at 750 °C. This was attributed to loss of absorbed moisture [12]. In EP, FA and BD, there is only small mass loss, which is expected as these do not have any components which can decompose or be oxidised in air as explained in Section 3.1.4 (Chapter 3). In EP, 2.8 % mass loss occurred between 70-690 °C leaving 97.2% residue at 750 °C. FA lost 4.1% of its mass during 420 to740 °C [16], producing 95.9% residue at 750 °C. BD lost only 1.8% mass during the test. These mass losses arise from loss of moisture. It can be observed from these TGA and DTA results that EP, FA and BD have a good thermal stability.
Figure 5.10: TGA (a), DTA (b) curves of NC, DE, EP, FA and BD from room temperature to 850 °C in air

Table 5.7: TGA and DTA results of NC, DE, EP, FA and BD

<table>
<thead>
<tr>
<th>Sample</th>
<th>TGA</th>
<th>DTA peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp Range</td>
<td>Mass loss</td>
</tr>
<tr>
<td></td>
<td>(°C)</td>
<td>(%)</td>
</tr>
<tr>
<td>NC</td>
<td>230-370</td>
<td>22.2</td>
</tr>
<tr>
<td></td>
<td>370-710</td>
<td>16.1</td>
</tr>
<tr>
<td>DE</td>
<td>70-260</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>260-700</td>
<td>2.4</td>
</tr>
<tr>
<td>EP</td>
<td>70-690</td>
<td>2.8</td>
</tr>
<tr>
<td>FA</td>
<td>420-740</td>
<td>4.1</td>
</tr>
<tr>
<td>BD</td>
<td>70-730</td>
<td>1.8</td>
</tr>
</tbody>
</table>

5.3.2 Form-stable PA composites in PL

The TGA and DTA results of PA-NC, PA-DE, PA-EP, PA-FA and PA-BD composites are presented in Figure 5.11 and Table 5.8. It can be seen from the results that there were three steps of mass loss for the sample PA-NC. The first step occurred in the range of 100-240 °C with mass loss of 59.5%, representing the release of the added PA. This main mass loss step was accompanied by the endothermic DTA peak at 215 °C. The second step took place from 240 to 360 °C with mass loss of 7.8%, assigned to the decomposition of the organic modifier of NC, showing an exothermic DTA peak at 358 °C. This was followed by the third mass loss step between 550 to 680 °C with mass loss of 5.5%, corresponding to the dehydroxylation of the clay layers as discussed in previous section, giving 26.9% residue at 750 °C. In all of these samples, there is a sharp mass loss between 100 -240 °C, which relates to the amount of PA present in each sample. In PA-DE, PA-EP, PA-FA and
PA-BD there is only one stage of mass loss. These results show that mass losses in these composites are as expected from a physical mixture of the components, shown by the calculated residue values in Table 5.8, which are similar to the experimental values. This indicates that there is no interaction between two components in these composites.

When this form stable composites was added to PL (samples PL+PA-NC, PL+PA-DE, PL+PA-EP, PL+PA-FA and PL+PA-BD), the shapes of the curves are very similar to that of the PL+PA as seen from Figure 5.12 and Table 5.9.

![Figure 5.11: TGA (a), DTA (b) curves of PA-NC, PA-DE, PA-EP, PA-FA and PA-BD from room temperature to 850 °C in air](image)

![Figure 5.12: TGA (a), DTA (b) curves of PL+PA-NC, PL+PA-DE, PL+PA-EP, PL+PA-FA and PL+PA-BD compared to PL+PA from room temperature to 850 °C in air](image)
Table 5.8: TGA and DTA results of PA, PA-NC, PA-DE, PA-EP, PA-FA and PA-BD

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp Range (°C)</th>
<th>Mass loss (%)</th>
<th>Residue (%)</th>
<th>Residue at 750 °C (%)</th>
<th>Max Temp (°C)</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>100-230</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>190</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA-NC</td>
<td>100-240</td>
<td>59.5</td>
<td>27.2</td>
<td>26.9 (24.7)</td>
<td>215</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>240-360</td>
<td>7.8</td>
<td></td>
<td></td>
<td>358</td>
<td>Exo</td>
</tr>
<tr>
<td></td>
<td>550-680</td>
<td>5.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA-DE</td>
<td>100-240</td>
<td>63.4</td>
<td>36.6</td>
<td>35 (35.9)</td>
<td>223</td>
<td>Endo</td>
</tr>
<tr>
<td>PA-EP</td>
<td>100-238</td>
<td>62.5</td>
<td>37.5</td>
<td>35.4 (38.9)</td>
<td>215</td>
<td>Exo</td>
</tr>
<tr>
<td>PA-FA</td>
<td>100-238</td>
<td>39.7</td>
<td>60.3</td>
<td>57.6 (57.5)</td>
<td>215</td>
<td>Endo</td>
</tr>
<tr>
<td>PA-BD</td>
<td>100-220</td>
<td>19.7</td>
<td>80.3</td>
<td>79.6 (78.6)</td>
<td>203</td>
<td>Endo</td>
</tr>
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</table>

Values in italics and brackets are calculated from individual component results.

Table 5.9: TGA and DTA results of PL+PA, PL+PA-NC, PL+PA-DE, PL+PA-EP, PL+PA-FA and PL+PA-BD

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp Range (°C)</th>
<th>Mass loss (%)</th>
<th>Residue (%)</th>
<th>750 °C (%)</th>
<th>Max Temp (°C)</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+PA</td>
<td>100-220</td>
<td>20</td>
<td>76.3</td>
<td>76.3</td>
<td>156</td>
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<tr>
<td></td>
<td>710-750</td>
<td>3.7</td>
<td></td>
<td></td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>PL+PA-NC</td>
<td>100-220</td>
<td>22.2</td>
<td>73.3</td>
<td>73.3</td>
<td>150</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>640-720</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PL+PA-DE</td>
<td>100-220</td>
<td>21.6</td>
<td>75.3</td>
<td>75.3</td>
<td>150</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>640-720</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PL+PA-EP</td>
<td>100-220</td>
<td>24.2</td>
<td>73</td>
<td>73</td>
<td>150</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>630-710</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PL+PA-FA</td>
<td>100-210</td>
<td>21.3</td>
<td>75.8</td>
<td>75.8</td>
<td>150</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>630-720</td>
<td>2.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PL+PA-BD</td>
<td>100-210</td>
<td>16.3</td>
<td>81.7</td>
<td>81.7</td>
<td>150</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>630-710</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From TGA and DTA results, the samples PL+PA-FA and PL+PA-BD showed best thermal stability in terms of residual mass, this is because the amount of BD and FA used was higher in these samples compared with the amounts of absorbents. The presence of organic modifier NC in PL+PA-NC decreased thermal stability. The thermal stability of PL+PA-DE was better than those of PL+PA-NC and PL+PA-EP.

5.3.3 Form-stable EM composites in PL

The obtained results of EM-EP and EM-BD composites from TGA and DTA analysis are
presented in Figure 5.13 and Table 5.10. EM-EP had one stage of mass loss between 100 to 210 °C losing 56% of its mass, which represented the amount of EM used in this mixture. The endothermic DTA peak was observed at 178 °C, corresponding to the release of EM, its residue was observed to be 43.4% at 750 °C. One mass loss step also has been observed in EM-BD between 100 –185 °C which represents the total amount of EM added. Its residue was higher than that of EM-EP because the percentage of BD used was much more than that of EP. EM-EP and EM-BD had calculated residue values close to their experimental values at 750 °C (see Table 5.10) which indicated no interaction between the components mixed. With the addition of PL, the mass loss steps have been changed to three in both PL+EM-EP and PL+EM-BD and the curves were similar to PL+EM. PL+EM-BD lost just 21.5% less than that of PL+EM-EP due to the percentage of BD added to EM is much higher than of EP to meet the percentage of EM used (10 wt%) in order to incorporate in PL as shown in Table 5.2. Both of them had residues higher than that of PL+EM due to the thermal stabilities of EP and BD.

![Figure 5.13: TGA (a), DTA (b) curves of PL+EM, EM-EP, PL+EM-EP, EM-BD and PL+EM-BD from room temperature to 850 °C in air](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>TGA</th>
<th>DTA peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp Range (°C)*</td>
<td>Mass loss (%)</td>
</tr>
<tr>
<td>EM</td>
<td>100-210</td>
<td>100</td>
</tr>
<tr>
<td>EM-EP</td>
<td>100-210</td>
<td>56</td>
</tr>
<tr>
<td>EM-BD</td>
<td>100-210</td>
<td>20.5</td>
</tr>
<tr>
<td>PL+EM</td>
<td>100-185</td>
<td>18.7</td>
</tr>
<tr>
<td></td>
<td>280-360</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>710-740</td>
<td>3.1</td>
</tr>
<tr>
<td>PL+EM-EP</td>
<td>100-180</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>280-360</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>650-720</td>
<td>2.5</td>
</tr>
<tr>
<td>PL+EM-BD</td>
<td>100-165</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>280-360</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>650-720</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Values in italics and brackets are calculated from individual component results

5.3.4 Form-stable BS composites in PL

Figure 5.14 and Table 5.11 exhibit the TGA and DTA results for BS-EP and BS-BD. It can be observed from these results that BS-EP and BS-BD had one stage of mass loss between 150-265 °C, with an exothermic DTA peak at 230 °C, representing the release of BS. BS-BD (80.5%) had a higher residue than BS-EP (40.6%) due to the amount of BD used which was higher than EP. These results were in agreement with the percentage of BS added and no interactions between components were observed from the calculated residue values which were close to the experimental values as shown in Table 5.11. Whereas, the incorporation of BS-EP and BS-BD in PL changed the mass loss steps from one to three, the shapes of the curves were very similar to that of the PL+BS. The only difference between them is the amounts of residue which were almost the same in PL+BS-EP and PL+BS, whereas the amount of residue from PL+BS-BD was higher due to the amount of BD being higher.
Figure 5.14: TGA (a), DTA (b) curves of PL+BS, BS-EP, PL+BS-EP, BS-BD and PL+BS-BD from room temperature to 850 °C in air

Table 5.11: TGA and DTA results of BS, PL+BS, BS-EP, PL+BS-EP, BS-BD and PL+BS-BD

<table>
<thead>
<tr>
<th>Sample</th>
<th>TGA</th>
<th>DTA peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp range</td>
<td>Mass loss (%)</td>
</tr>
<tr>
<td>BS</td>
<td>150-270</td>
<td>100</td>
</tr>
<tr>
<td>BS-EP</td>
<td>150-265</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BS-BD</td>
<td>150-265</td>
<td>18.4</td>
</tr>
<tr>
<td>PL+BS</td>
<td>100-170</td>
<td>14.4</td>
</tr>
<tr>
<td>PL+BS-EP</td>
<td>100-170</td>
<td>15</td>
</tr>
<tr>
<td>PL+BS-BD</td>
<td>100-170</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Values in italics and brackets are calculated from individual component results

From TGA and DTA results, it can be seen that the carrier materials EP, DE, FA and BD had good thermal stability at high temperatures but they did not change the thermal decomposition ranges of PCMs. Due to the decomposition of the organic modifier in NC, the thermal stability of NC was much lower than the others. The slight differences between PL+PA-EP, PL+EM-EP and PL+BS-EP could due to the non-uniformity of PCM absorbed or the experimental error.
5.4 Mechanical performance of PL containing form-stable PCM composites

5.4.1 PL-Form-stable PA composites

The flexural and compression properties results of the PL+PA-NC, PL+PA-DE, PL+PA-EP, PL+PA-FA and PL+PA-BD are presented in Figure 5.15 and the derived results are reported in Table 5.12 and compared with the control sample, PL+PA. It can be observed from Figure 5.15(a) that the trend of the curves was linear with R-squared ranging between 0.91 and 0.99. The flexural properties of PL were considerably decreased with the addition of form-stable composite PA compared to the control sample PL+PA. All PL samples containing form-stable composites failed to withstand the stress > 1.35 – 1.9 MPa and broke at the centre. This may be because the incorporation of any additives reduces the coherence between PL particles [17]. The highest flexural strength and modulus were observed in PL+PA-FA, which may be because the FA contains very fine particles as shown in the SEM results which increases the compactness in the PL by filling the spaces [18] and can be used to improve the workability of the PL. The flexural strengths measured for other tested samples were decreased compared to the control sample, although PL+PA and PL+PA-FA were almost the same after taking standard deviation into consideration for three replicate results. Whereas, the modulus of PL+PA-NC was similar to that of PL+PA-BD, it was less than those of PL+PA-DE and PL+PA-EP. These moduli were much lower than that observed for PL+PA and PL+PA-FA

It can be also observed that the compression properties of modified PL were lower compared to PL+PA due to the added form-stable composites, as shown in strain-stress behaviour of samples (Figure 5.15(b)) and Table 5.12. PL+PA-FA and PL+PA-NC samples had the maximum values of crushing strength and modulus, very close to the control PL+PA after taking standard deviation into account, whereas, the crushing strength results were significantly reduced (32.5%, 50.7% and 74%, respectively) for PL+PA-BD, PL+PA-DE and PL+PA-EP, and for modulus by 18%, 57.4% and 68.8%, respectively. From these results, PL+PA-FA showed good mechanical properties compared to the others as explained before. It can be concluded that the mechanical properties of samples were influenced by the particle size and decreased as also reported in literature [19-22] for DE, NC and EP. This is obvious in the PL+PA-EP compressive properties, due to the size of EP particles being of 0.8 mm thus contributing to the presence of large voids from which cracks could propagate as a result of applied load (see section 3.1.4).
Figure 5.15: Strain-stress curves from a) Three-point bending test and b) Compression test for control PL+PA and PL with form-stable PA composite

Table 5.12: Mechanical properties of control PL+PA and PL with form-stable PA composite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural properties</th>
<th>Compression properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stress-at-failure (MPA)</td>
<td>Modulus (GPA)</td>
</tr>
<tr>
<td>PL+PA</td>
<td>3.07±0.12</td>
<td>2.64±0.12</td>
</tr>
<tr>
<td>PL+PA-NC</td>
<td>1.36±0.15 (-55.7%)</td>
<td>1.13±0.04 (-57.2%)</td>
</tr>
<tr>
<td>PL+PA-DE</td>
<td>1.46±0.03 (-52.4%)</td>
<td>1.31±0.07 (-50.4%)</td>
</tr>
<tr>
<td>PL+PA-EP</td>
<td>1.53±0.08 (-50.2%)</td>
<td>1.34±0.05 (-49.2%)</td>
</tr>
<tr>
<td>PL+PA-FA</td>
<td>1.90±0.02 (-38.1%)</td>
<td>1.86±0.21 (-29.5%)</td>
</tr>
<tr>
<td>PL+PA-BD</td>
<td>1.39±0.12 (-54.7%)</td>
<td>1.13±0.08 (-57.2%)</td>
</tr>
</tbody>
</table>

- Average of three replicate results
- Values between brackets are the % reduction in mechanical properties of form-stable PA composite compared to PL+PA

5.4.2 PL- Form-stable EM composite

It can be observed from the results of PL+EM-EP and PL+EM-BD presented in Figure 5.16 and Table 5.13 that the addition of EP and BD significantly decreased the flexural...
strength of samples compared to PL+EM. The reductions were 47.5% and 51.3% in PL+EM-EP and PL+EM-BD, respectively and they had an almost similar trend to PL+PA-carrier materials (see Figure 5.15). Moreover, the reduction in flexural modulus was 59.6% and 24.4% in PL+EM-EP and PL+EM-BD, respectively. In compression mode, the compression properties were also drastically reduced as shown in Figure 5.16(b) and Table 5.13. The reduction for PL+EM-EP was higher than that for PL+EM-BD. The mechanical properties in PL+EM-BD were better than those of PL+EM-EP except for flexural strength. This because the diameter of EP particles used was much larger (0.8mm) than those of BD generating large voids in PL which weakened the coherence between PL particles leading to cracks as the result of applied load. Similar reductions have also been reported in the literature [23-24].

![Figure 5.16: Strain-stress curves from a) Three-point bending test and b) Compression test for control PL+EM and PL with form-stable EM composite](image)

**Table 5.13: Mechanical properties of control PL+EM and PL with form-stable EM composite**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural properties</th>
<th>Compression properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stress at failure (MPa)</td>
<td>Modulus at failure (GPa)</td>
</tr>
<tr>
<td>PL+EM</td>
<td>1.6±0.23</td>
<td>1.56±0.18</td>
</tr>
<tr>
<td>PL+EM-EP</td>
<td>0.84±0.02 (-47.5%)</td>
<td>0.63±0.02 (-59.6%)</td>
</tr>
<tr>
<td>PL+EM-BD</td>
<td>0.78±0.04 (-51.3%)</td>
<td>1.18±0.1 (-24.4%)</td>
</tr>
</tbody>
</table>

- Average of three replicate results
- Values between brackets are the % reduction in mechanical properties of PL with form-stable composite EM compared to PL+EM

135
5.4.3 PL- Form-stable BS composite

The results of the PL+BS-EP and PL+BS-BD in flexural and compression modes are given in Figure 5.17 and Table 5.14. With the addition of EP in sample PL+BS-EP, the flexural strength and modulus were reduced by 65% and 57%, respectively compared to those of PL+BS. Whereas with BD, the flexural strength was less than that observed in PL+BS-EP and its reduction was 60% compared to that of PL+BS. Its flexural modulus, 1.12GPa (54% reduction) was close to that observed in PL+BS-EP after taking standard deviation into account. In compression mode, with the carrier materials EP and BD, the crushing strength has deteriorated compared to PL+BS; the reductions were 86% and 54%, respectively. The modulus was also significantly decreased and the reduction for PL+BS-EP was much higher. The mechanical properties of PL+BS-BD were better than those of PL+BS-EP for the same reasons as those mentioned in sections 5.4.1 and 5.4.2.

![Figure 5.17: Strain-stress curves from a) Three-point bending test and b) Compression test for control PL+BS and PL with form-stable BS composite.](image)

![Table 5.14: Mechanical properties of control PL+BS and PL with form-stable BS composite](table)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural properties</th>
<th>Compression properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stress at failure (MPa)</td>
<td>Modulus at failure (GPa)</td>
<td>R²</td>
</tr>
<tr>
<td>PL+BS</td>
<td>2.86±0.65</td>
<td>2.43±0.5</td>
<td>0.99</td>
</tr>
<tr>
<td>PL+BS-EP</td>
<td>1.1±0.8 (-65%)</td>
<td>1.05±0.03 (-57%)</td>
<td>0.74</td>
</tr>
<tr>
<td>PL+BS-BD</td>
<td>1.15±0.04 (-60%)</td>
<td>1.12±0.06 (-54%)</td>
<td>0.83</td>
</tr>
</tbody>
</table>
- Average of three replicate results
- Values between brackets are the % reduction in mechanical properties of PL with form-stable BS composite compared to PL+BS

### 5.5 Fire performance of Plasterboard with incorporated form-stable PCMs composites

The flammability of the prepared samples by form-stable PCMs composites has been investigated using cone calorimetry at 70 kW/m\(^2\) external heat flux as described in Section 3.4.5 (Chapter 3). The curves of heat release rate (HRR) and mass loss as a function of time are graphically presented in Figures 5.18, 5.21 and 5.24. The derived results from these curves are given in Tables 5.15, 5.17 and 5.19. The curves of the temperature change measured at unexposed surface to cone heater using thermocouples as a function of time are presented in Figures 5.20, 5.23 and 5.26. The derived times taken to reach the temperature of 140 °C, 300 °C and maximum temperature at maximum time as explained in Section 4.6.1 (Chapter 4) during a fire from these curves are reported in Tables 5.16, 5.18 and 5.20. The images of samples after cone testing are explained in Figures 5.19, 5.22 and 5.25. It can be clearly observed from all sample results that there were two peaks of heat release rate (PHRR). The first peak was attributed to the release of PCM added to carrier materials and the second peak represented the delayed release of the PCM.

#### 5.5.1 Form-stable PA composites in PL

All of samples where form-stable PA composites were added to PL, ignited slightly later than PL+PA except the sample PL+PA-EP, which ignited at a similar time. All samples showed similar heat release curves to the PL+PA sample, with two peaks, the intensities of which varied from sample to sample, but were higher than that of PL+PA, indicating that the carrier materials were not effective in encapsulating the PA for long, hence, affecting the flammability of the PA. In these samples while the PA content is the same as in PL+PA (10%), in the form composite the additional amount of carrier material reduced the overall PL content in the samples. Since PL is inherently fire resistant, the samples with less amount of PL show higher flammability.

The cone calorimeter results of PL+PA-NC [25] in Figure 5.18(a) and Table 5.15 showed that PL+PA-NC had the longest ignition time at 48 s, and burned with a high PHRR, which may be that the organic modifier of the NC, contributing to burning as seen from the TGA
results. The first peak was of 159 kW/m² at 123 s and the second peak was of 169 kW/m² at 370 s, showing the highest THR of 51 MJ/m² and its EHC produced was 8.4 MJ/kg. The maximum mass loss rate was found to be 26.5% for the sample of PL+PA-NC, which is in agreement with TGA results because of the burning of organic modifier on the NC particles. The sample of PL+PA-DE ignited earlier than PL+PA-NC at 27 s, showing two PHRR, 156 kW/m² almost similar to PL+PA-NC at 68 s and 150 kW/m² at 370 s. This burning was slightly lower than PL+PA-NC because of DE has better thermal stability than NC, according to the TGA results. Although the burning time was almost the same as PL+PA-NC, its THR of 48.9 MJ/m² was similar after taking standard deviation into account and its EHC was 9.7 MJ/kg.

In the case of PL+PA-EP, it had the shortest ignition time at 11 s. However, once ignited, it burned with the lowest PHRR compared to others because EP is a non-flammable material, corresponding to the TGA results. Two PHRR have been recorded, the first peak of 128 kW/m² at 65 s and the second peak of 96 kW/m² at 360 s, releasing the lowest THR of 37 MJ/m² in spite of having the same burning time of PL+PA-NC and PL+PA-DE, producing 8.9 MJ/kg of EHC. These results revealed that the PL+PA-EP had better fire performance than others shown by the lower PHRR and THR. PL+PA-FA and PL+PA-BD, ignited at the same time of 23 s similar to PL+PA-DE and burned with two peaks lower than those for PL+PA-NC and PL+PA-DE with lower burning times particularly for PL+PA-BD which was the lowest. This indicated that both of them were less flammable than PL+PA-NC and PL+PA-DE shown by the lower first PHRR value in PL+PA-BD and the second PHRR value in PL+PA-FA. THR of PL+PA-FA was slightly higher although similar to that of PL+PA and its EHC was almost the same as for PL+PA-BD. The mass loss rate of PL+PA-FA was almost the same as for PL+PA-DE and PL+PA-EP after taking standard deviation into account. Whereas, PL+PA-BD has the minimum mass loss of 17.2% because of the percentage of PA-BD added to PL was the highest compared to other form-stable PA composites, PL+PA-FA and PL+PA-BD had mass loss rates similar to that observed by the TGA (see Table 5.9), which is attributed to the ability of FA and BD particles to have a good thermal stability.

On the whole, the mass loss behaviour measured using cone calorimetry was almost the same as that measured by TGA although these the former samples were heated quickly. The slight difference between them could be attributed to the heating rate of 10 °C/min which started from room temperature in TGA test, non-uniformity of PA absorbed in
carrier materials particles, impurity of PA and the related experimental errors. In the comparison with PL+PA, the mass loss rate of PL+PA-DE, PL+PA-EP and PL+PA-FA was almost the same as PL+PA after taking standard deviation into consideration, which indicated that these carrier materials of DE, EP and FA gave better fire performance than NC. After cone testing, the cracks were clearly observed on the both sides of samples such as PL+PA-NC, PL+PA-DE and PL+PA-EP (see Figure 5.19). Also, the external surface damage and colour change of PL with form-stable PA composites was observed due to the added PA. The surface distortion in these samples was almost similar to that of the PL+PA sample (see Figure 4.16).

(a) ![Cone calorimetric results of PL with form-stable PA composites samples and control PL+PA at 70 kW/m²](image)

(b) ![Mass loss curves as a function of time](image)

Figure 5.18: Cone calorimetric results of PL with form-stable PA composites samples and control PL+PA at 70 kW/m²: (a) HRR and (b) mass loss curves as a function of time

Table 5.15: Cone calorimetric results of PL with form-stable PA composites compared to control PL+PA at 70 kW/m² external heat flux

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI</th>
<th>FO</th>
<th>Mass loss</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>THR</th>
<th>EHC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(s)</td>
<td>(s)</td>
<td>(%)</td>
<td>PHRR</td>
<td>TFHRR</td>
<td>PHRR</td>
<td>TFHRR</td>
</tr>
<tr>
<td>PL+PA</td>
<td>13±1</td>
<td>565±1</td>
<td>22.3±1.6</td>
<td>79±19</td>
<td>60±7</td>
<td>125±20</td>
<td>160±14</td>
</tr>
<tr>
<td>PL+PA-NC</td>
<td>48±4</td>
<td>467±3</td>
<td>26.5±0.6</td>
<td>159±13</td>
<td>123±80</td>
<td>169±5</td>
<td>370±3</td>
</tr>
<tr>
<td>PL+PA-DE</td>
<td>27±3</td>
<td>464±5</td>
<td>24.6±0.8</td>
<td>156±17</td>
<td>68±10</td>
<td>150±12</td>
<td>370±10</td>
</tr>
<tr>
<td>PL+PA-EP</td>
<td>11±1</td>
<td>463±3</td>
<td>24.2±0.8</td>
<td>128±9</td>
<td>65±10</td>
<td>96±5</td>
<td>360±7</td>
</tr>
<tr>
<td>PL+PA-FA</td>
<td>23±2</td>
<td>416±2</td>
<td>23.9±0.6</td>
<td>157±4</td>
<td>49±5</td>
<td>119±12</td>
<td>333±31</td>
</tr>
<tr>
<td>PA+PA-BD</td>
<td>24±1</td>
<td>384±5</td>
<td>17.2±0.1</td>
<td>121±1</td>
<td>41±2</td>
<td>145±20</td>
<td>243±4</td>
</tr>
</tbody>
</table>

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Figure 5.19: Images of PL with form-stable PA composites after cone test (70 kW/m²): (a) PL+PA-NC, (b) PL+PA-DE and (c) PL+PA-EP

Figure 5.20 demonstrates the temperature change at the unexposed surface to the cone heater as a function of time. The times taken to reach the specified temperature mentioned previously. From these curves are reported in Table 5.16. Carrier materials used had low thermal conductivities as reported in literature [26-32]. All samples took a longer time to reach the temperatures of 140 and 300 °C than PL+PA except PL+PA-BD. This shows that while carrier materials could not reduce the flammability of the PA containing samples, they acted as insulators due to their lower thermal conductivities relative to PL (0.25W/m.k), reducing the heat transfer through the sample. While the maximum temperature reached by composites were higher than for PL, they were reduced compared to the PL+PA sample, except for PL+PA-BD. The reason is that the difference in the porosity of NC, DE, EP and FA affected the thermal conductivity of PA (0.21-0.24 W/m.k) [33], the greater the porosity is, the lower the thermal conductivity is. This lower thermal conductivity affects the heat transfer rate between both surfaces. The inability of BD particles to retain absorbed PA increases the heat transfer rate between surfaces as a result of PA being released. In the case of PL+PA-NC, the burning of organic modifier of NC increased the heat transfer rate.

Once PA burnt, the cracks formed increased the heat transfer rate between both surfaces [34]. Hence, the particle size of carrier materials used influenced the heat transfer rate, which created more cracks during exposure to high temperatures in the cone, (see Section 3.1.4 (Chapter 3)).

The longest time to reach 140 °C was noticed in the sample of PL+PA-EP and the overall order is:

\[ \text{PL+PA-EP} > \text{PL+PA-DE} > \text{PL+PA-FA} > \text{PL+PA-NC} > \text{PL+PA-BD} \]

The time taken to reach 300 °C was ranked as:

\[ \text{PL+PA-DE} = \text{PL+PA-FA} > \text{PL+PA-EP} > \text{PL+PA-NC} > \text{PL+PA-BD} \]
The maximum temperature measured during the test after dehydrations reaction was in the order of:

\[
\text{PL+PA-DE} < \text{PL+PA-NC} = \text{PL+PA-EP} = \text{PL+PA-FA} < \text{PL+PA-BD}
\]

Figure 5.20: Temperature versus time curves of the reverse surfaces of control PL+PA and PL with form-stable PA composite on cone exposure at 70 kW/m\(^2\) heat flux in vertical orientation

Table 5.16: Temperature changes measured at unexposed surface of PL+PA and PL with form-stable PA composites to cone heater

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time to reach</th>
<th>Maximum temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>140 °C (s)</td>
<td>300 °C (s)</td>
</tr>
<tr>
<td>PL</td>
<td>540</td>
<td>875</td>
</tr>
<tr>
<td>PL+PA</td>
<td>266</td>
<td>480</td>
</tr>
<tr>
<td>PL+PA-NC</td>
<td>375</td>
<td>580</td>
</tr>
<tr>
<td>PL+PA-DE</td>
<td>412</td>
<td>648</td>
</tr>
<tr>
<td>PL+PA-EP</td>
<td>435</td>
<td>590</td>
</tr>
<tr>
<td>PL+PA-FA</td>
<td>385</td>
<td>648</td>
</tr>
<tr>
<td>PL+PA-BD</td>
<td>273</td>
<td>420</td>
</tr>
</tbody>
</table>

5.5.2 Form-stable EM composites in PL

The flammability properties of the PL+EM-EP and PL+EM-BD are graphically demonstrated in Figure 5.21. The obtained results from these curves are summarized in Table 5.17. It can be observed from these results that PL+EM-EP ignited at 41 s similar to the control PL+EM with double peaks of 55 kW/m\(^2\) at 55 s and of 42 kW/m\(^2\) at 510 s. The THR and EHC values produced from this burning were 20 MJ/m\(^2\) and 2.9 MJ/kg, respectively. The mass loss rate of PL+EM-EP was similar to that of PL+EM as shown in Figure 5.21(b). PL+EM-BD ignited later than PL+EM-EP at 61 s, and burned with a higher PHRR as shown in Figure 5.21(a) similar to PL+EM because of the low porosity of BD
failing to encapsulate EM, as seen in the SEM results. The first peak was of 70 kW/m² at 105 s and the second peak was of 95 kW/m² at 318 s (see Figure 5.21), producing 29 MJ/m² of THR and 8.1 MJ/kg of EHC, which were higher than those observed in PL+EM-EP although the burning time was shorter. The mass loss rate of PL+EM-BD was less than that of PL+EM-EP due to the percentage of BD being higher, which reduced the amount of PL used. Moreover, the PHRR, THR and EHC values of PL+EM-BD were higher than those observed in the control PL+EM after taking standard deviation into account. These results illustrate that PL+EM-EP was less flammable than PL+EM-BD and PL+EM shown by the lower PHRR, THR and EHC values, due to EP being a non-flammable material. The cracks, colour change and surface damage were significantly observed on the sample surface for both PL+EM-EP and PL+EM-BD after the cone tests due to the EM added as shown in Figure 5.22. The surface distortion in these samples was similar to that of PL+EM (see Figure 4.16(c)).

![Figure 5.21: Cone calorimetric results of PL with form-stable EM composites samples compared to control of PL+EM at 70 kW/m²: (a) HRR and (b) mass loss curves as a function of time](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI (s)</th>
<th>FO (s)</th>
<th>Mass loss (%)</th>
<th>Peak 1 PHRR (kW/m²)</th>
<th>T_{PHRR} (s)</th>
<th>Peak 2 PHRR (kW/m²)</th>
<th>T_{PHRR} (s)</th>
<th>THR (MJ/m²)</th>
<th>EHC (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+EM</td>
<td>43±1</td>
<td>679±2</td>
<td>23.4±0.9</td>
<td>60±15</td>
<td>70±7</td>
<td>83±17</td>
<td>455±7</td>
<td>34±8</td>
<td>6.5±1.1</td>
</tr>
<tr>
<td>PL+EM-EP</td>
<td>41±1</td>
<td>618±2</td>
<td>23.2±0.8</td>
<td>55±5</td>
<td>55±14</td>
<td>42±5</td>
<td>510±7</td>
<td>20±1</td>
<td>2.9±0.3</td>
</tr>
<tr>
<td>PL+EM-BD</td>
<td>61±0.7</td>
<td>513±1</td>
<td>19±0.6</td>
<td>70±2</td>
<td>105±14</td>
<td>95±3</td>
<td>318±17</td>
<td>29±0.5</td>
<td>8.1±0.04</td>
</tr>
</tbody>
</table>
Figure 5.22: Images of PL with form-stable EM composites after cone testing (70 kW/m$^2$): (a) PL+EM-EP and (b) PL+EM-BD

The temperature change at the unexposed surface to the cone heater is presented in Figure 5.23, and the results are depicted in Table 5.18. The shortest time to reach 140 °C was observed in PL+EM-EP due to the high porosity of EP which absorbed and combined a large amount of EM used and then burned. PL+EM-EP had the longest time to reach 300 °C, indicating that the EP reduced the thermal conductivity of the sample, which could be because of the better dispersion of EM in the sample as explained in Chapter 4. This is also evident from the maximum temperature reached which was the lowest in PL+EM-EP.

![Figure 5.23: Temperature versus time curves of the reverse surfaces of control PL+EM and PL with form-stable EM composites on cone exposure at 70 kW/m$^2$ heat flux in vertical orientation](image)

Table 5.18: Temperature changes measured at unexposed surface of PL+EM and PL with form-stable EM composites to cone heater

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time to reach</th>
<th>Maximum temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>140 °C (s)</td>
<td>300 °C (s)</td>
</tr>
<tr>
<td>PL+EM</td>
<td>385</td>
<td>738</td>
</tr>
<tr>
<td>PL+EM-EP</td>
<td>337</td>
<td>795</td>
</tr>
<tr>
<td>PL+EM-BD</td>
<td>348</td>
<td>664</td>
</tr>
</tbody>
</table>
5.5.3 Form-stable BS composites in PL

The obtained results are shown in Figure 5.24 and Table 5.19 which indicate that PL+BS-EP ignited at 61 s, and burned with the lowest two peaks of heat release rate. The first and second peaks of heat release rate were 62 kW/m² at 50 s and 90 kW/m² at 402 s, respectively, producing 23 MJ/m² of THR and 8.2 MJ/kg of EHC with mass loss rates similar to PL+BS as illustrated in Figure 5.24(b). Whereas, PL+BS-BD ignited earlier than PL+BS and PL+BS-EP at 17 s, and burned with a higher PHRR than that of PL+BS-EP, the first and second PHRR were found to be 96 kW/m² at 64 s and 166 kW/m² at 437 s, respectively. The first peak was almost close to the control sample PL+BS and the second peak was higher after taking standard deviation into consideration. Hence, the flammability of PL+BS-BD was higher than that of control sample PL+BS and its mass loss was the lowest. This means the amount of BD, which did not burn, was much higher than that of EP. The mass loss results of PL+BS, PL+BS-EP and PL+BS-BD were almost in agreement with their respective TGA results. Compared to PL+BS-EP, PL+BS-BD had a higher THR of 46 MJ/m² and EHC of 9.2 MJ/kg, and its burning time was longer as shown in Figure 5.24(a). It can be observed from these results that PL+BS-EP was less flammable than PL+BS-BD and the control sample, PL+BS, shown by the lower PHRR and THR values. Moreover, it had the lowest time-to-ignition time due to the non-flammability of EP as explained before.

The cracks, colour change and surface damage (see Figure 5.25) were noticed on the surfaces of both PL+BS-EP and PL+BS-BD samples after the cone tests. This distortion observed in these samples was almost the same as that of the PL+BS sample (see Figure 4.16(d)).
Figure 5.24: Cone calorimetric results of PL with form-stable BS composites compared to control of PL+BS at 70 kW/m²: (a) HRR and (b) mass loss curves as a function of time.

Table 5.19: Cone calorimetric results of PL with form-stable BS composites compared to control of PL+BS at 70 kW/m² external heat flux

<table>
<thead>
<tr>
<th>Samples</th>
<th>TTI (s)</th>
<th>FO (s)</th>
<th>Mass loss (%)</th>
<th>Peak 1 PHRR (kW/m²)</th>
<th>TPHRR (s)</th>
<th>Peak 2 PHRR (kW/m²)</th>
<th>TPHRR (s)</th>
<th>THR (MJ/m²)</th>
<th>EHC (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+BS</td>
<td>23±3</td>
<td>547±3</td>
<td>23.4±0.3</td>
<td>86±14</td>
<td>52±53</td>
<td>111±8</td>
<td>397±74</td>
<td>34±0.04</td>
<td>3.5±1.1</td>
</tr>
<tr>
<td>PL+BS-EP</td>
<td>61±1</td>
<td>473±5</td>
<td>23.5±0.3</td>
<td>62±5</td>
<td>50</td>
<td>90±3</td>
<td>402±17</td>
<td>23±2</td>
<td>8.2±0.1</td>
</tr>
<tr>
<td>PL+BS-BD</td>
<td>17±1</td>
<td>528±2</td>
<td>19.9±0.4</td>
<td>96±16</td>
<td>64±7</td>
<td>166±14</td>
<td>437±4</td>
<td>46±1.2</td>
<td>9.2±0.3</td>
</tr>
</tbody>
</table>

Figure 5.25: Images of PL with form-stable BS composites after cone testing (70 kW/m²): (a) PL+BS-EP and (b) PL+BS-BD

The temperature shown for samples in Figure 5.26 and Table 5.20 rose from 32 °C until maximum values of 440 and 445 °C for the PL+BS-EP and PL+BS-BD respectively, which were close to each other and less than that of PL+BS. Furthermore, the longest time to reach 140 and 300 °C was found in sample of PL+BS-BD, indicating that the BS particles reduced the thermal conductivity of PL+BS-EP.
Figure 5.26: Temperature versus time curves of the reverse surfaces of control PL+BS and PL with form-stable BS composite on cone exposure at 70 kW/m² heat flux in vertical orientation

Table 5.20: Temperature changes measured at unexposed surface of PL+BS and PL with form stable BS composites to cone heater

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time to reach 140 °C (s)</th>
<th>Time to reach 300 °C (s)</th>
<th>Max (s)</th>
<th>Maximum temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+BS</td>
<td>330</td>
<td>475</td>
<td>831</td>
<td>459</td>
</tr>
<tr>
<td>PL+BS-EP</td>
<td>330</td>
<td>495</td>
<td>1050</td>
<td>440</td>
</tr>
<tr>
<td>PL+BS-BD</td>
<td>355</td>
<td>605</td>
<td>1050</td>
<td>445</td>
</tr>
</tbody>
</table>

5.6 Thermal energy storage performance of form-stable PCMs composite in plasterboard

5.6.1 Form-stable PA composites in PL

The variations of temperatures measured at the bottom of the top board of the cube as a function of time of PL+PA (control sample) and PL with form-stable PA composites are shown in Figure 5.27. All form-stable PA composite containing samples showed similar curves to that of PL+PA, showing that PA integrated into carrier materials has similar phase transition temperatures, i.e. when the PA changes its phase from solid to liquid to absorb heat and release it when the PA changes its phase from liquid to solid, corroborating the DSC results. In the heating process, all samples had the same trend of storing heat until ~50 °C as shown in Table 5.21. The lowest peak temperature was observed for PL+PA-BD compared to others. PL+PA-NC had almost the same peak temperature as PL+PA. As can be seen from the results that the maximum peak
temperature was in the order of PL+PA-BD<PL+PA-DE<PL+PA-FA<PL+PA-EP<PL+PA-NC.

These results indicated that the carrier materials used to retain PA increased the stored heat compared to PL+PA and PA thus acting effectively as thermal energy storage materials in their own right. In the cooling process, the set point was selected 4 °C below the onset of freezing temperature of PA when the PA had completely released the stored heat as shown in Figure 5.27 and Table 5.21. It can be clearly observed from the results that the stored heat in PL+PA-FA was released over a longer period of time (1080 s). The elapsed time to reduce the temperature according to the set point in PL+PA-EP and PL+PA-BD was less than that of PL+PA. Although the thermal conductivity of EP [21,31,35] is lower than all others including BD [36], the PL+PA-EP showed lower elapsed time than others, the reason for which is not known. The use of carrier materials of NC, DE and FA in retaining PA could slow down the heat transfer rate into inner surface of board compared to PL+PA, thus, the time to release the stored heat was longer. The obtained results were in the order: PL+PA-FA>PL+PA-DE>PL+PA-NC>PL+PA-BD>PL+PA-EP. These results showed the highest stored heat was in PL+PA-FA, and so it may be that the addition of FA particles with PA reduces the thermal conductivity of PL [27]. The delayed heat release values were calculated as the areas under the temperature-time curves between chosen points subtracted from the reference material, PL between the same set-points as shown in Table 5.21. The delayed heat release of PL+PA-NC, PL+PA-DE and PL+PA-BD was decreased compared to PL+PA, whereas, this heat release was increased using PL+PA-FA and PL+PA-EP. The negative values for PL+PA-NC and PL+PA-BD are due to experimental error as seen from the deviation of the curves’ baselines compared to other samples.

Figure 5.27: Comparison of temperatures measured at the bottom of top board of cube as a function of time between control sample PL+PA and PL with form-stable PA composites
Table 5.21: Peak temperature of PA samples during heating cycle, time interval and delayed heat release under the curves determined between 28-24 °C during cooling cycle.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak temperature (°C)</th>
<th>Time taken from 28 - 24 °C (s)</th>
<th>Delayed heat release (AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+PA</td>
<td>50.4</td>
<td>840</td>
<td>2782</td>
</tr>
<tr>
<td>PL+PA-NC</td>
<td>50.2</td>
<td>858</td>
<td>-3249</td>
</tr>
<tr>
<td>PL+PA-DE</td>
<td>48.7</td>
<td>870</td>
<td>691</td>
</tr>
<tr>
<td>PL+PA-EP</td>
<td>49.6</td>
<td>720</td>
<td>3309</td>
</tr>
<tr>
<td>PL+PA-FA</td>
<td>49</td>
<td>1080</td>
<td>7303</td>
</tr>
<tr>
<td>PL+PA-BD</td>
<td>48.4</td>
<td>780</td>
<td>-168</td>
</tr>
</tbody>
</table>

5.6.2 Form-stable EM composites in PL

The results of stored latent heat through comparing the temperatures at the bottom of the top board of the cube between PL+EM and PL with form-composites EM are presented in Figure 5.28 and Table 5.22. The temperature rise in all samples is similar during heating cycle, indicating no effect of PCM. This is because the experiment was started from 20 °C and at that temperature EM is already in molten phase (~18 °C). Moreover, both of PL+EM-EP and PL+EM-BD slightly decreased the peak temperature (0.6 °C) compared to PL+EM as a result of using EP and BD. The reducing of peak temperature using EM-EP was reported in the literature [37-38]. The elapsed time was measured during the cooling cycle in form-stable composite EM at the onset temperature of the solidification process (18 °C) until 14 °C when the stored heat was fully discharged. The value for PL+EM-EP was slightly higher than those of PL+EM and PL+EM-BD as shown in Table 5.22. The reason being that the EP added increased the duration of release of the stored heat compared to PL+EM as a result of efficiency of porous EP as reported in the literature [21] to absorb EM as previously explained in SEM and DSC results and its lower thermal conductivity (see Sections 5.1.2 and 5.2.2). Whereas, the inability of BD to absorb EM which decreased the percentage of PL used, produced results close to those of PL+EM. It can be also seen from results that the releasing of stored latent heat in the sample prepared by form-stable composite EM-EP is more slowly than by the direct incorporation method. This is probably because the acidic components of EM molecularly separate in PL during the direct incorporation method as discussed in SEM and DSC results (see Sections 4.2.1 and 4.3.1), whereas the carrier materials, particularly the highly porous EP, absorb the EM preventing its dispersion in PL. The delayed heat release rate of PL+EM-EP was much higher than PL+EM-BD and both of them were less than that of PL+EM.
Figure 5.28: Comparison of temperatures measured at the bottom of top board of cube as a function of time between control sample PL+EM and PL with form-stable EM composites.

Table 5.22: Peak temperature of EM samples during heating cycle, time interval and delayed heat release under the curve determined between 18-14 °C during cooling cycle.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak temperature (°C)</th>
<th>Time taken from 18-14 °C (s)</th>
<th>Delayed heat release (AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+EM</td>
<td>50.4</td>
<td>810</td>
<td>1332</td>
</tr>
<tr>
<td>PL+EM-EP</td>
<td>49.8</td>
<td>860</td>
<td>306</td>
</tr>
<tr>
<td>PL+EM-BD</td>
<td>49.8</td>
<td>790</td>
<td>-1225</td>
</tr>
</tbody>
</table>

5.6.3 Form-stable BS composites in PL

No significant difference was observed between the trend of PL+BS-EP, PL+BS-BD and PL+BS during heating cycle and also their peak temperatures as shown in Figure 5.29 and Table 5.23 were very similar. This is because the experiment was started from 20 °C and at that temperature BS is already in the molten phase (~18 °C), hence there is no phase change during heating. During the cooling cycle, which was determined from the onset temperature of BS (~21 °C) until the total of stored heat released at ~17 °C, all samples had almost the same duration of releasing stored heat. The slight difference was in the order of PL+BS-EP > PL+BS > PL+BS-BD. These results indicated that the PL+BS-EP had a higher stored heat due to the EP slightly reducing the thermal conductivity of sample compared to others. The delayed heat release rate of PL+BS-BD was increased compared to PL+BS-EP and PL+BS.
These results indicate that the ability of form-stable PCM composite to decrease the fluctuation temperature (difference between the peak and the minimum temperature) and increase the duration of releasing latent heat stored. The fine particles of carrier materials such as FA showed good energy storage results compared to others.

### 5.7 Conclusion

In this study, The SEM results showed that the amount of PCM partitioned between the selected carrier materials and the PL varied depending on the porosity of the carrier material. From DSC results, the phase transition temperatures of PCM in the carrier materials with/without PL were still similar to pure PCM except PL+EM-EP and PL+EM-BD which showed reductions in their latent heats after mixing with PL. The TGA results showed that the carrier materials did not change the thermal stability of PCM. All carrier materials have a good thermal stability except NC.
The mechanical tests showed that the sample of PL+PA-FA in the PA set has the best mechanical properties. PL+PCM-EP has the lowest mechanical performance because of the relatively large particles of EP acting as points of weakness in the PL matrix. The cone calorimeter test revealed that the carrier materials did not encapsulate the PCMs and hence, reduce its flammability compared to control PL+PCM except EP. It has been shown that form-stable PCMs composites had good thermal energy storage results particularly for PL+PA-FA and PL+BS-EP compared to others in their sets. In order to obtain less flammable materials, flame-retardants carrier materials with or without flame retardant will be studied in Chapter 6.

5.8 References


CHAPTER SIX

Flame-retardant form-stable phase change composite materials in plasterboards

In Chapter 5 it was shown that the plasterboard samples containing form-stable PCM composites have similarly good thermal energy storage performances as respective PCM containing PL samples. From a number of tested samples, PL+PA-FA and PL+BS-EP showed the best performance. Here their energy storage performance is studied further by measuring the indoor and wall temperatures of test rooms (PL cubes) prepared with 5 sides of these PCM containing samples. In order to reduce their flammability two approaches have been undertaken: (i) expanded graphite (EG), a flame-retardant, used as a carrier material for PA and BS, and (ii) resorcinol bis(diphenyl phosphate), (RDP) used as an additional flame retardant in samples from (i). The samples were named as PL+PA-EG with/without RDP and PL+BS-EG with/without RDP. These samples are discussed with reference to SEM, DSC, TGA, mechanical performance, cone calorimetry and thermal energy storage performances.

6.1 Thermal energy storage performance of form-stable composite PCMs in plasterboard: Indoor and wall temperatures of test rooms

In Chapter 5 the thermal energy storage performances of form-stable phase change composite materials incorporated in plasterboard were studied by measuring the back surface temperature of the top board of the cube (test room) made of PL, where only the top board had PCM. From Chapter 5, PL+PA-FA and PL+PA-EP were selected for further study because of their good thermal energy performance, flammability and mechanical performances compared to others. The tests room (cubes) with 5 sides of PL containing these two form stable PCM composites were prepared. A thermocouple placed in the centre of the cube measured the indoor air temperature in heating and cooling modes as explained in Chapter 3. The results of indoor and interior wall temperatures of cube prepared with/without form-stable composite PCMs are presented in Figures 6.1 and 6.2. Derived data from the curves are given in Tables 6.1 and 6.2.

6.1.1 Form-stable PA composites in PL

During heating cycles, the rise of the indoor air temperature in PL+PA and PL+PA-FA
before melting temperature of PA was almost as fast as that of PL as shown in Figure 6.1(a). But when the PA started melting at 28 °C, PL+PA-FA temperature rose slower than others. The indoor air temperature fluctuated from 51.5 (the peak) to 4.5 °C (minimum temperature) for the control sample of PL (see Table 6.1). In comparison to the PL, PL+PA samples indoor temperature varied from 51.5 to 4.7 °C, reducing the fluctuation (the difference between the peak and the minimum temperature) temperature by 0.2 °C. With the addition of FA, the temperature has varied from 50.1 to 5 °C. The reduction in peak temperature was 1.4 °C and the variation in the indoor thermal temperature was 2.1 °C compared to PL+PA. Thus, it can be inferred that FA has enhanced the ability of PA to absorb and release heat. During the cooling cycle, the results of the indoor thermal temperature profile represent the time when the PA started to release the absorbed heat at its onset freezing temperature of 28 °C until 24 °C by which temperature the PA had completely released the latent heat absorbed as shown in Table 6.1. The results indicate that the samples prepared with PA cooled at a slower rate than PL because the latent heat released was greater. PL+PA took 465 s (42 s longer than PL) to release the energy absorbed. This time was higher with the addition of FA, 485 s, due to the FA decreased the thermal conductivity of PA which reduced the heat transfer rate between both surfaces. Furthermore, the delayed heat release of PL+PA-FA was the highest compared to PL and PL+PA. This indicated the ability of PA to maintain the indoor thermal comfort temperature for longer. The negative value for PL+PA is due to experimental error as seen from the deviation of the curve’s baseline compared to those of other samples.

(a)
Figure 6.1: Comparison of a) indoor temperatures measured at the centre of cube and b) wall temperatures measured at the interior wall of cube as a function of time for PL+PA-FA and PL+PA compared to control sample PL.

Table 6.1: Indoor peak temperature of PA samples during heating cycle, time interval and the delayed heat release under the curves determined between 28-24 °C during cooling cycle.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak temp (°C)</th>
<th>Fluctuation temp (°C)</th>
<th>Peak reduction (°C)</th>
<th>Fluctuation reduction (°C)</th>
<th>Time taken from 28 - 24 °C (s)</th>
<th>Delayed heat release (AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>51.5 (51.7)</td>
<td>47 (47)</td>
<td>---</td>
<td>---</td>
<td>423 (409)</td>
<td>---</td>
</tr>
<tr>
<td>PL+PA</td>
<td>51.5 (51.7)</td>
<td>46.8 (47)</td>
<td>0 (0)</td>
<td>0.2 (0)</td>
<td>465 (890)</td>
<td>-445 (-1268)</td>
</tr>
<tr>
<td>PL+PA-FA</td>
<td>50.1 (49.8)</td>
<td>44.9 (44.9)</td>
<td>1.4 (1.9)</td>
<td>2.1 (2.1)</td>
<td>485 (1198)</td>
<td>3991 (15181)</td>
</tr>
</tbody>
</table>

- Values in italics and brackets are interior wall temperature.
- Fluctuation is the difference between the peak and the minimum temperature.
- Delayed heat release has been calculated by integrating the areas under the temperature-time curves between chosen points and subtracting the area under the temperature-time curve for the reference material, PL between the same set-points.

The wall temperature shown in Figure 6.1(b) and Table 6.1 depicted the same trend of temperature rise as the indoor temperature, though the values are much higher in the wall as is expected. This can be more clearly seen from the cooling curves where time taken from 28 to 24 °C is almost double in interior wall than indoor temperature and the delayed heat release values are fourfold in PL+PA-FA sample.

6.1.2 Form-stable BS composites in PL

The thermal performances of PL, PL+BS and PL+BS-EP are shown in Figure 6.2 and
Table 6.2, and the rise of indoor thermal temperature in the sample of PL+BS was the fastest during heating cycle, whereas, for the samples of PL+BS-EP and PL they were almost the same. The BS reduced the peak and fluctuation temperatures in PL+BS compared to PL. However, in PL+BS-EP there is no further significant decrease. This can also be seen from the cooling cycle, where PL+BS showed results better than PL and PL+BS-EP. The difference in the indoor thermal temperature between PA and BS containing samples is due to the latent heat of PA being much higher than that of BS, as indicated by the DSC results (see Section 4.1).

Figure 6.2: Comparison of a) indoor temperatures measured at the centre of cube and b) wall temperatures measured at the interior wall of cube as a function of time for PL+BS-EP and PL+BS compared to control sample PL.
Table 6.2: Indoor peak temperature of BS samples during heating cycle, time interval and the sum of temperatures under the curves determined between 21-17 °C during cooling cycle

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak temp</th>
<th>Fluctuation temp</th>
<th>Peak reduction</th>
<th>Fluctuation reduction</th>
<th>Time taken from 21-17 °C (s)</th>
<th>Delayed heat release (AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL</td>
<td>51.5 (51.7)</td>
<td>47 (47)</td>
<td>---</td>
<td>---</td>
<td>527 (503)</td>
<td>---</td>
</tr>
<tr>
<td>PL+BS</td>
<td>50.9 (51.6)</td>
<td>46 (47)</td>
<td>0.6 (0.1)</td>
<td>1 (0)</td>
<td>544 (788)</td>
<td>-2172 (-8712)</td>
</tr>
<tr>
<td>PL+BS-EP</td>
<td>50.7 (50.7)</td>
<td>45.9 (46)</td>
<td>0.8 (1)</td>
<td>1.1 (1)</td>
<td>525 (716)</td>
<td>-655 (5535)</td>
</tr>
</tbody>
</table>

Note: Values in italics and brackets are interior wall temperature

Figure 6.2(b) shows the wall temperature profile of PL, PL+BS and PL+BS-EP. During heating cycle, the rise of temperature has been slowed in PL+BS and PL+BS-EP than PL because of the BS, which can store heat and also the ability of porous EP to retain BS. No difference was noticed between PL+BS and PL in temperature reduction but in releasing the energy absorbed as illustrated in Table 6.2, PL+BS was slower. Whereas, EP added to retain BS caused a reduction of 1°C in peak and fluctuation temperature compared to PL and PL+BS, its elapsed time to release the stored energy from 21 to 17 °C in cooling cycle was also less than that of PL+BS, assigned to the indoor thermal temperature results. It can be seen from comparing heating and cooling cycles that the heating cycle showed a slower response when the PCM changes its phase from solid to liquid to absorb heat than that of cooling cycle when the materials changes its phase from liquid to solid to release the heat. This is due to the duration of heating cycle according to controlled incubation chamber available is much faster than cooling cycle. The carrier material FA showed its effectiveness to retain the PA, reducing the fluctuation temperature and increase the time to release the energy stored compared to direct incorporation (PL+PA). Whereas, EP in sample PL+BS-EP did not show much difference in the results compared to PL+BS.

Some flame retardants such as APP and FR370 were added to PL+PA-FA and PL+BS-EP to decrease their flammability as explained in Chapter 3, but no change was observed in the fire behaviour of those samples. Hence, EG as mentioned previously and a liquid flame retardant, RDP were used.

6.2 Flame-retardant form-stable PCMs composite and incorporation in plasterboards: physical and morphological properties

PA and BS were mixed separately with porous flame-retardant form-stable EG, the maximum fraction of PCM was determined by the leakage test and latent heat of fusion.
Then, flame retardant RDP was added to the PCM-EG composite.

### 6.2.1 Form-stable PA composites

Liquid PA was mixed with EG at room temperature. The optimum mass fraction of PA without leakage was observed to be 80%. For the sample containing additional RDP (PA-EG-RDP), 20% (by weight) of RDP with respect to PA was added to the composite PA-EG (section 3.3.2). The SEM images of EG, PA-EG, PA-EG-RDP, are shown in Figure 6.3. It can be seen from the morphology of EG shown in Figure 6.3(a) that EG has a layered porous structure [1] with different sizes of pores [2]. In EG’s pores, PA can be uniformly absorbed due to the capillary action of the porous EG [3], porosity of EG being >80% [4]. The SEM image of PA-EG sample is shown in Figure 6.3(b). The shape of EG was maintained even when PA added. With the addition of RDP, see Figure 6.3(c), no significant difference is observed and the EG was covered by PA and RDP. These two flame-retardant form-stable composites, PA-EG and PA-EG-RDP were incorporated in PL, the concentration of each was adjusted to maintain 10% of PA in the PL. 12.5 wt% of PA-EG with/without 20% of RDP was mixed with PL and water in the ratio of 0.31:2.19:1 to form the samples of PL+PA-EG and PL+PA-EG-RDP, respectively. The SEM images of the PL+PA-EG and PL+PA-EG-RDP are shown in Figures 6.3(d) and 6.3(e), which indicates that the flame-retardant form-stable composite PAs were uniformly dispersed in PL.

![SEM images](image)

Figure 6.3: SEM images (a) EG, (b) PA-EG, (c) PL+PA-EG, (d) PA+EG-RDP and (e) PL+PA-EG-RDP

### 6.2.2 Form-stable BS composites

The optimum mass fraction of BS contained in EG was found to be 80% according to leakage test and their latent heat, from which BS-EG sample was prepared. For preparing
sample BS-EG-RDP, 20% of RDP was mixed with BS, prior to adding to EG. The SEM images of BS-EG and BS-EG-RDP in Figures 6.4(a) and 6.4(b) illustrate that their morphologies were similar to respective PA samples. BS looks well dispersed in the porous structure of EG flakes. Moreover, the presence of RDP showed a minimum effect on SEM images. On addition of these composites in PL, these form stable composites seem to be uniformly dispersed as shown in Figures 6.4(c) and 6.4(d) for the samples PL+BS-EG and PL+BS-EG-RDP, respectively.

![SEM images of BS-EG, BS+EG-RDP, PL+BS-EG, and PL+BS-EG-RDP](image)

Figure 6.4: SEM images (a) BS-EG, (b) BS+EG-RDP (c) PL+BS-EG, and (d) PL+BS-EG-RDP

6.3 Thermal characterization of form-stable PCMs composites with/without flame retardant

6.3.1 Form-stable PA composite

The thermal properties of PA-EG, PA-EG-RDP, PL+PA-EG and PL+PA-EG-RDP are shown in Figure 6.5 and the derived data of thermal properties from these curves of DSC are depicted in Table 6.3. The onset of melting and freezing temperatures of PA in PA-EG were 27.3 and 27.5 °C, respectively, and were almost similar to pure PA. The values remained unchanged in PL+PA-EG. The latent heats of melting and freezing were greatly reduced to 191.7 and 192.7 J/g respectively in the sample of PA-EG but its calculated latent heat based on the mass fraction of PA was similar to the latent heat of pure PA measured using DSC. Moreover, the latent heat of PL+PA-EG was greatly decreased due to some of the PA leaking out during mixing. With the addition of flame retardant to PA-EG, the transition temperatures in melting and freezing phase were still similar to those of
pure PA and PA-EG, and were 27.6 and 27.8 °C, respectively. On the other hand, the latent heats of melting and freezing have been slightly decreased compared to PA-EG as a result of adding flame retardant RDP, they were 147.1 and 155.2 J/g, respectively. In the case of PL+PA-EG-RDP, the transition temperature was similar to PA and PA-EG-RDP with reduced latent heat compared to PL+PA-EG because of the RDP added. This indicated that while the RDP did not affect the melting and freezing temperatures, its presence reduced the latent heat.

Figure 6.5: DSC curves of the (a) PA-EG, (b) PL+PA-EG, (c) PA-EG-RDP and (d) PL+PA-EG-RDP composites

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Table 6.3: Thermal properties of flame-retardant form-stable PA composites by DSC

<table>
<thead>
<tr>
<th>PCM</th>
<th>Melting temp</th>
<th>Freezing temp</th>
<th>Latent heat of melting (J/g)</th>
<th>Latent heat of freezing (J/g)</th>
<th>*Derived Latent heat of melting (J/g)</th>
<th>*Derived Latent heat of melting (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-EG</td>
<td>27.3 (32.7)</td>
<td>27.5 (21.5)</td>
<td>191.7</td>
<td>192.7</td>
<td>239.6</td>
<td>240.9</td>
</tr>
<tr>
<td>PL+PA-EG</td>
<td>27.8 (32.1)</td>
<td>27.5 (23.2)</td>
<td>19.9</td>
<td>18.5</td>
<td>198.7</td>
<td>185.4</td>
</tr>
<tr>
<td>PA-EG-RDP</td>
<td>27.6 (32.9)</td>
<td>27.8 (23.8)</td>
<td>147.1</td>
<td>155.2</td>
<td>183.9</td>
<td>194</td>
</tr>
<tr>
<td>PL+PA-EG-RDP</td>
<td>27.5 (30.5)</td>
<td>27.4 (24.5)</td>
<td>16</td>
<td>15.7</td>
<td>160</td>
<td>156.7</td>
</tr>
</tbody>
</table>

* Values in italics and brackets are melting and freezing temperatures measured when PCM completely change its phase at the end of the peak

*= Calculated based on mass fraction of PCM in PL

The specific heat values of PA-EG with/without RDP shown in Figure 6.6(a) were in agreement with latent heat values during phase transition from solid to liquid even on addition in PL (See Figure 6.6(b) ).

![Figure 6.6: DSC curves showing specific heats vs. temperature of a) PA-EG with/without RDP b) PL+PA-EG with/without RDP](image)

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6.3.1 Form-stable BS composites

The DSC curves of the form-stable BS composite with and without RDP are shown in Figure 6.7. The thermal properties obtained by DSC are listed in Table 6.4. The onset of melting and freezing temperatures of BS-EG and PL+BS-EG were \( \sim17 \) and \( 21 \) °C respectively, similar to that of pure BS. The glass transition temperatures were also observed to be similar to that of BS. It can be seen from the results that the calculated latent heat of melting and freezing in BS-EG based on the mass fraction of BS was similar to that of BS. In addition, the latent heat of melting and freezing of PL+BS-EG has significantly decreased due to some of the BS leaking out into the PL. As can be seen from results, the temperatures of melting and freezing in BS-EG-RDP after adding the flame retardant RDP were reduced to 16.2 and 20 °C, respectively. The latent heat of BS has slightly decreased with adding RDP compared to BS-EG. Its latent heat was 75.8 and 76.1 J/g in the melting and freezing phase, respectively. Furthermore, no difference in the transition temperature of BS has been noticed after adding to PL compared to BS-EG-RDP but its reduction in the latent heat was higher than that of PL+BS-EG as a result of RDP addition.
Figure 6.7: DSC curves of a) BS-EG, b) PL+BS-EG, c) BS-EG-RDP and d) PL+BS-EG-RDP at 3 °C/min scanning rate.

Table 6.4: Thermal properties of flame-retardant form-stable BS composites by DSC

<table>
<thead>
<tr>
<th>PCM</th>
<th>Melting temp (°C)</th>
<th>Freezing temp (°C)</th>
<th>Latent heat of melting (J/g)</th>
<th>Latent heat of freezing (J/g)</th>
<th>*Derived Latent heat of melting (J/g)</th>
<th>*Derived Latent heat of freezing (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS-EG</td>
<td>17.8 (23.2)</td>
<td>21.1 (16)</td>
<td>84.4</td>
<td>85.8</td>
<td>105.5</td>
<td>107.3</td>
</tr>
<tr>
<td>PL+BS-EG</td>
<td>18.3 (22.5)</td>
<td>21.1 (16.9)</td>
<td>7.5</td>
<td>8.1</td>
<td>75.2</td>
<td>80.8</td>
</tr>
<tr>
<td>BS-EG-RDP</td>
<td>16.2 (22.1)</td>
<td>20 (14.5)</td>
<td>75.8</td>
<td>76.1</td>
<td>94.8</td>
<td>95.1</td>
</tr>
<tr>
<td>PL+BS-EG-RDP</td>
<td>15.9 (21.2)</td>
<td>20 (15.3)</td>
<td>6.9</td>
<td>7.2</td>
<td>69</td>
<td>72.4</td>
</tr>
</tbody>
</table>

Values in italics and brackets are melting and freezing temperatures measured when PCM completely changes its phase at the end of the peak.

* = Calculated based on mass fraction of PCM in PL.

Figure 6.8 shows the difference in specific heat values during phase transition from solid to liquid between BS in flame-retardant carrier-material EG, and in presence of the flame retardant RDP. It can be seen from the results that RDP reduced the specific heat of BS-EG compared to that of BS-EG without RDP and even after adding in PL, it showed a similar to the latent heat. It can be noticed from Figure 6.8(a) that the RDP decreases the ability of BS-EG to store heat compared to BS-EG without RDP. However, the specific heat value of PL+BS-EG was higher than that of PL+BS-EG-RDP (see Figure 6.8(b)), corresponding to the higher latent heat values.
Figure 6.8: DSC curves showing specific heats vs. temperature of a) BS-EG with/without RDP b) PL+BS-EG with/without RDP

6.4 Mechanical performance of PL containing flame-retardant form-stable PCM composites

The flexural results of PL+PA-EG, PL+PA-EG-RDP, PL+BS-EG and PL+BS-EG-RDP are portrayed in Figure 6.9, which show that the trend of the curves are linear with R-squared values ranging between 0.97 and 0.99. The derived data from these results are presented in Tables 6.5 and 6.6. All PL samples containing flame retardant PCM composites failed to withstand the stress > 0.86 – 1.83 MPa and broke at the centre. With the addition of PA-EG, the flexural properties have been significantly decreased compared to the control PL+PA as also reported by Li et al for cement with PA-EG [5]. The
reduction in flexural strength and modulus were 40.4% and 50.8%, respectively. The addition of PA-EG-RDP (i.e. RDP acted as a plasticizer) reduced slightly the flexural properties of PL and the reduction was 47.9% and 62.1% in flexural strength and modulus, respectively. The reason for this reduction compared to PL+PA is the effect of additives on coherence of PL particles.

For the BS samples, the flexural properties were also decreased compared to control PL+BS as a result of adding EG and RDP as shown in Figure 6.13(b) and Table 6.10. 69.9% and 74.5% were the reduction of PL+BS-EG in flexural strength and modulus, respectively. But the flexural properties have been reduced less on addition of RDP, the reduction being 54.5% and 52.7%, respectively. This is attributed to the affinity between BS and RDP because of the organic nature of both of them. It is also possible that RDP mixes with PL and ion exchange occurs between the calcium sulphate in PL and the phosphate group of RPD, hence better coherence of PL particles.

Figure 6.9: Stress-strain curves of three-point bending test of a) PL with flame-retardant form-stable PA and b) BS composites

Table 6.5: Mechanical properties of control PL+PA and PL with flame-retardant form-stable PA composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stress-at-failure</td>
<td>Modulus</td>
</tr>
<tr>
<td></td>
<td>(MPa)</td>
<td>(GPa)</td>
</tr>
<tr>
<td>PL+PA</td>
<td>3.07±0.12</td>
<td>2.64±0.12</td>
</tr>
<tr>
<td>PL+PA-EG</td>
<td>1.83±0.09</td>
<td>1.3±0.007</td>
</tr>
<tr>
<td>PL+PA-EG-RDP</td>
<td>1.6</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>(-47.9%)</td>
<td>(-62.1%)</td>
</tr>
</tbody>
</table>

- Values between brackets are the % reduction in mechanical properties of PL with flame-retardant form-stable PA composite compared to PL+PA
Table 6.6: Mechanical properties of control PL+BS and PL with flame-retardant form-stable BS composite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress-at-failure (MPa)</th>
<th>Modulus (GPa)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+BS</td>
<td>2.86±0.65</td>
<td>2.43±0.5</td>
<td>0.99</td>
</tr>
<tr>
<td>PL+BS-EG</td>
<td>0.86±0.05 (-69.9%)</td>
<td>0.62 (-74.5%)</td>
<td>0.98</td>
</tr>
<tr>
<td>PL+BS-EG-RDP</td>
<td>1.3±0.03 (-54.5%)</td>
<td>1.15±0.007(-52.7%)</td>
<td>0.99</td>
</tr>
</tbody>
</table>

- Values between brackets are the % reduction in mechanical properties of PL with flame-retardant form-stable BS composite compared to PL+BS

6.5 Fire performance of plasterboard with incorporated flame-retardant form-stable PCM composites

To study the effect of adding EG and RDP to PCM, the cone calorimetric results of PL+PA-EG and PL+BS-EG with/without RDP are graphically presented in Figures 6.10-6.15. The numerical data obtained from cone calorimetric results are summarized in Tables 6.7-6.10.

6.5.1 Flame-retardant form-stable PA composite in PL

On addition of EG, the sample PL+PA-EG ignited later than that of PL+PA at 41 s with double peaks of heat release rate, much higher than that of control PL+PA as shown in Figure 6.10 and Table 6.7. This indicates that the EG added increased the PHRR due to reduced PL content. The first peak of 215 kW/m² at 55 s could be because of the combustion of PA located on the surface of sample and the second peak of 192 kW/m² at 280 s due to the combustion of PA dispersed inside the P, which gets released when cracks appear in the structure. The burning time of PL+PA-EG was shorter than PL+PA with greater rate of mass loss, may be due to the reason that EG provides scaffold or wick to the PA and hence, sustains the burning. Its THR and EHC was similar to that of PL+PA. When RDP was combined in PL+PA-EG, the principal shape of the HRR curve was similar to sample without RDP, with two peaks, 207 kW/m² at 78 s and 225 kW/m² at 245 s. RDP did not reduce the PHRR of the sample. However, TTI has been delayed to 58 s with lower burning time, mass loss and THR. These changes indicated that EG provided a little bit of char layer as shown in Figure 6.11 to resist heat from the cone and prevented the sample
from further decomposition. The cracks, colour change and surface damage have been noticed on the sample surface after cone test (see Figure 6.11).

Figure 6.10: Cone calorimetric results of PL containing flame-retardant form-stable PA composites and control PL+PA at 70 kW/m²: (a) HRR and (b) mass loss curves as a function of time

Table 6.7: Cone calorimetric results of control PL+PA and PL with flame-retardant form-stable PA composites at 70 kW/m² external heat flux

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI</th>
<th>FO</th>
<th>Mass loss (%)</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>THR</th>
<th>EHC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(s)</td>
<td>(s)</td>
<td>(%)</td>
<td>PHRR</td>
<td>TPHRR</td>
<td>PHRR</td>
<td>TPHRR</td>
</tr>
<tr>
<td>PL+PA</td>
<td>13±1</td>
<td>565±1</td>
<td>22.3±1.6</td>
<td>79±19</td>
<td>60±7</td>
<td>125±20</td>
<td>160±14</td>
</tr>
<tr>
<td>PL+PA-EG</td>
<td>41±2.8</td>
<td>338±7</td>
<td>37±1.9</td>
<td>215±2</td>
<td>55±7</td>
<td>192±16</td>
<td>280±0.7</td>
</tr>
<tr>
<td>PL+PA-EG-RDP</td>
<td>58±0.7</td>
<td>275±7</td>
<td>28.5±0.5</td>
<td>207±19</td>
<td>78±3</td>
<td>225±8</td>
<td>245±15</td>
</tr>
</tbody>
</table>

Figure 6.11: Images of PL containing flame-retardant form-stable PA composites after cone testing (70 kW/m²): (a) PL+PA-EG and (b) PL+PA-EG-RDP

Due to the high thermal conductivity of EG of (4-70 W/m K) [6-9], the heat transfer rate between both surfaces has been greatly increased and the maximum temperature was much higher than for PL+PA. Both samples have almost similar temperature rise at 140 °C and

170
300 °C (see Table 6.8) measured at the unexposed surface to the cone heater as shown in Figure 6.12. The maximum temperature of PL+PA-EG-RDP (554 °C) was slightly higher compared to PL+PA-EG (540 °C).

![Temperature versus time curves of the unexposed surfaces of PL+PA-EG and PL+PA-EG-RDP compared to control PL+PA on cone exposure at 70 kW/m² heat flux in vertical orientation](image)

**Figure 6.12:** Temperature versus time curves of the unexposed surfaces of PL+PA-EG and PL+PA-EG-RDP compared to control PL+PA on cone exposure at 70 kW/m² heat flux in vertical orientation

**Table 6.8:** Temperature changes measured at unexposed surface of PL+PA-EG and PL+PA-EG-RDP to cone heater compared to PL+PA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time to reach</th>
<th>Maximum temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>140 °C (s)</td>
<td>300 °C (s)</td>
</tr>
<tr>
<td>PL+PA</td>
<td>266</td>
<td>480</td>
</tr>
<tr>
<td>PL+PA-EG</td>
<td>202</td>
<td>290</td>
</tr>
<tr>
<td>PL+PA-EG-RDP</td>
<td>206</td>
<td>300</td>
</tr>
</tbody>
</table>

6.5.2 Flame-retardant form-stable BS composite in PL

From the cone calorimetric results of the control PL+BS and flame-retardant form-stable BS composite shown in Figure 6.13 and Table 6.9, it can be seen that the EG improved the fire performance of PL+BS-EG by the increasing TTI from 28 s in PL+BS to 282 s. Additionally, the sample burnt giving a single PHRR value of 158 kW/m² at 320 s rather than two peaks as observed in the PL+BS with shorter burning time. The reason could be the significant expansion of the EG at the surface of sample, which acts as an effective barrier protects the underlying materials from the heat and flaming zone as shown in Figure 6.14. PL+BS-EG also produced much lower THR (15.7 MJ/m²) with higher mass loss rate and EHC. As can be seen from these results, EG is more effective with BS than with PA, and this may be because it encapsulates BS better than PA. Since in this work expanded graphite was made by heating expandable graphite (see Section 3.3.2, Chapter 3), it is possible that the complete expansion was not achieved. When tested as form stable
composites in PL during cone experiments, some expansion was observed. It could be possible that this expanded char has more affinity for BS than PA (which is a hydrocarbon), hence better encapsulating the former. The formation of an EG layer during combustion would resist heat from the cone calorimeter and inhibit materials from further degradation [10].

In the presence of RDP, PL+BS-EG-RDP burnt similar to PL+BS-EG but with a lower burning time and much lower THR due to RDP presence. The fire performance has been improved using EG and RDP by giving significant reductions in TTI, THR and EHC. Figure 6.14 illustrates the cracks, colour change and EG layer on both surfaces of sample after cone test. The effectiveness of RDP in BS is probably due to the chemical compatibility between RDP and BS, both being esters. Hence RDP associates with BS, acting as a flame retardant. PA, on the other hand, being non-polar in nature, has no affinity for RDP, hence RDP during mixing could migrate and mix preferentially with PL. There is also a possibility that there is ionic exchange between the calcium sulphate in PL and the phosphate group of RDP, hence RDP might become “locked” within PL resulting in it not acting as a flame retardant.

![Figure 6.14](image)

Figure 6.14: Cone calorimetric results of PL containing flame-retardant form-stable BS composite and control PL+BS at 70 kW/m²: (a) HRR and (b) mass loss curves as a function of time
Table 6.9: Cone calorimetric results of control of PL+BS and PL with flame-retardant form-stable BS composites at 70 kW/m² external heat flux

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI (s)</th>
<th>FO (s)</th>
<th>Mass loss (%)</th>
<th>Peak 1</th>
<th>THR (MJ/m²)</th>
<th>EHC (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+BS</td>
<td>23±3</td>
<td>547±3</td>
<td>23.4±0.3</td>
<td>86±14</td>
<td>52±53</td>
<td>34±0.04</td>
</tr>
<tr>
<td>PL+BS-EG</td>
<td>282±7</td>
<td>412±15</td>
<td>28.7±1.2</td>
<td>158±1</td>
<td>320±1</td>
<td>15.7</td>
</tr>
<tr>
<td>PL+BS-EG-RDP</td>
<td>278±7</td>
<td>357±7</td>
<td>33.9±0.5</td>
<td>154±27</td>
<td>300±14</td>
<td>12.5±0.7</td>
</tr>
</tbody>
</table>

Figure 6.14: Images of PL containing flame-retardant form-stable BS composite after cone test (70 kW/m²): (a) PL+BS-EG and (b) PL+BS-EG-RDP

The temperature measured at the unexposed surface to cone heater showed that the temperature rise for both samples are similar as seen in Figure 6.15 and Table 6.10 with maximum temperatures much higher than for PL+BS. This high heat transfer between both surfaces for both samples was attributed to the high thermal conductivity of EG.

Figure 6.15: Temperature versus time curves of the unexposed surfaces of PL+BS-EG and PL+BS-EG-RDP compared to control PL+BS on cone exposure at 70 kW/m² heat flux in vertical orientation
Table 6.10: Temperature changes measured at unexposed surface of PL+BS-EG and PL+BS-EG-RDP to cone heater compared to control PL+BS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time to reach</th>
<th>Maximum temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>140 °C (s)</td>
<td>300 °C (s)</td>
</tr>
<tr>
<td>PL+BS</td>
<td>330</td>
<td>475</td>
</tr>
<tr>
<td>PL+BS-EG</td>
<td>231</td>
<td>324</td>
</tr>
<tr>
<td>PL+BS-EG-RDP</td>
<td>263</td>
<td>297</td>
</tr>
</tbody>
</table>

6.6 Thermal stability of flame-retardant form-stable PCM composite in Plaster

6.6.1 Flame-retardant form-stable PA composites in PL

To further understand the effect of flame-retardant carrier material EG and the flame retardant RDP on flammability of form-stable PCM composites when incorporated in PL, the thermal decomposition of EG, RDP, PA-EG, PA-EG-RDP, PL+PA-EG and PL+PA-EG-RDP samples were studied using DTA-TGA. The TGA and DTA curves are graphically presented in Figure 6.16 and the derived data from these curves are listed in Table 6.11.

EG lost 82% of its mass in the range of 540-820 °C with an exothermic DTA peak at 755 °C, representing the oxidation of any residual species from the commercial products and of other elements within the graphite structure, producing 18% residue at 830 °C. RDP started to decompose at 240 °C and 79.3% mass loss occurred up to 480 °C with an endothermic DTA peak at 418 °C. Another mass loss step (18.2%) was observed between 500-810 °C, and is assigned to the thermal oxidation of EG. This step was accompanied by an exothermic DTA peak at 765 °C, leaving a residue of 2.8% at 830 °C.

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The PA added to EG changed the mass loss steps of EG from one to two, the first main mass loss step occurred in the range of 115-245 °C, losing 77.5% of its mass, following the release of the added PA with an endothermic DTA peak at 204 °C. The second mass loss step (19.5%) was observed between 650-820 °C, and is assigned to the thermal oxidation of EG. This step was accompanied by an exothermic DTA peak at 765 °C, leaving a residue of 2.8% at 830 °C. With the addition of RDP to PA-EG, the results showed better thermal stability than PA-EG, 70% of its mass was lost between 100-245 °C and this loss was attributed to the PA, accompanied by an endothermic DTA peak at 224 °C. As can be seen from the results, there was a significant reduction in mass loss in PA-EG-RDP.
compared to PA-EG. Combining EG and RDP improved the thermal stability of PA-EG and they work as a barrier to prevent further degradation, and shifted the second step of mass loss to be between 245-395 °C, decreasing the thermal decomposition of EG. The mass loss in the second period was 10%, giving 17.4% residue at 830 °C, much higher than that of PA-EG which indicates that RDP is acting in the condensed phase in addition to its gas phase activity to reduce the flammability of PA [11-14].

On addition of PA-EG in PL, two mass loss steps were also observed. The first step occurs between 100-220 °C, losing 22.7% of its mass with DTA peak at 145 °C, corresponding to the main dehydration reaction of PL and decomposition of PA. This is followed by a second mass loss step between 670-770 °C with mass loss of 5.3%, assigned to the second dehydration reaction of PL and decomposition of EG with a DTA peak at 760 °C, producing 71.3% residue at 830 °C. PL+PA-EG-RDP showed almost similar mass loss steps as observed in PL+PA-EG except its residue of 72.4% was higher due to the RDP added, providing slightly more residue.
Figure 6.16: TGA (a), DTA (b) curves of EG, PA-EG, PL+PA-EG and TGA (c), DTA (d) curves of RDP, PA-EG-RDP and PL+PA-EG-RDP from room temperature to 850 °C in air.

Table 6.11: TGA and DTA results of flame-retardant form-stable PA composites in PL.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp range (°C)</th>
<th>Mass loss (%)</th>
<th>Residue (%)</th>
<th>Residue at 830 °C (%)</th>
<th>Max temp (°C)</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDP</td>
<td>240-500</td>
<td>79.3</td>
<td>20.7</td>
<td>2.5</td>
<td>418</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>500-810</td>
<td>18.2</td>
<td>2.5</td>
<td></td>
<td>630</td>
<td>Exo</td>
</tr>
<tr>
<td>EG</td>
<td>540-820</td>
<td>82.0</td>
<td>18.0</td>
<td>18.0</td>
<td>755</td>
<td>Exo</td>
</tr>
<tr>
<td>PA-EG</td>
<td>115-245</td>
<td>77.5</td>
<td>3</td>
<td>2.8</td>
<td>204</td>
<td>Exo</td>
</tr>
<tr>
<td></td>
<td>650-820</td>
<td>19.5</td>
<td></td>
<td></td>
<td>765</td>
<td>Exo</td>
</tr>
<tr>
<td>PL+PA-EG</td>
<td>100-220</td>
<td>22.7</td>
<td>72</td>
<td>71.3</td>
<td>145</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>670-770</td>
<td>5.3</td>
<td></td>
<td></td>
<td>760</td>
<td>Exo</td>
</tr>
<tr>
<td>PA-EG-RDP</td>
<td>100-245</td>
<td>70</td>
<td>20</td>
<td>17.4</td>
<td>224</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>245-395</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PL+PA-EG-RDP</td>
<td>100-220</td>
<td>21.1</td>
<td>73.4</td>
<td>72.4</td>
<td>145</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>670-780</td>
<td>5.5</td>
<td></td>
<td></td>
<td>775</td>
<td>Exo</td>
</tr>
</tbody>
</table>

*Values in italics and brackets are calculated from individual component results.

These results indicate that RDP should reduce the flammability of PL+PA-EG-RDP, but from the cone results this was not the case. This indicates that RDP during mixing might have migrated and mixed preferentially with PL. EG could be considered to be used as a carrier material as well as a flame retardant.

6.6.2 Flame-retardant form-stable BS composites in PL.

The TGA results of BS-EG, BS-EG-RDP, PL+BS-EG and PL+BS-EG-RDP are shown in Figure 6.17 and Table 6.12. BS-EG displays two stages of mass loss similar to those of
PA-EG with higher residue, 3.6% and an endothermic DTA peak at 200 °C. RDP added to BS-EG improves its thermal stability by increasing the decomposition temperature and reducing the mass loss in the first stage between 150-285 °C to 66.7% compared to 77.2% in BS-EG. The second stage was shifted compared to that of BS-EG to be 285-400 °C with mass loss of 11.3%. These stages were accompanied by an exothermic DTA peak at 266 °C, giving 18.5% residue at 830 °C, almost the same as PA-EG-RDP. RDP significantly improved the thermal stability of BS-EG by increasing the residue (18.5%) compared to that of BS-EG. This indicates that RDP has efficiently reduced the flammability of BS. EG helps in encapsulating and degrading material in its porous structure, hence slowing down the degradation process as reported in literature for EG with other materials [15].

When form-stable BS composite is added to PL, the mass loss steps have changed from two to three, these steps of mass loss were similar to those of PL+BS and PL+BS-EP (see section 4.4.2, chapter 4 and section 5.3.4, chapter 5). PL+BS-EG-RDP left a residue of 73.3% at 830 °C, greater than that of PL+BS-EG (70.4%) due to the presence of RDP, which acts as a flame retardant as explained earlier.

(a)  
(b)

Figure 6.17: TGA (a), DTA (b) curves of BS-EG, PL+BS-EG, BS-EG-RDP and PL+BS-EG-RDP from room temperature to 850 °C in air
Table 6.12: TGA and DTA results of flame-retardant form-stable BS composites in PL

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp range</th>
<th>Mass loss</th>
<th>Residue</th>
<th>Residue at 830 °C</th>
<th>Max temp</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(%)</td>
<td>(%)</td>
<td>(%)</td>
<td>(°C)</td>
<td></td>
</tr>
<tr>
<td>BS-EG</td>
<td>100-250</td>
<td>77.2</td>
<td>3.6</td>
<td>3.6</td>
<td>200</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>650-830</td>
<td>19.2</td>
<td></td>
<td></td>
<td>755</td>
<td>Exo</td>
</tr>
<tr>
<td>PL+BS-EG</td>
<td>100-170</td>
<td>14.6</td>
<td>70.5</td>
<td>70.4</td>
<td>150</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>170-245</td>
<td>7.5</td>
<td></td>
<td></td>
<td>745</td>
<td>Exo</td>
</tr>
<tr>
<td></td>
<td>650-750</td>
<td>7.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BS-EG-RDP</td>
<td>150-285</td>
<td>66.7</td>
<td>22</td>
<td>18.5 (3.64)</td>
<td>266</td>
<td>Exo</td>
</tr>
<tr>
<td></td>
<td>285-400</td>
<td>11.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PL+BS-EG-RDP</td>
<td>100-170</td>
<td>14.3</td>
<td>73.9</td>
<td>73.3</td>
<td>150</td>
<td>Endo</td>
</tr>
<tr>
<td></td>
<td>170-245</td>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>650-775</td>
<td>6.6</td>
<td></td>
<td></td>
<td>772</td>
<td>Exo</td>
</tr>
</tbody>
</table>

_values in italics and brackets are calculated from individual component results

6.7 Thermal energy storage performance of flame-retardant form-stable PCMs composite in plasterboard

6.7.1 Flame-retardant form-stable PA composite in PL

Figure 6.18 represented the indoor air and wall temperature of the test rooms made of PL+PA-EG and PL+PA-EG-RDP respectively against time compared to PL+PA. The derived data from these figures are shown in Table 6.13. The rise of temperature during heating cycle from ~5 to ~50 °C is similar for all samples. At the onset of melting temperature of PA (28 °C), PA started melting to absorb energy as also seen from the DSC results. EG is known to be employed to enhance the heat transfer in PCMs due to its high thermal conductivity [11-14,16]. Its good compatibility with PA has been noticed when the temperature reaches ~50 °C, EG reduced the peak temperature by 0.4 °C as also reported in literature [5] compared to PL+PA and no reduction in fluctuation temperature has been observed. Despite its high thermal conductivity it has a function of storing energy through retaining the PA which is observed by taking more time (480 s) to release the energy absorbed during cooling cycle compared to PL+PA as reported for other PCMs with EG [17].

This can also be seen from the delayed heat release, calculated by integrating the areas under the temperature-time curves between the onset of freezing temperature, 28 °C until 24 °C (when approximately the latent heat was completely released) and subtracting the area under the temperature-time curve for the reference material, PL between the same set-
points. With the addition of flame retardant RDP, the thermal properties of sample were still similar to that in the DSC results. RDP shows better results than others by having reduction of 1.4 and 1.3 °C in peak and fluctuation temperature respectively compared to PL+PA.

The wall temperatures measured confirmed the efficiency of EG and RDP to reduce the peak and fluctuation temperatures. The reduction was 1.8 and 1.2 °C for PL+PA-EG respectively, higher at 2.5 and 2.4°C for PL+PA-EG-RDP respectively compared to PL+PA. During the cooling cycle, PL+PA-EG took longer time to release the energy absorbed than the others and had a higher delayed heat release.

Figure 6.18: Comparison of a) indoor temperatures measured at the centre of cube and b) wall temperatures measured at the interior wall of cube as a function of time between control sample PL+PA and PL with flame-retardant form-stable PA composites
6.13: Indoor peak temperature of PA samples during heating cycle, time interval and the delayed heat release under the curves determined between 28-24 °C during cooling cycle

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak Temp (°C)</th>
<th>Fluctuation Temp (°C)</th>
<th>Peak reduction (°C)</th>
<th>Fluctuation reduction (°C)</th>
<th>Time taken from 28 - 24 °C (s)</th>
<th>Delayed heat release (AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+PA</td>
<td>51.5 (51.7)</td>
<td>46.8 (47)</td>
<td>---</td>
<td>---</td>
<td>465 (890)</td>
<td>---</td>
</tr>
<tr>
<td>PL+PA-EG</td>
<td>51.1 (49.9)</td>
<td>46.8 (45.8)</td>
<td>0.4 (1.8)</td>
<td>0 (1.2)</td>
<td>480 (1220)</td>
<td>2549 (8677)</td>
</tr>
<tr>
<td>PL+PA-EG-RDP</td>
<td>50.1 (49.2)</td>
<td>45.5 (44.6)</td>
<td>1.4 (2.5)</td>
<td>1.3 (2.4)</td>
<td>480 (1040)</td>
<td>1868 (8442)</td>
</tr>
</tbody>
</table>

Note: Values in italics and brackets are interior wall temperature

6.7.2 Flame-retardant form-stable BS composite in PL

It can be observed from the indoor thermal temperature results of PL+BS-EG and PL+BS-EG-RDP shown in Figure 6.19 and Table 6.14 that both of them had the same trend of temperature rise. The onset of melting temperature remained ~17 °C for all samples in the heating cycle similar to the DSC results. No significant difference was noticed in the peak and fluctuation temperature of internal except reduction of 0.3 °C in the samples prepared with flame retardants compared to PL+BS. In case of cooling cycle when the BS started to release the energy absorbed at the onset ~21°C until ~17 °C when the heat absorbed was approximately released, there was a slight difference in the elapsed time as a result of adding EG and RDP. The results showed that the longest time of 600 s was for PL+BS-EG-RDP and then for PL+BS-EG at 560 s. In contrast, the delayed heat release of PL+BS-EG was higher. These results indicated that the EG with or without RDP did not affect the absorption and release of energy which could be because of the high thermal conductivity of EG, which accelerated the heat transfer rate between external and internal regime [16]. Moreover, the latent heat of BS is much lower than that of PA as can be seen from DSC results (see section 4.1, chapter 4).
Figure 6.19: Comparison of a) indoor temperatures measured at the centre of cube and b) wall temperatures measured at the interior wall of cube as a function of time between control sample PL+BS and PL with flame-retardant form-stable BS composites.

Table 6.14: Indoor peak temperature of BS samples during heating cycle, time interval and delayed heat release under the curves determined between 21-17 °C during cooling cycle

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak temp (°C)</th>
<th>Peak reduction (°C)</th>
<th>Fluctuation temp (°C)</th>
<th>Fluctuation reduction (°C)</th>
<th>Time taken from 21 - 17 °C (s)</th>
<th>Delayed heat release (AU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL+BS</td>
<td>50.9 (51.5)</td>
<td>---</td>
<td>46 (47)</td>
<td>---</td>
<td>544 (788)</td>
<td>---</td>
</tr>
<tr>
<td>PL+BS-EG</td>
<td>50.6 (50.2)</td>
<td>0.3 (1.3)</td>
<td>46 (46.3)</td>
<td>0 (0.7)</td>
<td>560 (960)</td>
<td>479 (1617)</td>
</tr>
<tr>
<td>PL+BS-EG-RDP</td>
<td>50.6 (50)</td>
<td>0.3 (1.5)</td>
<td>46 (45.8)</td>
<td>0 (1.2)</td>
<td>600 (740)</td>
<td>-443 (-591)</td>
</tr>
</tbody>
</table>

Note: Values in italics and brackets are interior wall temperature.

The wall temperature illustrated much higher differences between samples compared to indoor temperatures as shown in Figure 6.19(b) and Table 6.14. The onset of temperature changed due to melting of BS during the heating cycle which can be seen more clearly as a shoulder at 17 °C. The reduction in peak and fluctuation temperatures was 1.3 and 0.7 °C respectively for PL+BS-EG, but was increased to 1.5 and 1.2 °C respectively after the addition of RDP. During the cooling cycle, the time taken between the onset temperature of freezing 21 °C and 17 °C when BS released all the stored energy was longer for PL+BS-EG to below compared to PL+BS, but when adding RDP the results were decreased below that of PL+BS. This could be because the increase in heat transfer rate.

From the results it can be said that the addition of EG and RDP reduced the fluctuation temperature measured at the wall but when measured in the interior, the additives just reduced the peak temperature as a result of the increase in the thermal conductivity of BS-EG due to the presence of EG.
6.8 Conclusion

To reduce the PCM flammability, several samples of PL and flame-retardant form-stable composite PCM have been prepared. The use of EG to retain the PA and BS did not significantly affect the melting points but reduced the latent heats of melting and freezing of the PCMs. Furthermore, addition of RDP had no effect on the phase transition temperatures and the latent heats of PCMs. The mechanical performance has been reduced after adding EG and even after adding RDP, except for PL+BS-EG-RDP, which gave better results than in the absence of RDP due to the compatibility between RDP and BS, both of which are esters. TGA results show that the addition of RDP to samples increases the amount of char residue, indicating that RDP is acting in the condensed phase and so should reduce the flammability of PA and BS. The fire behaviour of PL+BS is significantly improved with the addition of EG and RDP as a result of organic nature between BS and RDP, but EG with/without RDP did not have any effect on the HRR of PA containing samples, whereas, overall THR was unchanged, considering the error range. The presence of EG and RDP did not affect the thermal energy storage properties of PA and BS.

6.9 References


CHAPTER SEVEN

Conclusions and recommendations for future work

The aim of this research was to develop energy efficient and fire safe construction materials, such as PL, incorporating PCMs. The PCMs selected in this research are paraffin (PA), eutectic mixture (EM) and butyl stearate (BS) because their melting temperatures are close to human comfort temperature 17-28 °C and they have favourable latent heat storage capacity. To be applied in PL, immersion and direct incorporation methods are used. To improve the thermal energy storage and prevent the leakage of PCMs, carrier materials of nanoclay (NC), diatomaceous earth (DE), expanded perlite (EP), fly ash (FA) and brick dust (BD) are used to retain PCMs through vacuum impregnation. To reduce the flammability of PCMs, EG as a flame retardant carrier material was studied. Furthermore, flame retardant RDP was added. At the beginning of the project, the research question was: Is it possible to incorporate PCMs in building materials such as PL in order to improve the thermal energy storage performance of PL and can flame retardants be used to reduce the flammability of PCMs? To address this research question a series of experiments was carried out in a systematic manner in order to: (i) study the effect of impregnation of PCMs into PL by immersion and direct incorporation methods on thermal energy storage and flammability (chapter 4), (ii) incorporate PCMs in carrier materials (chapter 5) for easier processing and reducing flammability, and (iii) identify suitable flame retardant carrier materials and chemicals to reduce the flammability of PCMs (chapter 6).

The experimental techniques used were SEM for morphology; DSC and TGA for thermal transitions and stability, compression and flexural tests for mechanical performance, cone calorimetric testing for flammability, and heating and cooling in a temperature-controlled incubation chamber for energy storage evaluation. The main conclusions from the above experiments are presented in the following sections.

7.1 Plasterboard impregnated with phase change materials (chapter 4)

Two techniques were used to integrate PA, EM and BS into PL by immersion and direct incorporation. The range of PCMs absorbed in immersion was between ~18-22 wt% and 10 wt% by the direct incorporation method:
• SEM results show the PL particles are uniformly coated by PCM except for EM, which may be because EM, being composed of ionic small molecules, is better dispersed in PL.

• DSC results indicate that PA has the highest latent heat among the PCMs used. The onset of melting and freezing temperatures of PCMs used are as expected from their datasheets and literature, being in the temperature range 17-28 °C. This temperature range is within human comfort range, hence these PCMs are suitable for thermal energy storage applications. When these PCMs are incorporated in PL, the measured latent heat values are reduced compared to the values observed for pure PCMs and the reduction is related to the % PCM used. This is due to the separation and dispersion of molecules of PCMs during mixing with PL. When they are finely dispersed, not enough material is available to melt with considerable latent heat. However, samples prepared by the immersion method show higher measured latent heat than those prepared by the direct incorporation. This is because in the immersion method the PCM is absorbed in the interstices of PL, hence exist as a distinct phase to melt compared to PCM molecules which get dispersed in the direct incorporation method. With both methods the highest latent heat is observed in PA samples and the lowest is observed in EM samples. No changes in the onsets of melting and freezing temperatures of PCMs on their addition in PL have been observed.

• TGA results reveal that the PCMs are thermally stable at room temperature but they start to volatilize after 100 °C with one mass loss step. In PL-PCM samples, three mass loss steps due to volatilization of PCM, the dehydration reactions of PL, and the decomposition of calcium carbonate and magnesium carbonate are observed. The mass loss values are similar to that of control PL with the additional mass loss being due to the added PCM.

• The mechanical properties of PL are reduced by adding PCMs. In direct incorporation, the reduction in mechanical properties is much greater than for the immersion technique, particularly when using EM. In flexural mode, PL_PA and PL_BS show results better than PL. This is due to the PCM filling the pores of the PL without affecting the structure in the immersion method, whereas with direct incorporation the distributed PCMs affect the PL structure.
• Cone calorimetric tests indicate that the addition of PCM makes the PL (which does not burn) flammable. The immersion samples show worse fire performance than the direct incorporation samples, particularly with PA, because the % PCMs absorbed are higher and also the concentration of the PCM on the surface of sample is greater. Moreover, the heat transfer rate between exposed and unexposed surfaces in the cone calorimeter in these samples is greater compared to PL and also samples prepared by the direct incorporation technique. The reason for use of the immersion technique resulting in higher heat transfer is because burning of PCM on the surface is higher and when the absorbed PCMs are burnt, voids are created, causing more heat transfer.

• With regards to thermal energy storage performance, the PCMs reduce the fluctuation temperature of PL by decreasing the peak temperature during heating cycle particularly for samples containing PA (2.7 °C decrease observed in PL_PA). The samples from the immersion technique are more efficient in this respect than those prepared by direct incorporation, due to higher PCM contents in the former. The lowest reduction was found in PL_EM (0.2 °C) which indicates that this sample does not absorb much heat.

This work has shown that while PCMs help in energy storage in building materials their high flammability is the limiting factor for commercial applications.

7.2 Form stable phase change composite materials in plasterboard (chapter 5)

In order to obtain more compatibility between the PL matrix and PCMs, carrier materials of NC, DE, EP, FA and BD were used to give form-stable composite PCMs, which were then added to PL. Based on the testing results, the following conclusions can be drawn:

• Using a vacuum impregnation method 60, 60, 60, 40 and 20 wt% of PA can be retained in the carrier materials NC, DE, EP, FA and BD, respectively. Form-stable composites could not be obtained for EM and BS with NC, DE and FA, whereas, 60 and 20 wt% EM/BS could be retained in EP and BD, respectively. 10 wt% of PCM of form-stable PCM composites were mixed with PL to make samples.
- SEM results show that the amount of PCM partitioned between the selected carrier materials and the PL varies depending on the porosity of the carrier material; EP has the highest porosity and BD has the lowest porosity.

- From DSC results, no change is observed in the phase transition temperatures of PCM in the carrier materials with/without PL except for PL+EM-EP and PL+EM-BD in which the ionic EM molecules probably disperse separately. The latent heats of form-stable composites PCMs are similar to those of pure PCM after allowing for the mass fraction of PCM. After mixing with PL, the latent heat is greatly reduced because some leakage from carrier material into PL, particularly for BD.

- TGA analysis shows that the carrier materials are thermally stable at high temperatures except for NC. This is due to the thermal decomposition of the organic modifier in NC. These carrier materials do not change the thermal transition and decomposition behaviours of PCMs, indicating that there is no chemical interaction between the two components of these composites.

- The mechanical properties of PL containing form-stable composite PCM are considerably decreased compared to those of the control sample. This may be because the incorporation of any additives reduces the coherence between PL particles. PL+PA-FA in the PA-containing set shows the best results. PL+PCM-EP is the worst. The mechanical properties of samples are influenced by the particle sizes of carrier materials.

- Cone calorimetry revealed that the carrier materials used did not help in reducing the flammability of PCMs, except for EP, the use of which leads to notable decreases of the PHRR and THR, (particularly in PL+BS-EP). On the other hand, from the temperature measured at the unexposed surface during cone experiments, it appeared that the carrier materials reduce the thermal conductivity of those composites compared to control PL+PCM, except for PL+PA-BD. This shows that while carrier materials can not reduce the flammability of the PCM containing samples, they act as insulators due to their lower thermal conductivities, reducing heat transfer through the sample. The greater the porosity is, the smaller the thermal conductivity is, cracks, colour changes and significant surface damage are noticed on the samples’ surfaces.
It has been shown that form-stable composite PCMs reduce the peak temperature during a heating cycle and take longer time to release the stored heat during the cooling cycle than do samples prepared by the direct incorporation method. The samples of PL+PA-FA from the PA set and PL+BS-EP from the BS set show good results compared to others in their sets.

Out of all the samples studied, PL+PA-FA and PL+BS-EP show the best properties in terms of energy storage and flammability performance. Their energy storage performance was studied further by measuring the interior and wall temperatures of test rooms (PL cubes) prepared with 5 sides of these PCM containing samples. They helped in reducing the interior temperature as well, supporting the above mentioned results.

### 7.3 Flame-retardant form-stable phase change composite materials in plasterboard (chapter 6)

To reduce PCM flammability two approaches were undertaken: (i) use of expanded graphite (EG) as a flame-retardant carrier material for PA and BS, and (ii) use of resorcinol bis(diphenyl phosphate), (RDP) as an additional flame retardant in samples from (i). Several samples of PL and flame-retardant form-stable composite PCM with/without RDP were prepared.

- Using a vacuum impregnation method, 80 wt% of PA and BS can be retained in EG. The SEM results show that the PCM and RDP are dispersed well in EG due to the high porosity of EG. Because EG has the capacity to absorb useful amounts of PCM this can be used as a carrier material to incorporate PCMs into building materials without changing the “feel” of these materials. EG itself has significant FR properties so that PCMs containing reduced levels of FRs incorporated into the EG should have useful fire resisting behaviour.

- The use of EG to retain the PA and BS does not significantly affect the thermal properties of PCMs. The onset of melting and freezing temperatures are similar to those of pure PA, slightly decreased in BS, but the latent heat values in both samples are as expected based on the mass fraction of PCM in PA-EG and BS-EG. With further addition of RDP in PA-EG, the phase transition temperature is still similar to that of pure PA (although there is a slight shift in BS) and that the latent
heats of PCMs with RDP are similar to those of samples without RDP. The latent heat values are reduced though when these composites are added to PL.

- TGA results show that on mixing PA or BS with EG, there is no obvious interaction between the two components. The addition of RDP to samples though increases the amount of residue, indicating that RDP should reduce the flammability of the PCM.

- The mechanical properties are reduced after adding EG, and are reduced further after adding RDP as in PL+PA-EG-RDP. PL+BS-EG-RDP on the other hand gives better results than the sample without RDP, which could be due to the compatibility between RDP and BS, both of which are esters.

- The addition of EG and RDP has no effect on the flammability of PA-containing samples. The flammability of PL+BS however, is significantly reduced with the addition of EG and RDP, shown by a significant increase in TTI (~280s compared to 23s in PL+BS) and reduction in THR and EHC values. The effectiveness of RDP in BS is probably due to chemical compatibility between RDP and BS, both being esters. Hence RDP associates with BS, and acts as a flame retardant. PA, on the other hand, being non-polar in nature, has no affinity for RDP, hence RDP during mixing could migrate and mix preferentially with PL. There is also a possibility that there is ionic exchange between the calcium sulphate in PL and the phosphate group of RPD, hence RDP might become “locked” within PL resulting in it not acting as a flame retardant.

- The temperature measured at the unexposed surface to the cone heater illustrates that the heat transfer rate between both surfaces has been greatly increased due to the high thermal conductivity of EG. The cracks, colour change and surface damage have been noticed on the samples’ surface after the cone test.

- The energy storage performance of these samples shows that the presence of EG and RDP in PL+PA samples improves the energy storage capability (shown by reductions in the peak and fluctuation indoor temperature during heating cycle, and increase in the time taken to release the energy absorbed during cooling cycle). In the case of PL+BS, while EG slightly improves the values, RDP had no effect, indicating again that RDP could have migrated from the form-stable composite.
Overall this work has shown that PL containing form-stable PCM composites can be used for thermal energy storage applications and, with appropriate use of flame retardants, that these can be rendered fire safe.

7.4 Suggestions for future work

The potential of using phase change materials in wall-lining on the surface of a room to improve the thermal performance of the room has been demonstrated. To render them fire safe, some flame retardant treatment is required. To take this research forward the following recommendations can be made:

- **Effect of different FRs on PCMs**

  The addition of liquid flame retardants to the PCMs should be investigated. In order to do this the miscibility of the selected FRs must be established with chosen PCM to ensure that the FR is miscible over the entire temperature range. In the present work, RDP has been incorporated into BS with good effect. This suggests that other phosphate FRs should be effective and the use of smaller quantities of FRs containing higher levels of phosphorus should be considered.

- **Encapsulation of PCMs with flame retardant materials**

  The encapsulation of PCMs with flame retardant materials is a way forward to keep flame retardants in proximity to the PCMs. One example is making urea-formaldehyde microspheres with inherent flame retardant properties.

- **Testing for environmental effects**

  Due to time constraints the effect of environmental ageing could not be performed on PCM-containing samples. Selected samples should be subjected to cycle heating and cooling conditions and then tested for their thermal energy and fire performances, and specified time periods.

- **Large scale test installation**

  The thermal performance of flame retarded phase change materials integrated in building materials needs to be evaluated in a real room in different seasons, particularly in winter.
and summer. This will provide crucial performance data on how effective the phase change material is at improving thermal performance and the resulting thermal comfort conditions.

- **Thermal model**

Performance results obtained from further test studies and a large scale test could be used to develop a thermal model. The developed computer model would enable designers and engineers to study the thermal energy performance of the building with the PCMs. This will lead to greater confidence in specifying a PCM for a particular condition and would be likely to lead to a greater commercial success.