

QATAR UNIVERSITY  
COLLEGE OF ARTS AND SCIENCES

HEAT ABSORBERS BASED ON RECYCLED POLYETHYLENE AND  
PARAFFIN WAX FOR ENERGY STORAGE

BY

HANEEN WADI ABDELRAZEQ

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## COMMITTEE PAGE

The members of the Committee approve the thesis of Haneen Wadi Abdelrazeq defended on May 26 2016.

---

Dr. Igor Krupa  
Thesis Supervisor

---

Dr. Mariam Al-Maadeed  
Committee Member

---

Dr. Adriaan Luyt  
Committee Member

---

Dr. Mabrouk Ouederni  
Committee Member

---

Dr. Ilias Belharouak  
Committee Member

Approved:

---

Dr. Eiman Mustafawi, Dean, College of Arts and Sciences

## **ABSTRACT**

The building sector is one of the main sectors in Qatar; however, it consumes a huge portion of primary energy sources. Today, there is a worldwide trend to utilize renewable sources of energy to cover buildings' energetic needs using local climate conditions. The common source of energy, the sun, can be efficiently utilized in covering energetic supplies of buildings. To be able to consume energy of the sun, various components and materials are designed. This thesis is focused on the preparation and complex physical characterization of heat absorbers based on Phase Change Materials Heat Absorbers (PCM-HA). The materials are designed based on recycled high-density polyethylene (W-HDPE) obtained directly from a local industrial company in Qatar, paraffin wax and expanded graphite (EG) which can all be used together as the main components in improving the passive heating or cooling of buildings. Thus, this work is directly related to environmental protection and energy conservation in buildings. A big attention is given to the long term stability of the PCM-HA. The materials were artificially aged at selected conditions (temperature, UV irradiation, humidity) to characterize their long term behavior. This type of characterization was rarely reported in literature. Thus, the obtained results conveyed valuable benefits. This long-term experimentation confirmed the significant reduction in paraffin leakage from the thermal system up to 9.83%. Thus, this also confirms the high ability of the materials to absorb and release reaching 70 J/g of heat energy. Samples mixed with EG did not lose their mechanical integrity and compactness even after 100 days of accelerated artificial aging. Adding to this, various PCMs are applicable not only in building sectors, but also in thermal protection of electronic devices. For this reason, the dielectric behavior of the developed materials are explored and results confirmed an increase in electrical conductivity due to addition of EG to the materials.

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## **Dedication**

I dedicate the success of this work to my lovely mother: *Laila*; my precious father: *Wadi*; and dear siblings: *Hanan, Ahlam, Motasem and Mohieb*; for the endless love and care.

*Most importantly...*

“To my dear husband, *Omar*, for being the shining star in my life.”

# Chapter 1. INTRODUCTION

## 1.1 General background

Enormous efforts are devoted towards advancements in use of various sources of energy [1]. Economists, scientists, and engineers are striving to successfully develop technologies that can increase the efficiency of power systems taking into consideration new and renewable sources of energy to minimize the negative effects of greenhouse gas emissions [2,3]. The development of such unique energy storage systems are becoming as important as developing new sources of energy. Energy storage plays an important role in conserving energy to overcome the mismatch between supply and demand [4–6]. Implementation of such energy storage systems helps smooth out temperature fluctuations. Therefore, storage of energy can be employed either by sensible heat (increasing and decreasing of the system's temperature) or by latent heat (presence of phase change materials to raise thermal inertia) [7,8].

Interestingly, organic polymers are currently occupying the second place, behind steel, in being the most important set of materials used majorly in latent heat systems [9]. Polymer matrices, based on both thermoplastics and thermosetting resins, are considerably abundant with desirable mechanical and thermal properties [10]. Yet, polyethylene (PE) seems to be the most commonly used polymer for blending with paraffin waxes, as the phase change material (PCM), due to their high structural and chemical similarity. This match ensures high compatibility of the two components [11][12]. It is worth noting that PCMs have been the subject of rigorous studies in the past few decades [13]. Researchers worldwide focused on the PCMs' numerous advantages as high-energy storage systems that can effectively store thermal energy. Many types of PCMs melt and solidify at different temperature ranges. This makes them more attractive for use in numerous applications [14].

Lately, significant research studies have been focusing on preparing novel PCMs taking into consideration utilization of waste polymers as mentioned in Chapter 2. Due to the huge generation of waste polymers from industrial areas and manufacturing companies, the world is becoming in need of positive utilization of such waste materials. For instances,

instead of disposing the waste elements in landfills and causing more harm to the environment, we can wisely utilize these recycled materials and simply incorporate them in the making of efficient heat absorbing composites. In this study, we work on utilizing waste high-density polyethylene obtained as a recycled component directly from industry. This waste polyethylene is blended with paraffin wax, as the phase change material, along with expanded graphite filler to obtain a novel stabilized composite suitable with good thermal, mechanical and electrical properties suitable for energy storage applications.

## **1.2 Objectives of research**

This research focuses on preparation and characterization of new composite PCMs utilizing local Qatari HDPE waste, blended with paraffin wax and expanded graphite for the purpose to get well processable material with desirable thermal characteristics such are high specific enthalpy of melting of PCM component (paraffin wax) at selected temperature, high thermal conductivity and appropriate mechanical properties which enable a simple manipulation with the material in selected applications. Such special materials may greatly take part in reducing the overall energy consumption, particularly in building industry maintaining the thermal comfort inside buildings. Hence, the main scope of this work involves the following three parts:

- 1- The preparation of PCM composites from recycled HDPE, paraffin wax and expanded graphite by hot molding process and to optimization of the components' ratio. This is very important tasks as each component has different functionality in the system. HDPE fix material in the compact shape, paraffin wax enables the absorption/release of heat energy and expanded graphite improves thermal conductivity in the system.

- 2- Study of the long-term thermophysical properties of prepared composite phase change materials and measuring the overall level of enhancement which makes our materials suitable for thermal storage applications. A significant effort was put in dealing with the artificial aging of materials.
- 3- Study the influence of the highly conductive filler, expanded graphite, on the electrical performance of the composites.

## Chapter 2. LITERATURE SURVEY

### 2.1 Energy Storage

Thermal energy storage (TES) in materials is an excellent way in enhancing the heating, cooling, and other energy consuming processes. In fact, thermal energy storage helps lower the cost of generating electricity in terms of thermal power. Therefore, thermal energy storage has the great advantage of allowing the system operate at lower capacities [15][16]. In terms of conservation of energy, numerous energy saving methods were developed due to the rapid increase in energy demands and its utilization [17]. Farid et al. explained that it is definitely required to have short term storage systems for only a few hours for some applications, and other systems lasting for a couple of months for other essential cases. In some heat recovery systems, energy storage would be necessary especially when the consumption periods and waste heat availability are altered. Thermal storage units exist in various applications (Figure 1) as they offer less temperature fluctuations at larger storage densities [18][19].

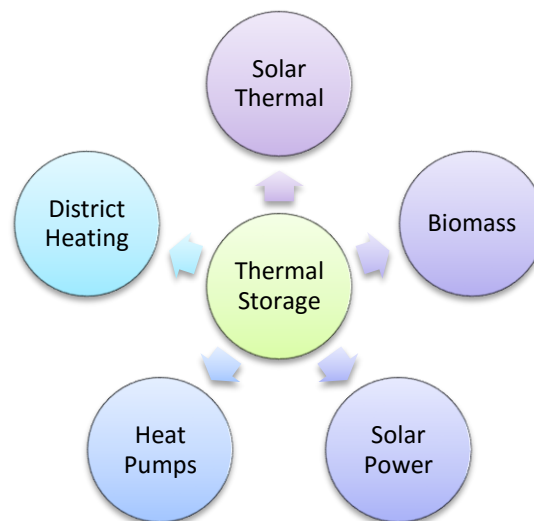


Figure 1: Positions of thermal energy storage [18]

Whenever a material is heated up, excess thermal energy is stored in two different forms, sensible or latent heat. When the same material is cooled down, the stored heat can be utilized for desired applications. Some possible applications for thermal energy storage include solar thermal systems, energy management in buildings, and thermal protection for electronic devices [20][21].

### **2.1.1 Latent Heat Storage Materials**

The rapid rise in applying different research procedures in improvement of latent heat storage materials (LHSM) has become of global interest [17]. In practical terms, latent heat is described as an attractive method in supplying high-energy storage density with the ability to store energy at temperatures of specific ranges. Latent heat energy storage is generally based on the capture and release of energy during a material's phase change process. Large potential benefits were gained in the building sector while releasing and storing heat energy at lower overall energy [22–24]. Latent heat storage systems are mainly functioning to improve thermal system performance. This is mainly dependent upon the energy size [25][26][27].

Both sensible and latent heat are depicted by the temperature-time plot in Figure 2 [28]. As energy is added into a substance in the form of heat, its internal kinetic energy will rise; resulting in its temperature increase. This is defined as sensible heat. A point is then reached where addition of heat will no longer cause change in temperature (melting point A and boiling point C in the figure below). This energy being added is no longer kinetic. It is called potential energy. This type of energy is required to break all attraction forces of the substances during melting and boiling processes, resulting in change of phase. Heat storage and release occurring throughout this process is defined as latent heat [29][30][31].



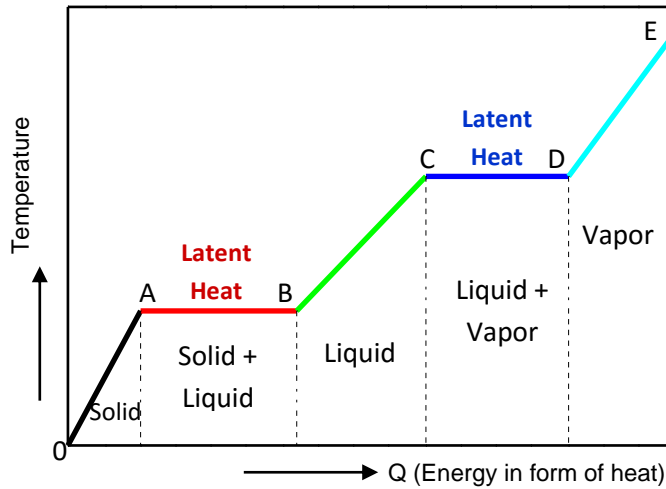


Figure 2: Temperature-time diagram for the heating of a substance [28]

When the material changes phases from solid to liquid (or vice versa), transfer in thermal energy occurs. Socaciu [33] mentioned that the conversion of water to ice is the most common example of a phase change process. In general, ice storage cooling systems possess a greater advantage in compared to chilled-water units of the same capacity. This is due to the huge quantity of stored energy during the change of phase.

Simply, in terms of latent heat, when temperature is above the phase transition temperature of the material, energy is absorbed and stored changing the state of the material from solid to liquid (i.e. melting). Whereas, when this amount of absorbed energy is released, the phase changes back from liquid to solid.

Farid et al. compared latent heat storage with sensible heat storage as summarized in Table 1. Verma et al. explained that latent heat would be favorable over sensible heat in terms of both the mass and volume of storage units. It is also shown that the inorganic compounds possess latent heat of fusion and densities that are much higher than the organic

compounds [10][17]. These combined effects can reduce the storage size and cost significantly.

Table 1: Comparison between the latent heat storage and sensible heat storage [18]

Property	Latent heat storage		Sensible heat storage	
	Organic	Inorganic	Rock	Water
Latent heat of fusion (kJ/kg)	190	230	—*	—*
Density (kg/m <sup>3</sup> )	800	1600	2240	1000
Specific heat (kJ/kg)	2.0	2.0	1.0	4.2
Storage mass for 10 <sup>6</sup> kJ (kg)	5300	4350	67,000	16,000
Storage volume for 10 <sup>6</sup> kJ (m <sup>3</sup> )	6.6	2.7	30	16
Relative mass	1.25	1.0	15	4
Relative volume	2.5	1.0	11	6

\*Latent heat of fusion is not of interest for sensible heat storage.

Latent heat storage systems are attractive due to their high storage densities along minor temperature intervals [7]. Whereas, in sensible heat storage systems, a significant rise in the material's temperature takes place. This allows the storage size to be compact in storing heat [34]. As an efficient thermal storage medium, phase change materials (PCMs) are considered effective in storage and release of high quantities of energy at specific temperature ranges taking place in less volume [35][36].

### 2.1.2 Desired Characteristics of Heat Storage Systems

Heat storage systems are dependent of storage size and are mainly functionalized upon specific properties. The diagram in Figure 3 below shows the favored characteristics for both sensible and latent thermal energy storage systems [28][37].

Compact	Efficiency	Temperature	Performance	Lifetime	Cost
<ul style="list-style-type: none"> <li>• Large storage capacity per unit mass and volume</li> </ul>	<ul style="list-style-type: none"> <li>• High storage efficiency</li> </ul>	<ul style="list-style-type: none"> <li>• Uniform operating temperature range</li> </ul>	<ul style="list-style-type: none"> <li>• Small self-discharging rate without heat loss</li> </ul>	<ul style="list-style-type: none"> <li>• Maintains a long storage lifetime</li> </ul>	<ul style="list-style-type: none"> <li>• Inexpensive system</li> </ul>

Figure 3: Desired characteristics of a thermal storage system [28]

## 2.2 Phase change materials (PCMs)

### 2.2.1 Definition

PCMs are latent heat storage materials of which consist of chemical bonds that work on storage and release of thermal heat. Materials employed as PCM should possess large thermal conductivities as well as high latent heat of fusion. The common phase change process of PCM is shown in Figure 4.

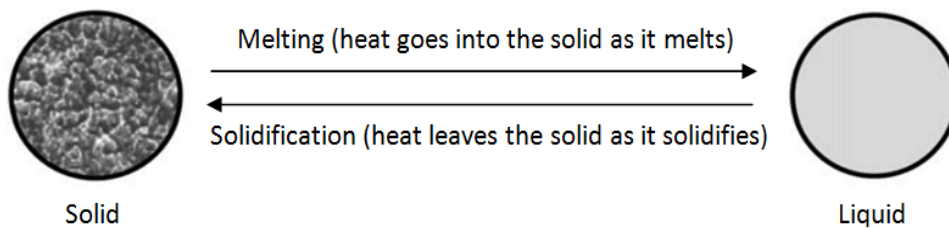


Figure 4: Schematic of a phase change process [33]

### 2.2.2 Classifications of PCMs

In 1983, Abhat presented the classifications of PCMs as in figure 5 [38].

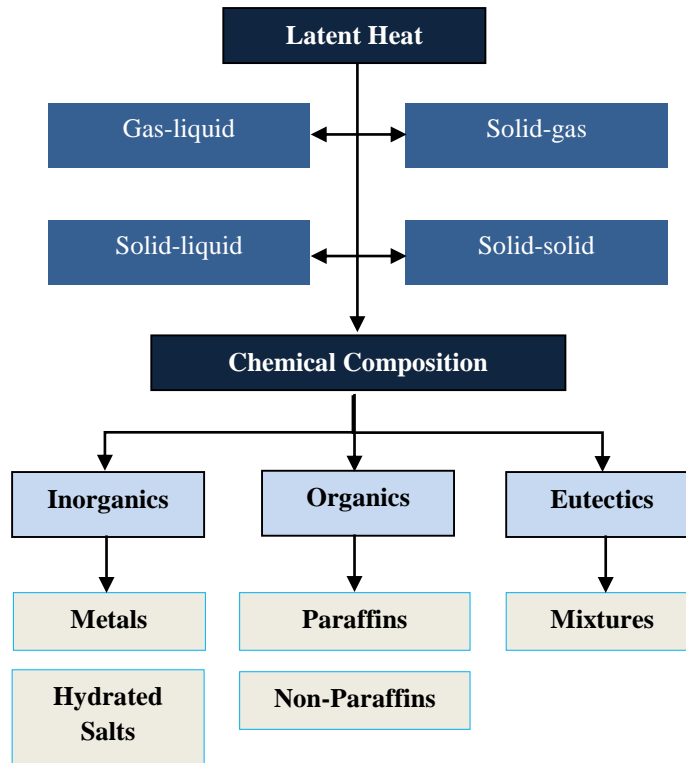


Figure 5: Classifications of PCMs [42]

Many types of organic and inorganic substances melt at desired temperatures ranging from 20 °C to 80 °C. At the same time, such substances should exhibit certain chemical and thermodynamics specifications to be suitable for use in latent heat storage systems [24][39][40]. Mehling and Cabeza [41] provided a detailed discussion on

thermodynamic, chemical and economic criteria; as listed in Table 2. Table 5 also shows the differences between organic, inorganic and eutectics base on literature studies.

Table 2: Desired properties of phase change materials [24]

<b>Thermodynamic criteria</b>	
1. Melting point should be in the desired operating temperature range.	4. Less volume change in phase transition: Simple container can be used.
2. High latent heat of fusion: Smaller amounts of material storing a set quantity of energy.	5. High thermal conductivity: Small temperature gradients required for charging and discharging the storage material.
3. High density: A smaller container volume holding the material.	6. High specific heat: To assure good sensible heat storage effects.
<b>Chemical criteria</b>	<b>Economic criteria</b>
1. Chemical stability with no chemical decomposition: Assuring a high LTES system life.	1. Should be accessible and available in large quantities.
2. Non-corrosiveness to construction materials.	2. Inexpensive.
3. Material should be non-poisonous and nonexplosive.	

#### 2.2.2.1 Organic compounds

A lot of interest was showed in recent studies, showing the evolution of a unique class of organic materials that would support the inherent disadvantages present in inorganic PCMs. Such organic materials maintain good chemical stability and physical properties. In addition to having excellent thermal behavior along with modifiable transition regions [42]. Organic phase change materials are known to possess congruent

melting (repeated melting and freezing) with no phase segregation. They also crystallize with negligible supercooling (self-nucleation) [43]. Organic PCMs are more chemically stable and have higher latent heat in compared to inorganic PCMs. Also, they are considered as recyclable elements [33]. These organic PCMs function over temperature ranges between 0°C to 200 °C. Most of these PCMs are non-stable at elevated temperatures due to the existing covalent bonds. The density of organic PCMs is generally less than that of organic materials, reaching values no more than 103 kg/m<sup>3</sup> [41][44].

#### 2.2.2.1.1 *Paraffin Organics*

Organics such as paraffins greatly take part in heat storage systems due to their numerous advantages they possess [28][45]. Waxes are quite attractive due to several advantages: chemical resistivity, limited solubility, and low viscosity under melting temperatures. The molecular weight of wax ranges from hundreds to thousands grams per mole [48]. In terms of materials selection, paraffins are generally safe, noncorrosive and very reliable. However, the major drawback would be the low thermal conductivities and flammability; which at some points may limit their efficiency.

Paraffins are substances that is made up of a waxy consistency at ambient temperatures. Chemically, paraffin waxes are mainly composed of straight hydrocarbon chains with little branches near the end of the chains. The main element present in paraffin waxes is known as alkanes. The structural formula of paraffins mainly controls their chemical properties. The most chemically stabled paraffins are the ones with normal straight chains and symmetric branches [46]. The most abundant and economical paraffins consist of even numbers of carbon atoms. The normal paraffins are known as saturated hydrocarbons; characterized by C<sub>n</sub>H<sub>2n+2</sub>. Commercial waxes consist of carbons in the range of 8-15 [38]. Paraffins below C<sub>5</sub> (< 5 Carbons) are gases, between 5-15 are liquids, and the rest are solid waxes [46]. Molten paraffins should be retained in secure containers to suppress leakage of the wax. This can be achieved through mixing of the paraffin wax with suitable polymers [11][46]. Manoo and Hensel [47] presented some variations in conductivities and enthalpies of some paraffins corresponding to change in temperature.

#### *2.2.2.1.2 Non-Paraffin Organics*

This category contains numerous organic materials with different design parameters, unlike the paraffins that possess similar characteristics [46]. Non-paraffin organics are considered as the major set of materials suitable for thermal storage. During the past decades, many research groups have extensively worked on identifying various organic elements (i.e. fatty acids, esters, glycols and alcohols). However, their major drawback is flammability. Non-paraffins should not be bare to extreme temperatures or any kind of oxidizing agent [49].

#### *2.2.2.2 Inorganic Compounds*

Mehling and Cebaza [41] mentioned that inorganic compounds cover a larger range of temperature in compared to organic compounds. Both types of compounds compose of alike melting enthalpies per mass, however, inorganic materials possess higher densities and therefore exhibit higher melting enthalpies per volume. On main drawback is the high compatibility between the inorganics and metallic components. This leads to high occurrence of corrosion in some PCM-metal blends.

##### *2.2.2.2.1 Salt Hydrates*

These types of inorganics are good thermal conductors with large volumetric storage densities and reasonable expenses in compared to paraffins. When heated, the hydrated salts dissolve and start absorbing energy [15]. In spite of the high density of salt hydrates, some flaws take place after repetitive cycling. Further, what makes salt hydrates problematic as PCMs is the density differences between solid and aqueous phases of the salt throughout the process of melting. This forms a reduced hydrate of the same salt. Decomposition takes place at the container's bottom end where the solid phases gathers. This occurrence is permanent and cannot be reversed.

Due to incongruent melting and large subcooling effects, the functionality of salt hydrates become much slower. In cases where incongruent melting occurs, two phases of solid and liquid of saturated salt solutions both come to be in equilibrium. Thus, melting and freezing become irreversible. On the other hand, salt hydrates with congruent melting temperatures normally melt similar to all pure components [46]. Thus, both decomposition and corrosiveness act as strong lifetime reducers of the PCM [50]. Also, suitable actions must be taken to reduce supercooling effects to the least [23][27].

*Table 3: Melting temperatures and heat of fusion for some common PCMs from different sources [49]*

PCM Name	Type of Product	Melting Temp. (°C)	Heat of Fusion (kJ/kg)	Source
Astorstat HA17	Paraffin waxes	21.7-22.8	-	Astor wax by
Astorstat HA18	Paraffin waxes	27.2-28.3	-	Honey well (PCM Thermal Solution )
RT26	Paraffin	24 - 26	232	Rubitherm GmbH
RT27	Paraffin	28	206	
Climsel C23	Salt Hydrate	23	148	Climator
Climsel C24	Salt Hydrate	24	108	
STL27	Salt Hydrate	27	213	Mitsubishi Chemicals
S27	Salt Hydrate	27	207	Cristopia
TH29	Salt Hydrate	29	188	TEAP
-	Mixture of Two Salt Hydrates	22-25	-	ZAE Bayern



### 2.2.2.3 Eutectics

A mixture is defined as a “eutectic” once the lowest melting temperature is obtained by altering the concentrations of the mixture’s components. Hence, in eutectics, melting takes place at constant points [15]. For example, the melting points of eutectic water-salt solutions are less than 0 °C. This is due to adding the salt into the water; which significantly reduced the overall melting point of the eutectic mixture.

Mainly, water-salt solutions consist of two components: water and salt. This gives an indication that phase separation would most probably take place. Thus, to overcome the segregation problem, eutectic compositions are used. Eutectic compositions are mainly consisted of at least two constituents, which solidify at the same lowest freezing point. Therefore, there would be no gathering of solid phases at the bottom of a sink due to any density deviations [41]. For this reason, eutectics would be more beneficial for use than inorganic PCMs in terms of segregation occurrence [49]. Table 4 shows some good examples of common water-salt mixtures [41].

Table 4: Examples of eutectic water-salt solutions that have been investigated as PCM [41]

Material	T <sub>m</sub> (°C)	Melting enthalpy (kJ/kg)	Density (kg/m <sup>3</sup> )
Al(NO <sub>3</sub> ) <sub>3</sub> (30.5 wt%)/H <sub>2</sub> O	-30.6	131	1283 (liquid)
			1251 (solid)
NaCl (22.4 wt%)/H <sub>2</sub> O	-21.2	222	1165 (liquid)
			1108 (solid)
KCl (19.5 wt%)/H <sub>2</sub> O	-10.7	283	1126 (liquid)
			1105 (solid)
H <sub>2</sub> O	0	333	998 (liquid, 20°C)
			917 (solid, 0°C)

Table 5: Comparison between organic, inorganic and eutectics [49]

	<b>Organic</b>	<b>Inorganic</b>	<b>Eutectic</b>
<b>Advantages</b>	Low Cost (120Euro/kWh) Self nucleating Chemically inert and stable No phase segregation Recyclable Available in large temperature range	Moderate cost (130 Euro/kWh), High volumetric storage density, (180-300 MJ/m <sup>3</sup> ), Higher thermal conductivity (0.6W/m°C), Non flammable, Low volume change	Sharp melting point, Low volumetric storage density
<b>Disadvantages</b>	Flammable, Low thermal conductivity (0.2W/m°C), Low volumetric storage density (90-200 MJ/m <sup>3</sup> )	Subcooling, Phase segregation, Corrosion of containment material	Limited available material property data

### 2.2.3 Applications of PCMs

Based on the desired use, the PCMs are chosen mainly upon the practical melting point. PCMs melting below 15 °C are majorly applied in coolness storage for air conditioners. The ones with melting points higher than 90 °C are used in refrigerating applications. Adding to this, PCMs that melt between 20 °C and 32 °C are highly advised for passive management of buildings [10][20].

#### 2.2.3.1 PCMs in Building Envelopes

Thermal energy storage is in rapid rise especially in building applications where space cooling and heating are of interest [52]. Due to the PCM's good thermal performance and long term stability while solidification and melting processes, they have become more attractive for use in building envelopes. Moreover, phase change materials may be

effortlessly mixed with other building elements forming stronger composite materials that work on enhancing the overall stability of their shapes. Resulting in more stabilized PCMs.

Figure 6 shows night cooling, active heating and passive solar heating effects on walls, roof and the floor using PCMs. Thus, PCMs incorporated in building envelopes can both lower and shift the highest heat load and reduce any fluctuations in room temperature. In other words, building envelopes base on PCMs have the ability to store heat with low-priced electricity during the evenings, then release that heat all through the daytime [52].

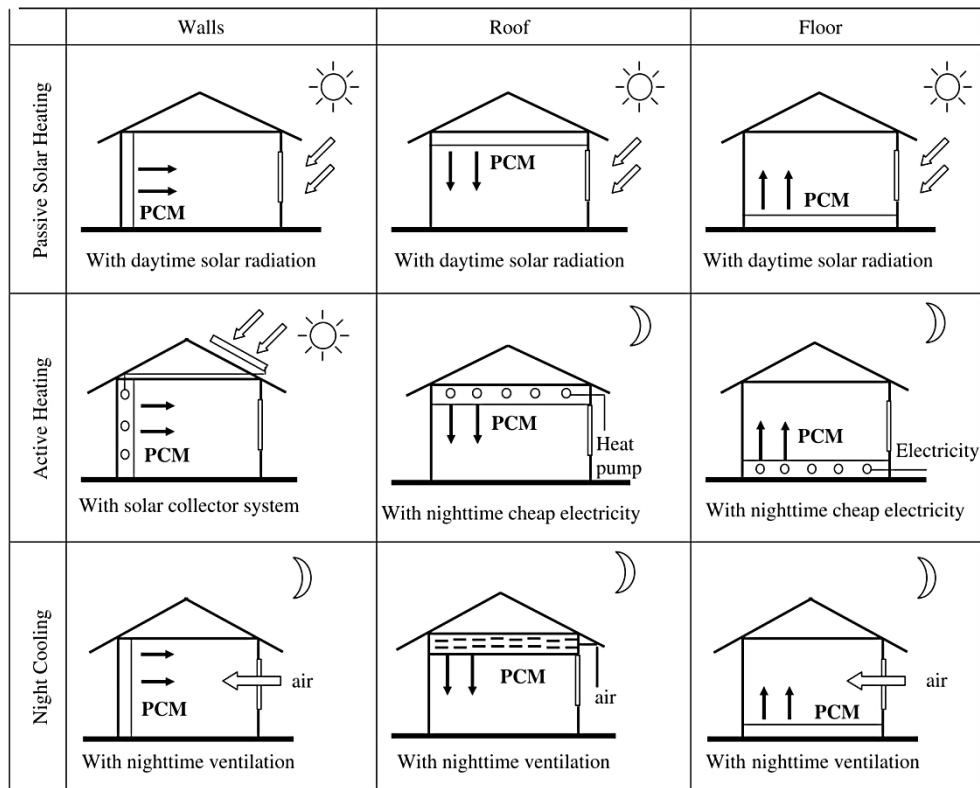


Figure 6: The forms and effects of PCM building envelope [52]

Stritih and Novak [9] worked on designing a wall consisting of black paraffin wax. Mainly, the stored heat in the PCM was used for actual heating in a household. Also, Peippo et al. well-thought-out a plasterboard incorporated with PCM in a lightweight passive solar house in Madison, Wisconsin. This insulated house was able to save an amount of 3GJ during one year. This is 15% of the yearly price of energy [42][53].

Xu et. al. [54] studied the thermal effect of a room made up of a PCM ground. It was generally pointed out that for the purpose of lowering inner room temperature, the PCM's melting point must be almost the same as ambient temperature of sunny cold days. The analysis of this study is useful for considering PCM floorboards in thermal solar applications.

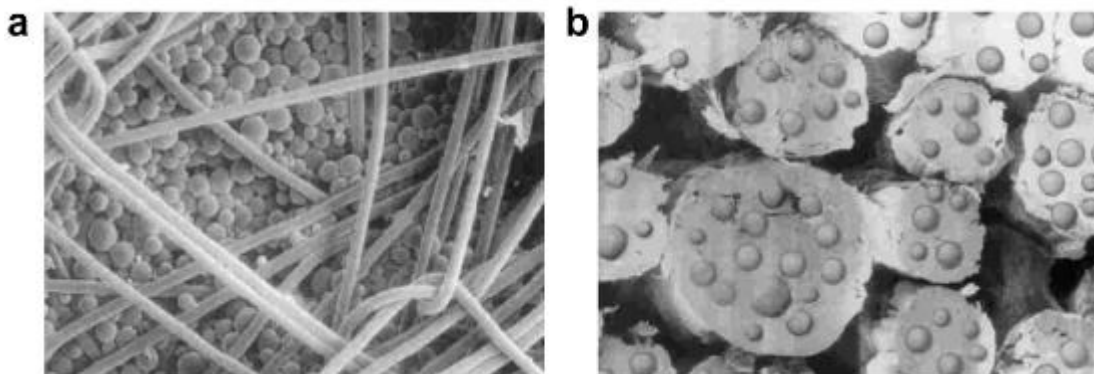
Dutil et. al. [17,55,56] reviewed the mathematical modeling in building applications, where phase change materials functioned at specific temperatures. Heat was allowed to be stored in a big amount in such a low volume. This directly lead to direct savings of energy, and so consumption of energy was largely lowered to the minimum. In some countries, such as inn GCC, the incorporation of such PCM materials would definitely lead to significant reduction in the consumer's consumption which in return would be considered cost-effective.

Wisconsin, Peippo et al. considered a PCM impregnated plasterboard as a storage component in a lightweight passive 120 m<sup>2</sup> solar house. The house was able to save up to 3G J in a year or 15% of the annual energy cost [42]. In other words, thermal storage systems consisting of high thermal conductive PCMs is vital to complement the occurrence of crystallization of the used PCM throughout the discharging process [53]. Adding to this, our PCM-HA would also be of great use in solar energy building applications. It was noted that Xu et. al. [54] studied the influence of various factors on thermal performance of a room with shape-stabilized PCM floor model.

On the other hand, thermal systems based on phase change materials may also be of great use in industry in order to further improve the heat transfer rates of some parts of a chemical plant. Similarly, Fukai [57] inserted brushes of thermal conductive carbon fibers on the shell side of a heat exchanger to increase the PCM's heat transfer conductivity. The reduction of thermally conductive fillers towards the cost of equipment in industry was also proven [58]. Furthermore, Dutil et al. [50][51][55] reviewed the mathematical modeling in building applications, where phase change materials undergo a phase change close to the desired room temperature. For instance, air-conditioning systems provide higher efficiency at night since ambient air temperatures are relatively low [15].

### ***2.3.2.2 PCMs in Smart textiles***

Some PCMs were investigated in interesting textile applications. Wang et al. [60] presented the effect of PCMs on smart thermal-protective textile materials. Study has shown that the electrical energy with no PCM was much higher than that with PCM. This confirms that PCM actually lowered the amount of electrical energy consumed by the textile element by 31%.



*Figure 7: PCM microcapsules coated on the surface of fabric (a) and embedded within fiber (b) [60]*

Chen et al. [61] was able to produce electrospun fiber composites composed of PEG and cellulose acetate. PEG functioned as the PCM. The PCM was dispersed throughout the surface and inside the fibres. Thermal measurements were confirmed to be regenerated after 100 cycles of heating followed by cooling.

### ***2.3.2.3 PCMs in Solar Energy Storage***

Researches have put lots of effort in employing latent heat storage material in thermal solar applications. In such solar energy systems, heat is stored along the day and released for use in the nights [37]. Along this area, Kurklu et al. [62] established a solar collector composed of water with PCMs. This was introduced as a substitute to the regular solar collectors used in heating the water. Both insulation and absorptions properties were enhanced for this purpose. Furthermore, Hammou and Lacroix [63] proposed a unique method in concurrently handling solar heat storage as well as electric energy. Detailed models were conducted for a period of four successive years. Results obtained showed that the whole PCM system was successfully able to lower consumption of energy consumption by 32% [64].

## **2.2 Composite Phase Change Materials**

Composite PCMs are mainly materials consisting of a PCM in addition to other one or two different materials. Added materials work on enhancing a specific property of the used PCM. A composite is formed by either inserting another material into the PCM or by inserting the PCM into another matrix [16][20]. In most cases, composites can: [7]

1. Develop the cycling stability of the whole material
2. Enhance thermal transfer of heat transfer. This may be achieved by incorporating materials with larger thermal conductivities (i.e. graphite).

Sari et al. [22] and Fang et al. [65] examined the thermal stability and chemical properties of PCMs. Studies revealed that composite PCMs have excellent thermal stability

after many thermal cycles. It was concluded that the PCMs can be largely used in waste heat recovery applications.

### ***2.2.1 PE/Wax PCM Composites***

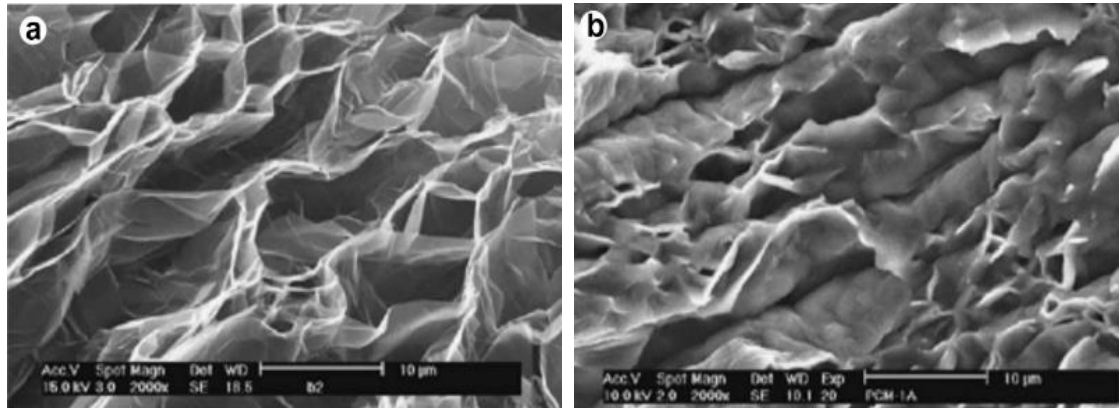
Polyethylene is the thermoplastic polyolefin which is one of the most widely used polymers suitable for a variety of applications. PCMs based on polyethylene were prepared and characterized by a number of research groups in order better understand the material's functionality at different conditions.

Alkan et al. [66] introduced a unique composite based on paraffin/polypropylene. In this composite, polypropylene was used as the supportive material for paraffin. Reliability of the thermal performance was investigated during an accelerated thermal cycling experiment (3000 cycles). AlMaadeed et. al. [67] explored the impact of adding waste wax on LDPE, HDPE and LLDPE. The study showed how the amorphous structure of the polymer allowed the wax to disperse easily between the chains. The increase in wax portions lead to an observed increase in miscibility and phase separation. An experimental study was done by Krupa and Luyt [68], where thermal properties of cross-linked and uncrossed-linked LLDPE/wax blends were investigated. A reduction in thermal stability of the blends was observed as the wax content increased.

### ***2.2.2 Wax/EG PCM Composites***

Zhang and Fang [69] have explored a thermal energy storage composite composed of paraffin wax and expanded graphite (EG). Preparation of the composites was based on the absorption of paraffin into the pores of EG. This occurred due to the presence of micro-porous layers in the expanded graphite. The morphology of EG is shown in Figure 8. Surface tension and capillary forces worked on preventing the wax leakage from the blend [69]. Wang et al. [70] examined a blend composed of polyethylene glycol (PEG) with expandable graphite. 90 wt% of PEG was the highest weight percentage of PEG added to

PCM leading to negligible leakage of the polymer. The conductive network of EG significantly increased the thermal conductivity performance of the whole blend.



*Figure 8: SEM photomicrographs of the expanded graphite and paraffin/expanded graphite composite PCM: (a) expanded graphite, (b) paraffin/expanded graphite composite PCM [69]*

Cabeza et. al. [34] worked on three techniques to further improve heat transfer in low-temperature storage unit with the PCM being water/ice. The prepared composites based on PCM and graphite showed the most significant rise in heat flux in compared to all other methods done. The study also showed that the volume content of water was always bigger or equal to 90% volume of the store, and that the heat or cold stored was dominated by latent heat, since sensible heat in all cases was between 15% and 25% of total heat stored. In addition, the increase in graphite composite material showed a much higher increase in the average power of the store: 280% on heating and 170% on cooling.

Zhang et al. [71] blended expanded to paraffin wax. Weight percentages varied from 0% to 10%. As per DSC measurements, some shifts were noted in the phase change temperatures. At the start, the paraffin's latent heat raised, then decreased back as more EG



was added. The expanded graphite distribution in the composite PCMs was detected using an optical microscope as shown in Figure 9.

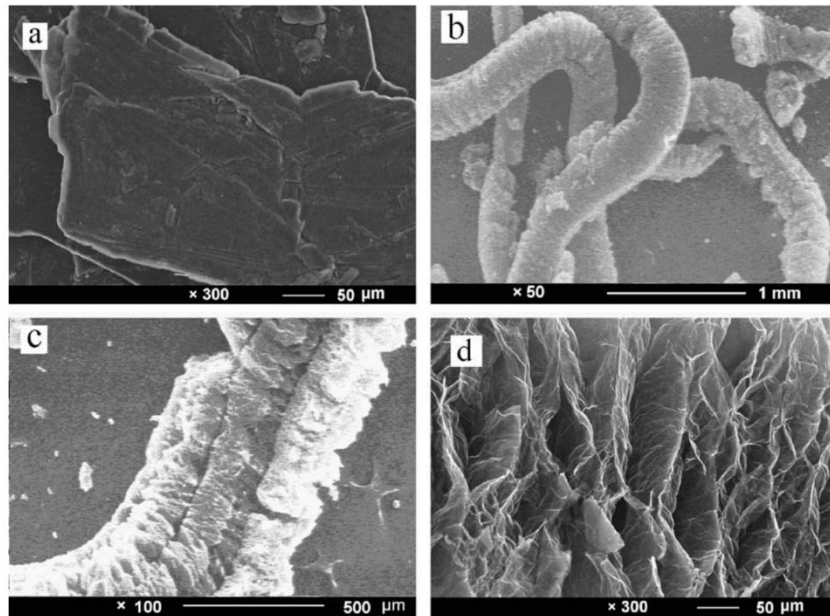


Figure 9: SEM images. (a) Raw expandable graphite (x300); (b) large spaces among worm-like EG particles (x50); (c) crevice-like pores on the surface of EG particle (x100); (d) net-like pores inside or on the surface of EG particle (x300). [71]

PEG and mesoporous active carbon (AC) were blended together via an impregnating method [72]. When lowering the content of PEG in the composite, the phase change temperatures and specific enthalpy of melting were decreased. It was concluded that phase change properties were highly affected by the confinement of PEG segment in the carbon's porous structure. This can be related to the carbon layer of expanded graphite. In another study, liquid paraffin was absorbed in expanded graphite in a study done by Sari and Karaipekli [73]. Composites with 10 wt% of EG were most stable. No leakage was observed during phase transition.

Another interesting study prepared composites based on fatty acid (as the PCM) and expanded graphite. The highest amount of PCM absorbed into the pores of EG was 80

wt%. Results obtained from DSC showed that the crystallization and melting points were more or less the same as those of the fatty acid. However, the latent heats of the pure fatty acids were higher than those of composite PCMs [74][75].

## **2.3 Characterization of Polyethylene Composites**

### **2.3.1 Thermal Characterization**

The thermal performance of the PCM can be enhanced via addition of fillers with high thermal conductivity values [41]. The one of the methods to improve a heat flux in PCMs is based on expanded graphite developed by ZAE Bayern and manufactured by SGL CARBON GmbH (Germany). It featured both high heat storage capacity due to 80–85% content of PCM; a 10% content of special, highly porous graphite provided the composite material a thermal conductivity in the rang 20–30 W/mK [2][16][27][30].

Zhong et. al. [80][81] investigated enhancement of heat transfer using graphite foam composites. The foam's pore size was the main cause in improving its thermal diffusivity. In addition, latent heat of Paraffin wax/graphite foam systems has shown an increase with the increasing of the portions of wax.

Sari and Karaipekli [73] examined the influence of expanded graphite addition to paraffin wax in obtaining form stable composites as phase change materials. Composite PCMs with weight percentage of 10% graphite consisted of satisfying range of melting temperature along with good thermal conductivity.

On the other hand, Wang et. al. [82] prepared a conductive phase change material by blending PEG, silica gel, and  $\beta$ -Aluminum nitride powder. Thermal conductivity increased with the increase in  $\beta$ -Aluminum nitride up to 30%. It was also confirmed that, in compared to pure PEG, this composite PCM had much higher heat storage and release rates.

### **2.3.2 Mechanical Characterization**

Many research groups have worked on developing various types of PCMs with great mechanical stability. For example, impregnating wood fiberboards into paraffin wax. The company, Rubitherm Technologies GmbH, developed several materials that consist of two main components: a stable and highly porous element, where paraffin is kept within its pores, and a supportive polymer matrix that holds the paraffin [41].

Krupa and Luyt [83] investigated the mechanical characteristics of linear low-density polyethylene (LLDPE)/wax blends. Young's modulus raised with an increase in wax content. This resulted in less elongation near the yield point. Krupa et. al. [84] also investigated phase change material blends based on LDPE and two waxes (hard, oxidized Fischer–Tropsch wax and soft paraffin wax). As portions of wax increased, both strength and elongation were reduced. This was because of the absence of tie molecules that are directly in charge of transferring mechanical stress across the wax molecules. Adding to this, it was also noted that the compactness of blends was reduced at elevated temperatures.

### **2.3.3 Electrical Characterization**

Polymers, in theoretical terms, consist of special characteristics which makes them flexible, electrically insulating, semi-crystalline or amorphous materials. Hence, polymers are being widely used as dielectrics due to their reliability, accessibility, and cost effectiveness. Information obtained from dielectric studies greatly assists in knowing the attenuation and phase change occurring in the material. Nevertheless, such accurate investigation of polymer composites has not been extensively studied due to existence of some limitations and complexities involved in data analysis [85].

In 1998, Singh and Gupta have reported two types of dielectric relaxation with respect to temperature and frequency for PVA-based materials in the form of thin films. The results were explored by means of dipole–segmental motion ( $\alpha$ -relaxation) and side chain dipole group motion ( $\beta$ -relaxation). In order to obtain the best conclusion for dielectric results for a polymeric system, a precise technique in data analysis should be

done for the most important dielectric parameters: Dielectric constant that demonstrates polarization, and tangent of dielectric loss angle, which expresses some relaxation occurrences. A comprehensive study of these two main parameters as a function of both frequency and temperature reveals great understanding of the material's conducting nature and presence of structural phase transition (especially around crystalline melting point,  $T_m$ ) [86]

The process of choosing a suitable dielectric polymer for a certain application is highly dependent upon the operating conditions of the applied system. In the main, enhanced electrical properties of polymers can be achieved via the addition of inorganic fillers forming new materials called polymer composites. Such polymeric materials with superior properties are gradually emerging worldwide as tremendous functional materials being suitable for dielectrics and electrical insulation applications. Although the efforts of adding fillers to polymers to enhance a particular dielectric property has been present for several decades [87][88], the effect of the filler's size on the dielectric behavior of the polymer composites has not been fully explained in literature [89].

Krupa et. al. [90] prepared composites of high electrical conductivity consisting of a styrene-isoprene styrene block copolymer occupied with expanded graphite. These polymeric composites were investigated in terms of use as oil sensors of different kinds. It was mainly pointed out, that a rise in the amount of graphite had lowered the sensors' response rate. Another investigation by Krupa et. al. [91] was the preparation of HDPE/microcapsule blends. It was mainly concluded that a strong melting point shift of HDPE occurred at lower temperatures. This indicated a plasticizing effect of the HDPE based capsules.

Recent researches have shown promising dielectric properties for polyethylene composites in compared to similar properties in traditional neat polymers. Zubkova studied the influence of 2 wt% polyethylene terephthalate on carbonization of coals with varying maximum fluidity (MF). It was concluded that the blend of the polymer with the coals caused a decrease in the polymer's thickness layer [88]. Gomaa et al, investigated the effect

of nitrile rubber (NBR) on pure and waste polyethylene using Positron Annihilation Lifetime Spectroscopy (PALS). The immiscibility of NBR was studied and the electrical properties were interpreted in free volume parameters [92]. Another similar study on miscibility was done by Mostafa and Mohamed [93]. Styrene butadiene rubber-polyethylene blends were prepared. The intensity of these blends interestingly showed a negative deviation from the linear relationship of initial polymers.

Gouda et al. [89] prepared and characterized high-density polyethylene consisted of various portions of Na-montmorillonite clay-nanofiller. Enhancements on electrical properties of the HDPE/clay blend occurred in compared to the pure HDPE. Similarly, Mohapatra et al. [86] reported the effect of an organo-modified clay concentration on the dielectric relaxation properties of polymer nanocomposites. The resulted dielectric analysis provided an insight into ion dynamics in the PS/clay system. The permittivity pattern in Figure 10 for PS at room temperature shows a typical low frequency dispersion followed by high frequency saturation with a decrease by 3 orders of magnitude moving from low frequency to a higher one. The main cause was explained as being due to the space charge polarization at sample-electrode interface whereas the saturation in the high frequency region may be related to the orientational polarization effects due to relaxing dipoles.

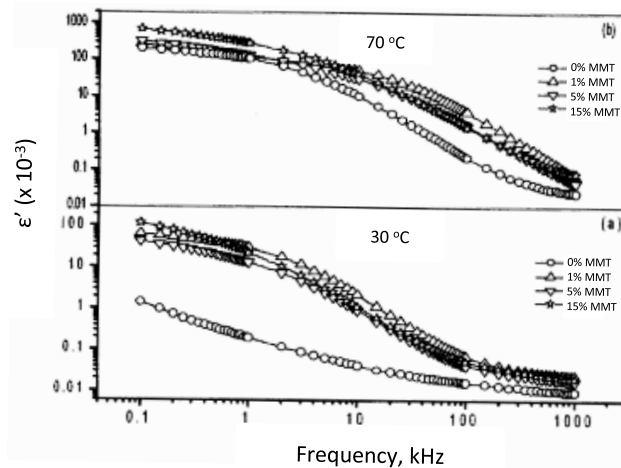


Figure 10: Frequency response of permittivity as a function of frequency for polymer-salt complex and clay composites of different clay concentrations [86]

Lately, recent studies are aiming towards utilizing waste polyethylene incorporated with various types of fillers to better investigate their electrical characteristics. Significant electrical and physical properties of polymeric specimens based on waste polyethylene was lately discussed. Los et al. studied the electromagnetic characteristics of waste polyethylene and polyvinyl acetate. A significant increase in dielectric constant was observed with increasing the content of Cu filler [94]. Another group studied the positron annihilation of a waste polyethylene terephthalate system filled with carbon black. The amorphousness of this composite was analyzed in the frequency range 0.1 Hz to 5 MHz and the percolation threshold was also determined [95]. Figure 11 presents the electrical conductivity versus carbon black content at elevated temperatures.

Shalaby et al. worked on utilizing waste plastics in cement pastes with a maximum amount of 10% waste polyethylene terephthalate in the prepared composites. The dielectric response of this plastic-filled cement material showed promising results at varying temperatures and different levels of hydration [96]. Adding to this, Abd-El-Messieh worked on studying dielectric properties of waste PE-natural rubber blends for electrical insulating purposes [97]. It was found that the addition of waste PE to natural rubber raised the permittivity,  $\epsilon'$ , and lowered the dielectric loss,  $\epsilon''$ , which in return enhanced the overall insulating characteristics of the blended materials.

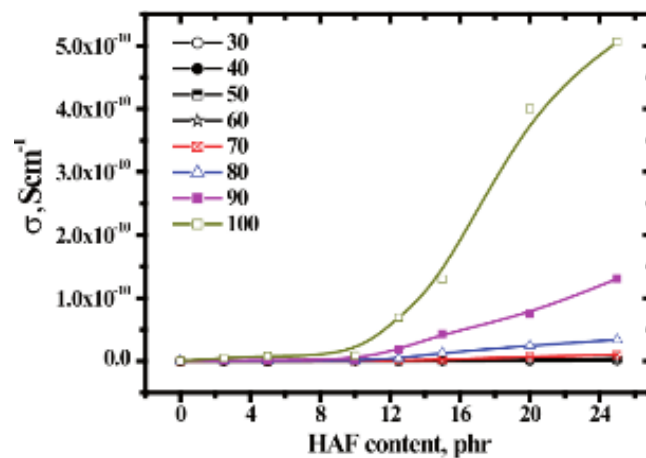


Figure 11: Electrical conductivity versus the HAF filler content at different temperatures [95]

Chand and Khare [98] have prepared polypropylene and waste recycled low-density polyethylene blends and measured the blends' dielectric constant in addition to the factor,  $\tan \delta$ . Three types of relaxation were found:  $\beta$ ,  $\alpha_c$  and  $\alpha$ ; and their activation energies were determined. Mohamed and Abd-El-Messieh [99] studied dielectric properties of waste low-density and waste high-density polyethylene filled with silica and asbestos. From this study, it was concluded that  $\epsilon'$  and  $\tan \delta$  for waste-HDPE materials was less than those for waste-LDPE. This was explained to be due to HDPE's higher crystallinity than LDPE. Table 6 summarizes some observed electrical properties with varying contents of filler.

Table 6: Summarized electrical properties notes when varying filler content in Waste Polyethylene Composites.

WPC	Filler	Change in Filler Content	Changed Elec. Prop.	Ref
Waste-PE/PVAc	Cu	Increased	Dielectric constant increased Electromagnetic shielding increased	[94]
Waste-PET	HAF	Increased	Electrical conductivity increased Relaxation time decreased	[95]
Waste-LDPE	Silica and asbestos	Increased	Permittivity and loss tangent rapidly increase Better insulation properties	[99]
Waste-HDPE	Clay-Nanofiller	Increased		[89]
Waste-HDPE	EG	Increased	Dielectric constant increased Electrical conductivity increased	This study

\* WPC: Waste Polyethylene Composite

### 2.3.3.1 Electrical Properties of Waxes

In 2013, Prava and Ahmed [85] have investigated new dielectric behavior of three types of waxes: bees wax (BW), paraffin wax (PW) and microcrystalline wax (MW). The dielectric constant and loss of the materials were calculated for the waxes after heat treatment with respect to varied frequencies. In line of our main interest our thesis work, a closer look on the dielectric specifications of the paraffin wax, as the phase change material, can be seen in Figure 12.

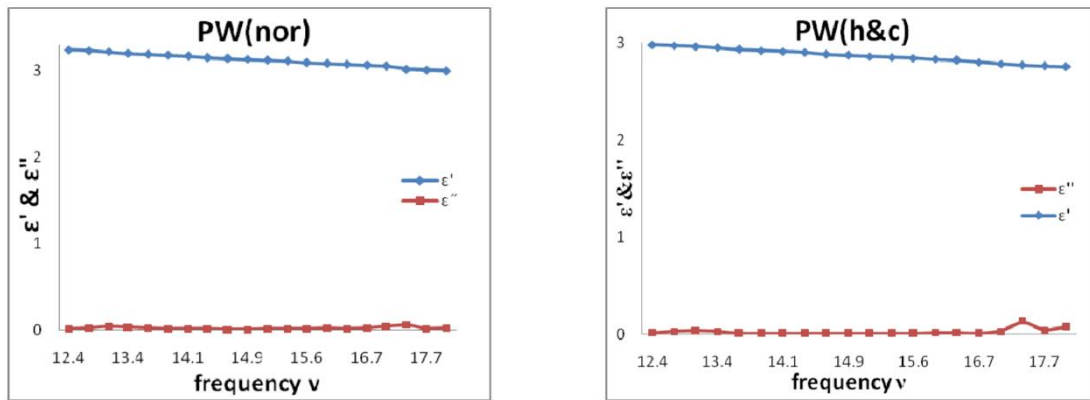


Figure 12: represent the variation of the dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) with frequency ( $\nu$ ) for paraffin wax in normal and after heat treatment [85]

The conductivity of the material was measured in terms of its resistivity. The study revealed an interesting change in dielectric loss and electrical conductivity with increase in frequency as shown in Table 7.



Table 7: Dielectric data for paraffin wax at normal and after heat treatment at different frequencies[85]

Wax Condition	Freq. (GHz)	$\epsilon'$	$\epsilon''$	$\sigma (\times 10^{-3} \text{ mho/cm})$
Normal	12.4	3.24	0.01	8.82
After heat treatment	12.4	2.98	0.02	11.58
Normal	17.9	3.00	0.02	15.62
After heat treatment	17.9	2.75	0.08	75.31

## **Chapter 3. MATERIALS AND METHODS**

Prior to conducting experimentation of the prepared samples, this study focused on employing specific types of raw components and have followed a well-planned methodology in order to be able to fully study the long-term properties of the PCMs.

### **3.1 Materials**

#### **3.1.1 Waste High-Density Polyethylene (W-HDPE)**

Waste HDPE (High-Density Polyethylene) with a melting point of 130 °C was supplied in granular forms from Doha Plastic Products & Recycling Co. (Mesaieed Industrial City (MIC), Qatar)

#### **3.1.2 Paraffin Wax**

A solid waxy PCM of Grade RT42 was employed as the phase change material in our composites. The paraffin wax was purchased from Rubitherm Technologies, Germany. It has a melting temperature of 41 °C.

#### **3.1.3 Expanded Graphite**

Expanded graphite (EG) was purchased from SGL Carbon, Germany. Some typical properties of this material are: Flexible and soft, chemically and thermally resistant, as well as thermally conductive. This powder material was of average size 200 mm (GFG200). EG was incorporated with our PCM as received without any additional treatment. Concentrations of expanded graphite were 5, 10 and 15 wt%.

### **3.2 Experimental Investigations**

#### **3.2.1 Sample Preparation**

The blends were prepared by mixing all components in the 50 ml mixing chamber of a Brabender Plasticorder PLE 331 (Germany) for 10 minutes at 140 °C and a mixing speed of 35 rpm. Table 8 shows the composition of Waste-HDPE, paraffin wax and expanded graphite (EG) for all 7 samples.

Table 8: Composition of prepared samples.

Sample ID	Waste-HDPE	Paraffin Wax	EG
	wt%	wt%	wt%
S1	100	0	0
S2	60	40	0
S3	50	50	0
S4	40	60	0
S5	45	50	5
S6	40	50	10
S7	35	50	15

### 3.2.2 Hot Press Machine

One-mm thick slabs were prepared by compression molding of the mixed composites using a laboratory press (Fontijne SRA 100, The Netherlands) at 150 °C for 1 minute. Then, the parallelepiped shaped PCMs were quenched between two thick metallic plates.

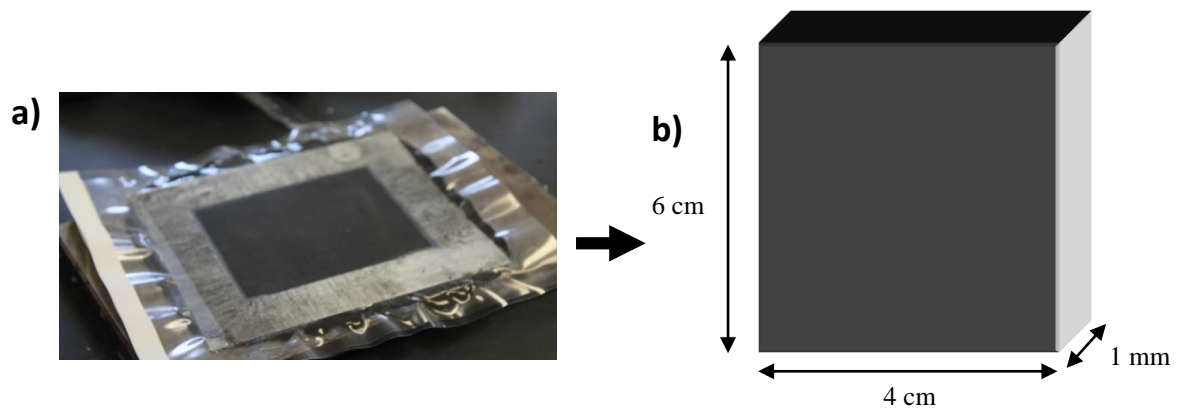


Figure 13: Parallelepiped molded PCMs after quenching (a) and dimensions (b)

### **3.2.3 Artificial Aging Accelerator**

Aging of the composite PCMs was carried out in an Accelerated Aging Tester (Q-Lab). The conditions of the aging were chosen according to ISO 4892-3 with one exception which is the changing of the temperature of the condensation step from 50 to 40 °C in order to ensure the solidification of paraffin wax during aging.

Artificial aging setup included UV irradiation at 340 nm with an irradiance of 0.76 W/m<sup>2</sup> at 60 °C for 8 h followed by a condensation step at 40 °C for 4 h. Those two steps were repeated for the entire duration of the test (100 days). Specimens were taken for characterization before aging (Day 0) and during aging (Day 5, 15, 30, 50, 100). All samples were exposed to harsh conditions and direct UV irradiation.

### **3.2.4 Scanning Electron Microscopy (SEM)**

The morphology of the composite PCMs was characterized using a FEI Quanta 200 environmental scanning electron microscope at 2.0 keV. The Scanning electron micrographs were taken for composite PCMs after the 100 days of artificial aging. This was done in order to understand the morphology and microstructure of the samples.

### **3.2.5 Fourier Transform Infrared Spectroscopy (FTIR)**

Fourier transform infrared (FTIR) spectrometry was used to identify the chemical changes and degradation (Photo-oxidation) in the PCMs structure during aging. FTIR data were recorded on FTIR spectrometer Spectrum 400 (Perkin Elmer). The spectra were characterized in wavenumbers. The carbonyl index (CI) was used to characterize the degree of degradation of the PCMs. The CI is defined as the peak area of absorbance of carbonyl band around 1740 cm<sup>-1</sup> and internal thickness band at 2020 cm<sup>-1</sup>.

### 3.2.6 Differential Scanning Calorimetry (DSC)

DSC measurements were performed using a Perkin Elmer model DSC 8500 (Perkin Elmer, USA) over a temperature range from 0 °C to 150 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Specific enthalpy of melting ( $\Delta H_m$ ) was calculated from the second heating curve in order to eliminate the thermal history of the samples, whereas, enthalpy of crystallization ( $\Delta H_c$ ) was calculated from the cooling curve. Nitrogen gas was passed through the instrument at a flow rate of 40 ml/min. Results obtained from DSC were calculated from 3 measurements and average values were presented. The weight of the tested samples varied from 3 to 5 mg.

### 3.2.7 Thermogravimetric Analysis (TGA)

thermogravimetric analysis (TGA) of a Perkin Elmer Pyris system was used. TGA is a thermal method that involves the measurement of weight loss as a function of temperature or time. In TGA, the change in the samples' weight was obtained while exposure to elevating heat. Temperature range applied in this test was from ambient room temperature 25 °C to 600 °C at a heating rate of 10 °C/min. Temperature was maintained at 600 °C for 20 minutes. All TGA tests were performed using a 10 mg sample under ambient pressure at nitrogen atmosphere. Loss in PCMs' weight versus temperature were plotted as thermograms in Chapter 4.

### 3.2.8 Leakage Analysis

Leakage analysis was performed as a method of characterizing weight loss of PCMs before aging (Day 0) and during aging at Day 5, 15, 30, 50 and 100. The PCMs were cleaned from excessive wax, using a clean cloth, then weighted via an analytical balance. The weight loss percentage of all aging samples were calculated according to the equation below:

$$\text{weight loss (\%)} = 100 - \frac{m_o - m_x}{m_o \times w} \times 100$$

Where:  $m_0$  is the initial mass of specimen.

$m_x$  is the actual mass of the specimen.

$w$  is the mass fraction of paraffin wax.

### **3.2.9 Thermal Conductivity Measurements (TC)**

The Transient Plane Source (TPS) method is one of the most precise and convenient technique for studying thermal transport properties [97]. It is an absolute technique, yielding information on thermal conductivity, thermal diffusivity as well as specific heat per unit volume of the material under study, in accordance with ISO 22007-2. The measurement of thermal conductivity and diffusivity has been performed by using parallelepiped-shape samples (45 mm • 45 mm • 5 mm). TPS Sensor with diameter 2 mm was sandwiched between two equivalent pieces of a sample. Various time, periods and power was used according the samples compositions. At least two measurements per each sample were performed in order to obtain reproducible values of thermal conductivity and diffusivity.

### **3.2.10 Tensile Mechanical Measurements**

For mechanical testing, dog-bone-shaped specimens with a working area of  $30 \times 4 \times 1 \text{ mm}^3$  were cut from the slabs. The mechanical properties in tensile mode were measured at room temperature using an Instron 3365 (England) universal testing machine at a deformation rate of  $10 \text{ mm} \cdot \text{min}^{-1}$ . Seven tensile measurements were done per sample, and the average values were recorded.

### **3.2.11 Dielectric Measurements**

The Dielectric Broadband Spectroscopy was used to investigate the dielectric loss and electrical conductivity properties of prepared PCMs. Prior to conducting dielectric measurements, the phase change materials were pressed using a hot press machine under  $150 \text{ }^\circ\text{C}$  for 2 minutes. The thickness values of the PCMs were reduced from 1 mm to ranges

of 0.02-0.08 mm (Table 9). This variation in the samples' thickness values after hot pressing may be due to the different compositions existing per component for each sample.

Table 9: Measurements of PCMs prior to Dielectric test

Sample ID	Diameter (mm)	Thickness (mm)	Constant Electrode Thickness (mm)
S1	2.00	0.35	2.00
S2	2.00	0.05	2.00
S3	2.00	0.02	2.00
S4	2.00	0.06	2.00
S5	2.00	0.06	2.00
S6	2.00	0.08	2.00
S7	2.00	0.08	2.00

After pressing the PCMs, round plate electrodes were prepared from these pressed PCMs via hammering a round-shaped mold on top of the surface of the thin PCM specimens. The detailed procedure is shown in the schematic below.

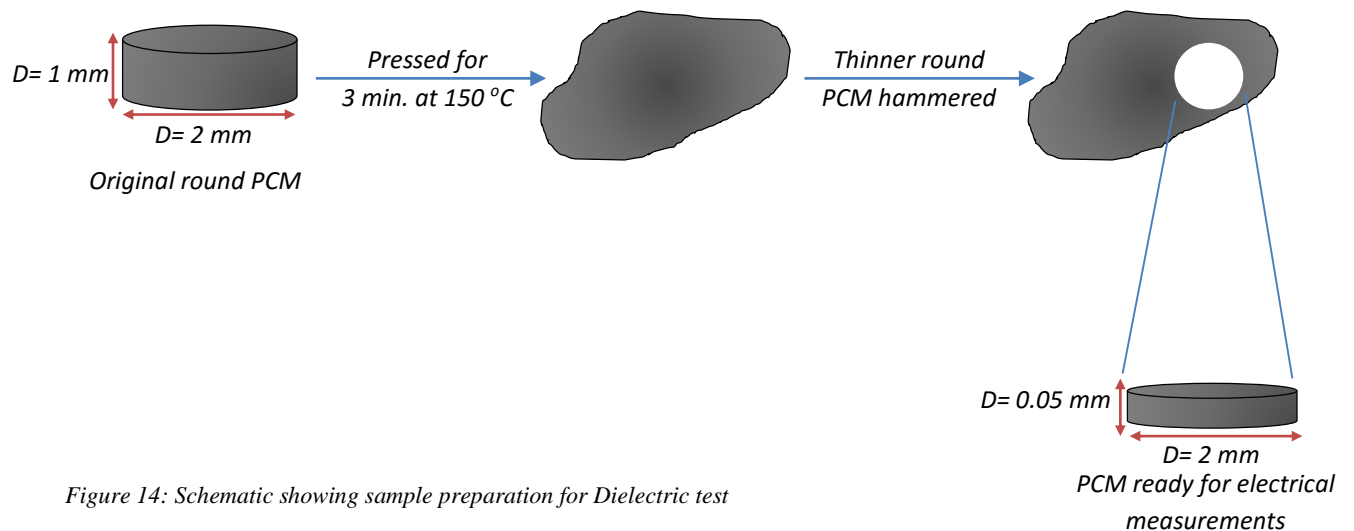


Figure 14: Schematic showing sample preparation for Dielectric test

The dielectric measurements of samples took an exact time of 5 hours and 30 minutes in the Dielectric Broadband Spectroscopy locked within a sealed chamber in a Liquid Nitrogen environment. After that, the device automatically cooled down to room temperature in order to be able to remove the sample, as per conditions and values entered to the Broadband Dielectric Spectroscopy. All data was obtained for temperatures from -100 – 150 °C with frequencies varying between the ranges 0.1 Hz – 3 MHz.



## Chapter 4. RESULTS AND DISCUSSION

### 4.1. Morphology of the PCMs

The micro-images were taken for the surface of samples after finishing the aging test (100 days) to observe the effect of harsh UV irradiation of which the samples were expose during the accelerated aging. There is a clear difference in the morphological behavior of materials. In case of the reference sample, Waste-HDPE, scratches in the surface of the material were visible in the micro level. These scratches are due to direct exposure of the UV irradiation, of which by time caused deterioration of the sample's surface. As low content of 40% wax was added to the blend, the miscibility of the wax within the W-HDPE matrix was very weak, and agglomeration of wax was noted at the surface.

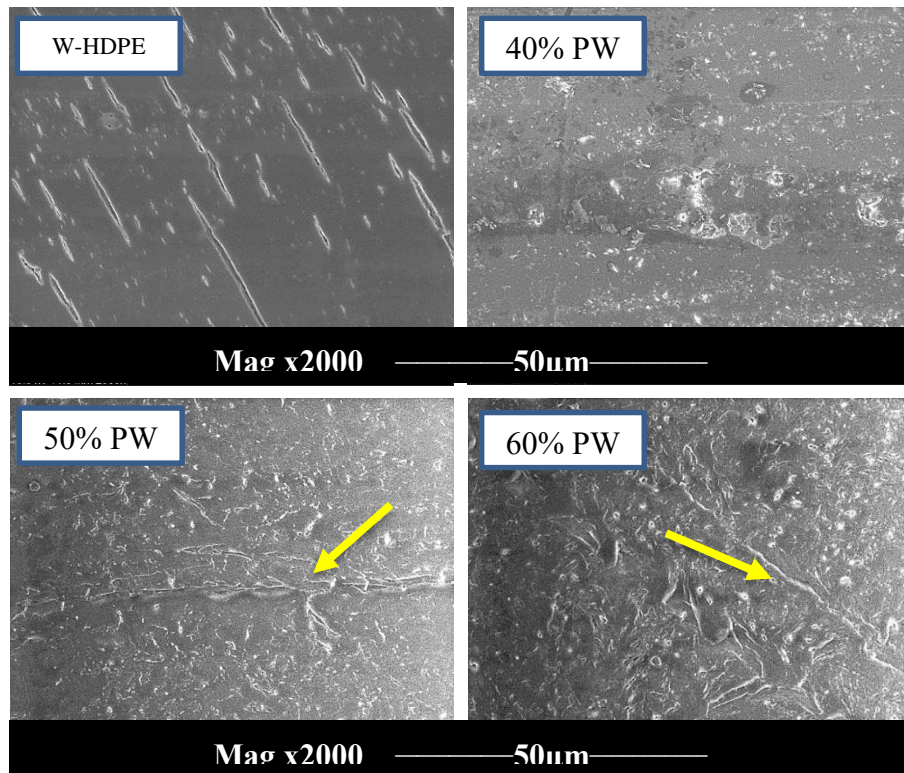
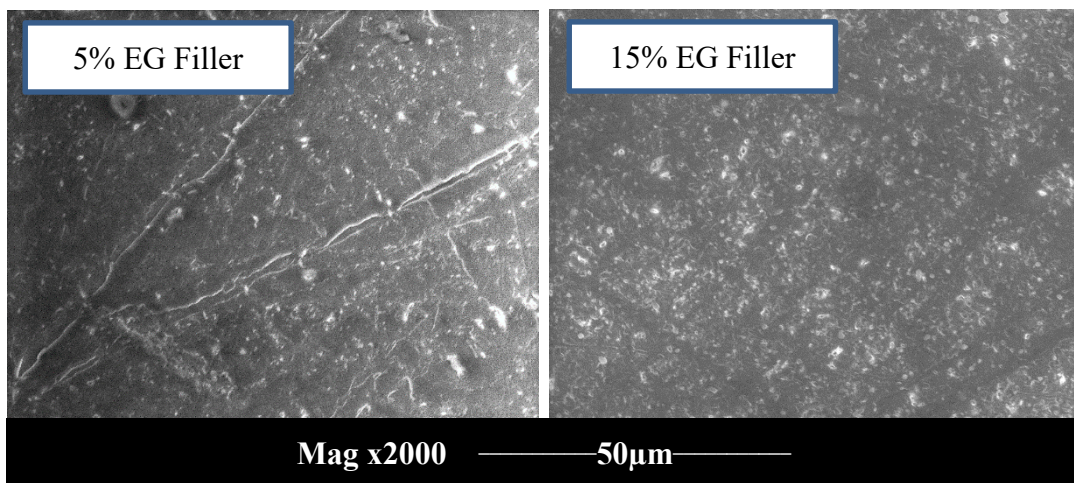


Figure 15: SEM images for W-HDPE as a reference and W-HDPE/wax blends

However, when adding the expanded graphite filler to fixed-50% Wax PCM composites with different contents (5%, 10% and 15%) clear changes in morphology were observed. Theoretically [69], expanded graphite contains a porous structure that allows the paraffin to be absorbed into the pores by capillary forces and surface tension. For the sake of comparison, the PCM containing only 5% EG, this small amount of filler does not contain enough pores to absorb the 50% wax. Whereas, when 15% EG was added, penetration of wax into the EG pores was observed.



*Figure 16: SEM images for PCMs with added EG fillers of 5 wt% and 15 wt% for comparison*

## **4.2 Leakage Analysis**

The leaching of paraffin wax from blend is caused by inherent immiscibility of wax and HDPE due to their different crystalline structures. Obviously, miscibility in amorphous phase was presented. All investigated samples showed the highest leaching in the first 5 days period, probably due to higher concentration gradient against later composition. At this period a significant amount of paraffin wax at the surrounding of the surface has been

leaked. In other words, it can be said that dispersion of wax in the blends highly depends on the structure of W-HDPE matrix. Hence, crystallinity of the polymer plays a big role in its leakage behavior. As per literature [100], HDPE has the lowest degree of chain branching. This means that it contains higher crystallinity areas and less amorphous regions.

The crystallinity structure of this waste polymer refers to more packing of the chains which may not allow for the low molecular paraffin wax chains to penetrate easily into the W-HDPE chain network. This, together with different crystalline structure of both components leads to a high phase separation between the structures of W-HDPE and wax. Therefore, after aging, when adding higher amounts of wax (up to 60 wt%), the wax chains were leaked out of the blends due to the difficult penetration into the polymeric chain network. As per calculations, the percentage of paraffin loss for the 40, 50 and 60 PCMs were 19, 18 and 20 percent, respectively. The lowest leakage of PCM for the W-HDPE/wax samples was the 50/50 blend. This trend is clearly shown in Figure 17.

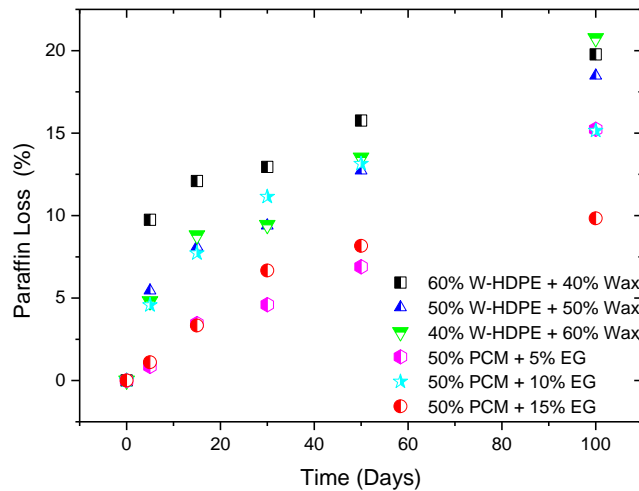


Figure 17: Leakage analysis of composite PCMs during days of artificial aging experiment

However, to explain the trend of the W-HDPE/wax/EG more specifically, the content of wax (50 wt%) was fixed and variations in EG added portions was studied. During artificial aging, where PCMs were directly exposed to both UV irradiation and heat, leakage of the wax took place in different rates for the different PCM compositions. Increasing amount of the EG filler from 5 wt% to 15 wt% also increased the amount of pores which allowed more wax to be absorbed into the graphite's porous structure via capillary forces. Also, due to the suppressing effect of expanded graphite and the capillary forces, the wax leakage decreased with increasing the content of expanded graphite. Parallel effect which decreases the leaching of paraffin from blends is that graphitic sheets represent a simple mechanical hindrance for paraffin movement. Finally, graphite resulted in an increase in the viscosity of the blends. This directly lead to suppressing of paraffin leakage. On the other hand, cracks formed by UV irradiation may enhance the paraffin leaching. From this reason, the leaching of paraffin from investigated materials is very complex phenomenon.

Therefore, as shown in Table 10, the percentage of paraffin loss was the least for the PCM of highest amount of EG with a loss percentage of 9.83%. Whereas it was 15.23% and 15.14% for the PCMs with 5 wt% and 10 wt% of EG filler.

*Table 10: Amount of paraffin wax left during the days of artificial aging experiment*

<b>Time (Days)</b>	<b>W-HDPE/Wax wt/wt</b>			<b>W-HDPE/Wax/EG wt/wt/wt</b>		
	<b>60/40</b>	<b>50/50</b>	<b>40/60</b>	<b>45/50/5</b>	<b>40/50/10</b>	<b>35/50/15</b>
<b>0</b>	50.00	50.00	50.00	50.00	50.00	50.00
<b>5</b>	45.13	47.27	47.59	49.57	47.71	49.44
<b>15</b>	43.95	45.95	45.60	48.28	46.14	48.33
<b>30</b>	43.52	45.30	45.28	47.70	44.43	46.67
<b>50</b>	42.12	43.64	43.24	46.55	43.43	45.92
<b>100</b>	40.11	40.76	39.62	42.39	42.43	45.08

### 4.3 FTIR analysis of PCMs

Fourier transform infrared (FTIR) spectrometry was used to identify the chemical changes in the degradation (photooxidation) of the PCMs during artificial weathering. The increase of carbonyl groups during artificial weathering has been observed. Decreasing of transmittance area can be attributed to the creation of carbonyl groups. A similar relation was observed by Sobolciak et al. [101].

In actual terms, the presence of two components of similar chemical composition would accelerate the photo-oxidation of the material. This was the case for the PCMs containing W-HDPE and paraffin wax. On the other hand, it became a different case once EG was added. The carbonyl index (CI) was a very important factor which identifies the degree of degradation of the PCMs. The CI was defined as the peak area of absorbance of carbonyl band around  $1700\text{ cm}^{-1}$ ; as shown in Figure 19.

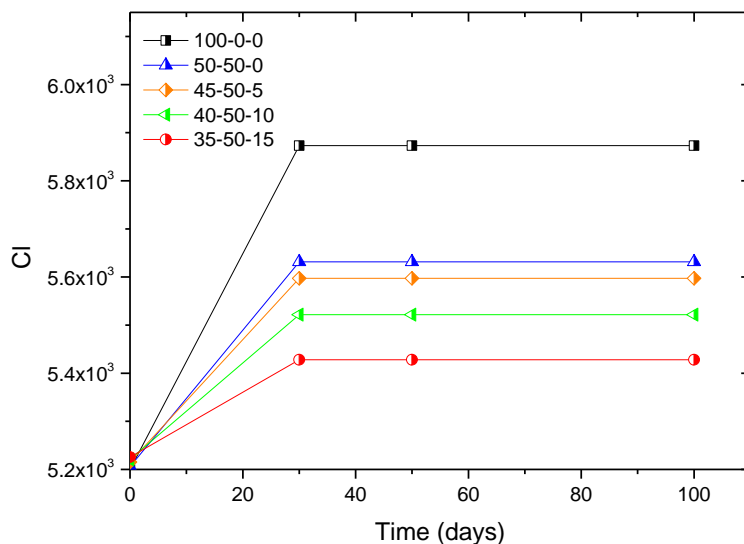


Figure 18: Carbonyl index vs time for W-HDPE as a reference, and PCM blends with 50 wt% of wax

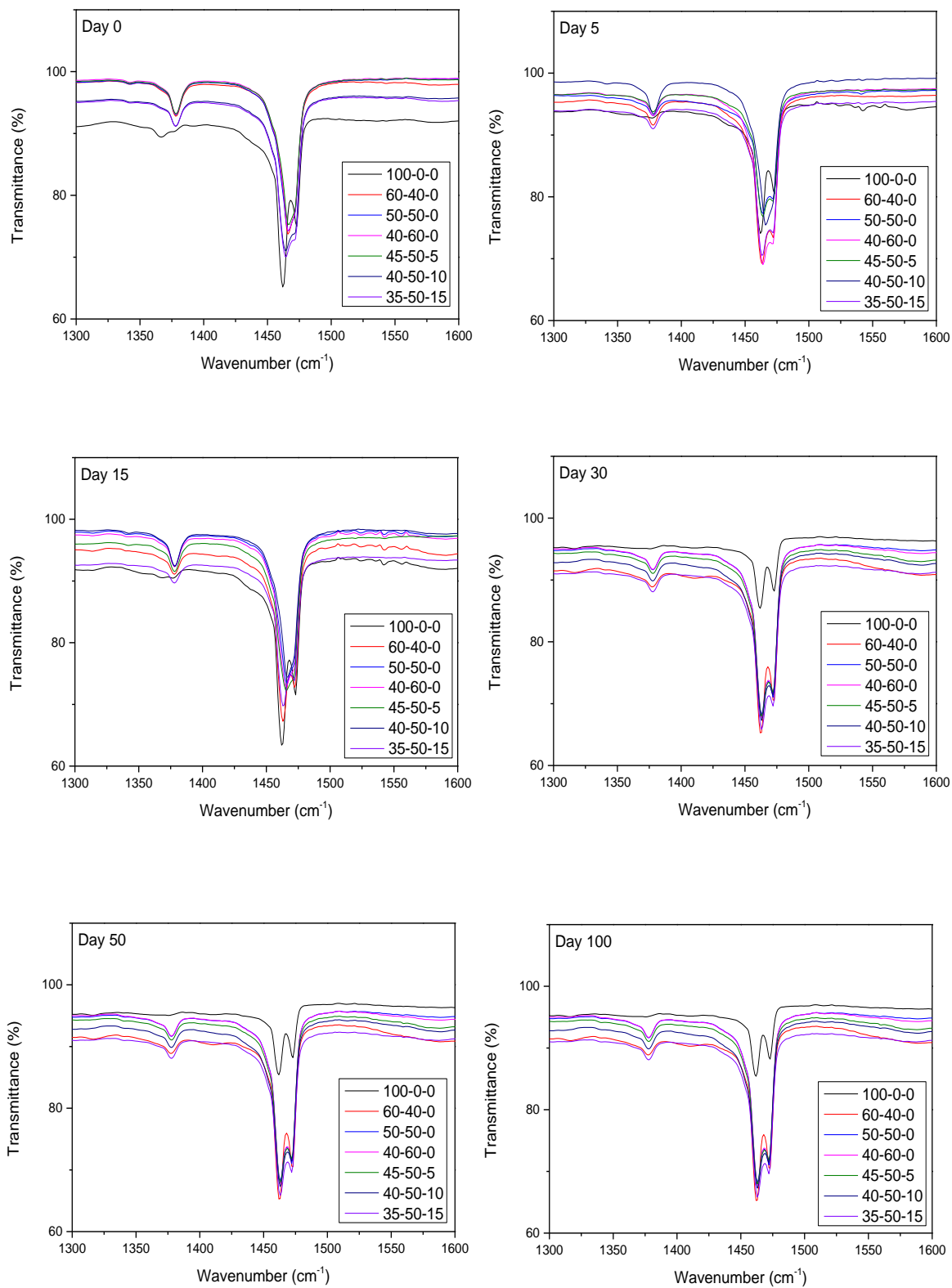


Figure 19: FTIR spectroscopy of PCMs based on W-HDPE, wax and EG during the days of artificial aging test where Carbonyl index was calculated.

Furthermore, from Figure 18, the degree of PCM degradation was very clear. It shows that PCMs with higher amounts of filler contained much less CI values, meaning less degradation occurred. It can be stated, that CI is reduced with more EG content. These experiments confirmed the well-known effect of carbon materials (i.e. graphite, carbon black and carbon nanotubes) on UV stability of the polymers. This phenomenon is caused by a conjugated system of  $\pi$ - $\pi$  bonds in those materials which were able to deactivate the free radicals (created by UV light, oxygen, etc.) as it is known for low molecular antioxidants and stabilizers commercially used in plastics.

## **4.4 Thermal properties of the PCMs**

### **4.4.1 Thermal Conductivity**

The investigation of thermal conductivity properties for PCMs was considered in this work for further enhancements in heat storage and release properties of prepared PCMs. Basically, thermal conductivity is related to the ability of materials to conduct heat. A high thermal conductivity denotes a good heat conductor, whereas a low thermal conductivity indicates a good thermal insulator [102].

Results showed that as the amount of wax added to the W-HDPE matrix is increased, the thermal conductivity was proportionally decreased. This is because wax has much lower conductivity than W-HDPE (0.24 W/m.K versus 0.5 W/m.K). Values of thermal conductivity of all blends are shown in figure 20. The blends of W-HDPE\Wax blends showed much lower thermal conductivity in compared to the ones with added EG.

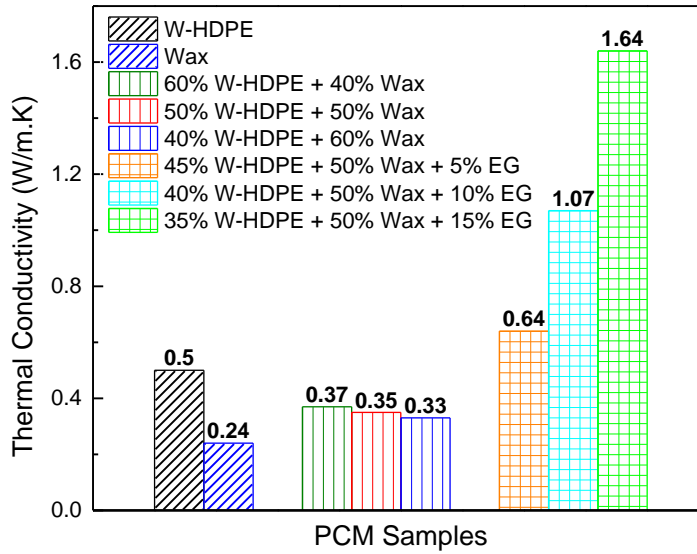


Figure 20: Thermal conductivity of pure components in compared to wt/wt/wt, W-HDPE/Wax/EG PCM composites

Furthermore, as shown in figure 20, the addition of the expanded graphite filler significantly enhanced the composite PCMs. This improvement in thermal properties of PCMs is due to the much higher conductivity of expanded graphite (129 W/m.K) compared to that of PCMs (0.24 W/m.K). Thus, as per literature, the contribution of paraffin wax to thermal conductivity was neglected in this case and the effect of graphite was much more pronounced. Also, as confirmed by Ling et al. [103], the particles of expanded graphite interlock to form a network to hold PCMs and hence conduct heat. This explains the raise in thermal conductivity when more amounts of EG was added to the composites; reaching the highest value of 1.64 W/m.K.



#### 4.4.2 Differential Scanning Calorimetry (DSC)

The DSC measurements were done to further study the thermal characteristics of the prepared composites. The specific enthalpies of melting and crystallization are characteristics of particular interest for PCM functionality because they have a direct relation to the ability to absorb and release the heat. In general, an increase in paraffin wax portion within blends lead to the increase in specific enthalpy of melting (in the case of immiscible components) due to inherently higher specific enthalpy of melting of paraffin against polyethylene. The data in Figure 21 below were calculated for all materials before, during and after the aging test for the sake of measuring the effect of wax and expanded graphite filler on the thermal properties of the composites. According to previous results from leakage tests, one can logically expect that the amount of wax within aged blends will decrease and therefore the specific enthalpy of melting of paraffin within blends will be continuously decreasing. Here we have to point out that only thermal characteristics of paraffin within blends were investigated. The influence of paraffin on the thermal characteristics of polyethylene phase was not involved in this study.

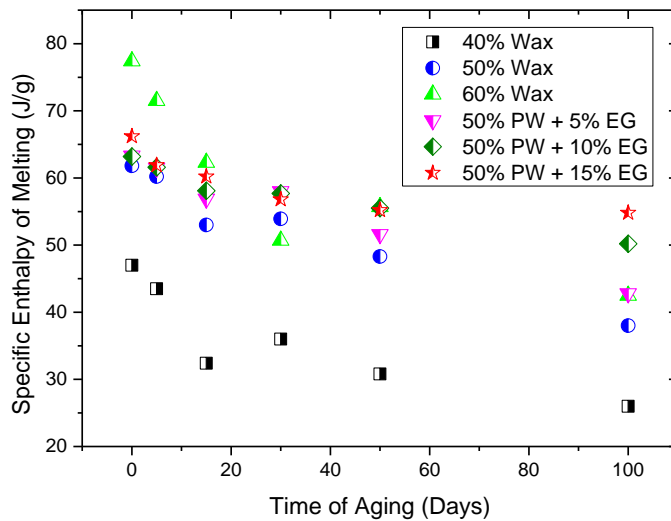


Figure 21: Specific enthalpy of melting versus days of artificial aging

The greatest reduction for specific melting enthalpy was noted for the blends without filler. This is due to the leakage effect of paraffin wax as mentioned earlier. As for the composites with added portions of EG (here we investigate only blends with 50% of wax), the melting enthalpies were higher. This phenomenon is caused by enhanced crystallinity of paraffin within composites caused by graphite particles which probably acted as promoters for crystallites growth [100].

It is seen that during artificial aging, and due to significant leakage of wax out of the materials, the specific enthalpy of melting decreased. This decrease is proportional to the paraffin reduction during leakage. The PCM with highest portion of filler (15% EG) showed the least reduction in thermal properties, and this is greatly due to the addition of the high conductive filler which worked as a stabilizer for the specimens with respect to the leakage suppression. The higher the amount of graphite, the more stabilized was the PCM [101].

Variations in melting and crystallization temperatures of the PCMs was observed during artificial aging as listed in Table 11 and Table 12. The data listed in the tables confirm the percentage drop in specific enthalpy for melting and crystallization (17.2% and 8.6%, respectively) were the minimum for PCMs with 15% expanded graphite.

Table 11: DSC melting temperatures and enthalpies for the different compositions of PCMs during aging

W-HDPE/W/EG	<b>60/40</b>		<b>50/50</b>		<b>40/60</b>		<b>45/50/5</b>		<b>40/50/10</b>		<b>35/50/15</b>	
Time (Days)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)
0	43.8	47	44.7	61.8	44.3	77.4	44.4	63.3	43.9	63.2	43.9	66.2
5	44.3	43.5	44.8	60.2	45.5	71.5	44.0	61.5	44.4	61.6	45.1	61.9
15	45.1	32.4	44.2	53	46.0	62.3	44.6	56.9	43.9	58.1	43.8	60.2
30	45.9	36	44.6	53.9	45.6	50.7	44.5	58	44.5	57.7	44.8	56.8
50	45.3	30.8	45.1	48.3	46.0	55.7	44.8	51.6	44.5	55.5	45.5	55.2
100	45.9	26	46.5	38	47.2	42.5	46.2	42.8	44.8	50.2	44.8	54.8
%Drop in ΔH <sub>m</sub>		44.7%		38.5%		45.1%		32.4%		20.6%		17.2%

Table 12: DSC crystallization temperatures and enthalpies for the different compositions of PCMs during aging

W-HDPE/W/EG	<b>60/40</b>		<b>50/50</b>		<b>40/60</b>		<b>45/50/5</b>		<b>40/50/10</b>		<b>35/50/15</b>	
Time (Days)	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (J/g)	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (J/g)	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (J/g)	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (J/g)	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (J/g)	T <sub>c</sub> (°C)	ΔH <sub>c</sub> (J/g)
0	36.7	-48.3	36.0	-73.3	36.1	-78.8	36.1	-62.7	36.7	-64.0	36.6	-63.8
5	36.4	-46.7	36.1	-66.9	36.7	-70.9	36.4	-61.9	36.4	-60.7	36.5	-60.7
15	38.5	-33.0	36.8	-53.8	39.0	-63.1	35.8	-65.2	36.6	-58.7	36.9	-61.5
30	39.0	-37.1	37.6	-54.7	38.2	-63.0	36.0	-64.2	36.5	-57.4	37.3	-58.1
50	38.5	-30.8	37.7	-48.9	37.5	-60.3	37.1	-55.3	36.5	-56.8	38.5	-55.8
100	38.4	-26.0	38.3	-39.8	39.9	-44.7	39.4	-43.9	37.0	-54.8	37.1	-58.3
%Drop in ΔH <sub>c</sub>		46.2%		45.7%		43.3%		30.0%		14.4%		8.6%

#### **4.4.3 Thermogravimetric Analysis (TGA)**

The TGA measurements were conducted to take a closer look on the mass loss of the PCMs at elevated temperatures. Figure 22 shows the thermographs of the PCM samples of only W-HDPE/Wax blends whereas Figure 23 shows the thermographs of the composites with EG filler. All data was obtained before, during and after 100 days of artificial weathering. Thermal degradation of paraffin wax for all PCMs was observed. The plots show that at Day 0 before aging, all samples contained 50% weight of wax. During aging, the percentage of weight loss started to shift and increase in terms of weight loss.

All plots demonstrate thermal degradation of the paraffin wax for all PCMs due to much lower thermal stability of paraffin against HDPE. The wax started to degrade starting from 190 °C to 350 °C. This means that approximately 40% reduction in mass took place for all specimens. At a temperature of 420 °C in the PCM, the waste HDPE began to degrade. At 500 °C the whole PCM was degraded. No char formation was observed for materials without graphite.

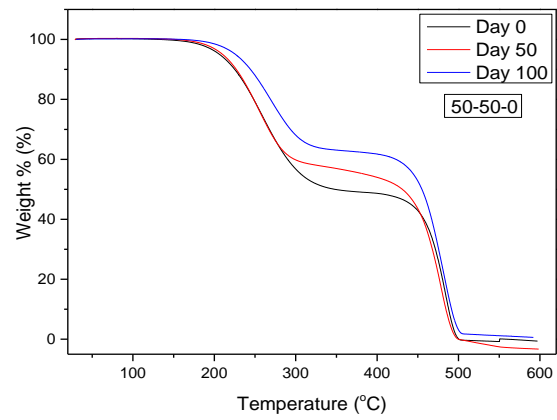
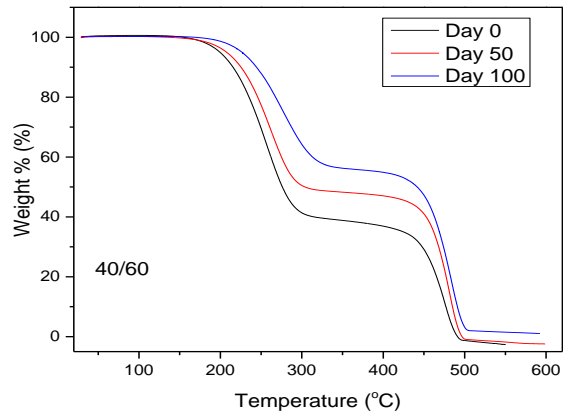
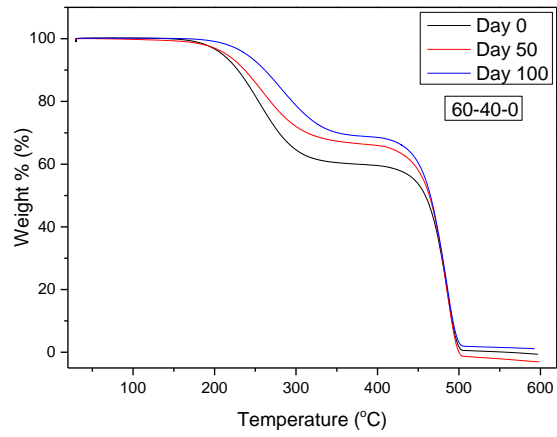


Figure 22: TGA of W-HDPE/Wax blends in N<sub>2</sub>

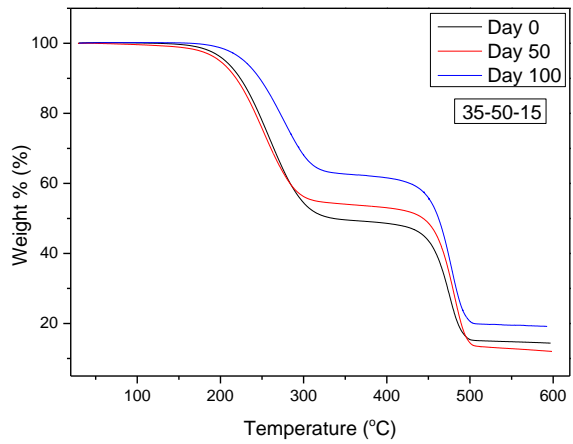
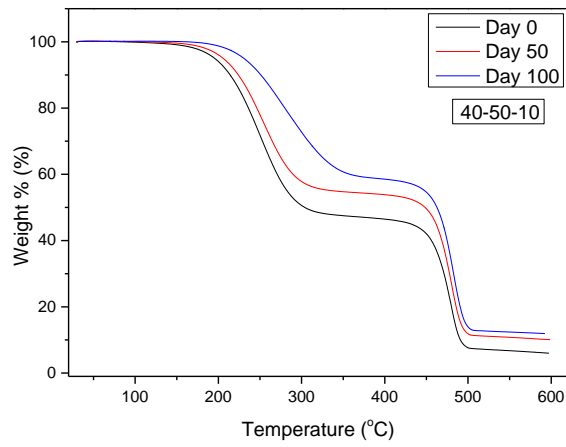
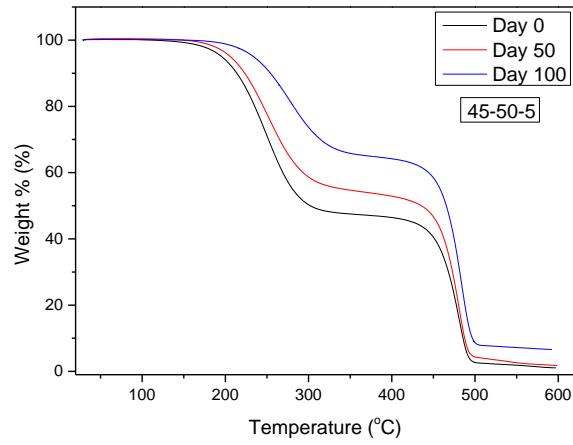


Figure 23: TGA of W-HDPE/Wax/EG composites in N<sub>2</sub>

Figure 24 shows a comparison between 50 wt% PCMs in compared to reference W-HDPE sample with no wax and no filler. Thermal degradation was clearly observed in this plot. It seems that expanded graphite particles have negligible effect on the degradation behavior of composites.

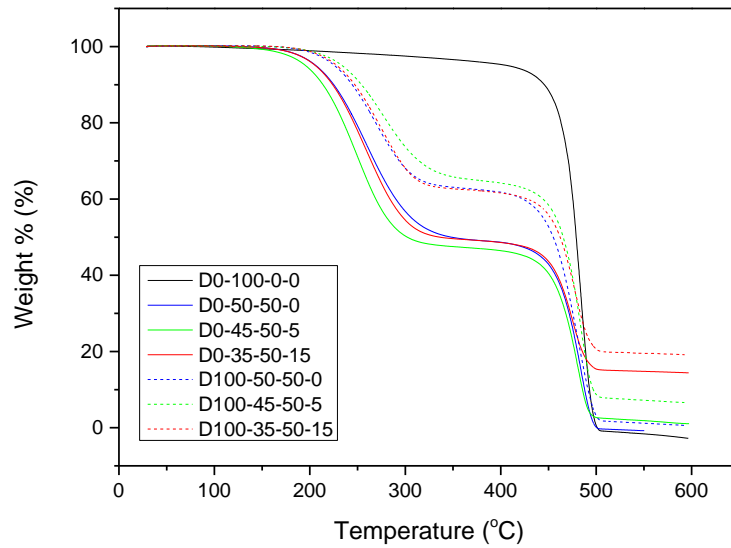


Figure 24: TGA of PCMs containing 50 wt% paraffin wax in compared to reference W-HDPE



## 4.5 Dielectric Behavior of PCMs

Most polymer composites consist of significant amount of electrical resistance. Therefore, the frequency-dependent trend of dielectric properties assists in fully understanding the important characteristics of our prepared PCM heat absorbers [104]. In waste high-density polyethylene, dielectric loss analysis was calculated. When the waste polymer was exposed to electric field, the energy storing capacity of the material was analyzed by means of polarization at varying frequencies.

Based on literature [105], at low frequencies, in a static region, the dipoles have enough time to align with the field before they change direction. Whereas, at very high frequencies the dipoles do not have time to align before the field changes direction. This explains the incapability of molecules to polarize under applied electric field, known as dielectric loss ( $\epsilon''$ ) at very low frequencies. This trend is clearly shown in Figure 25.

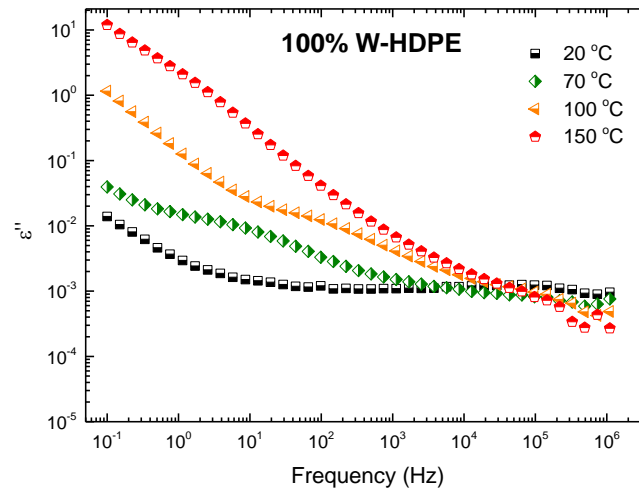


Figure 25: Dielectric loss vs frequency for waste HDPE at elevated temperatures

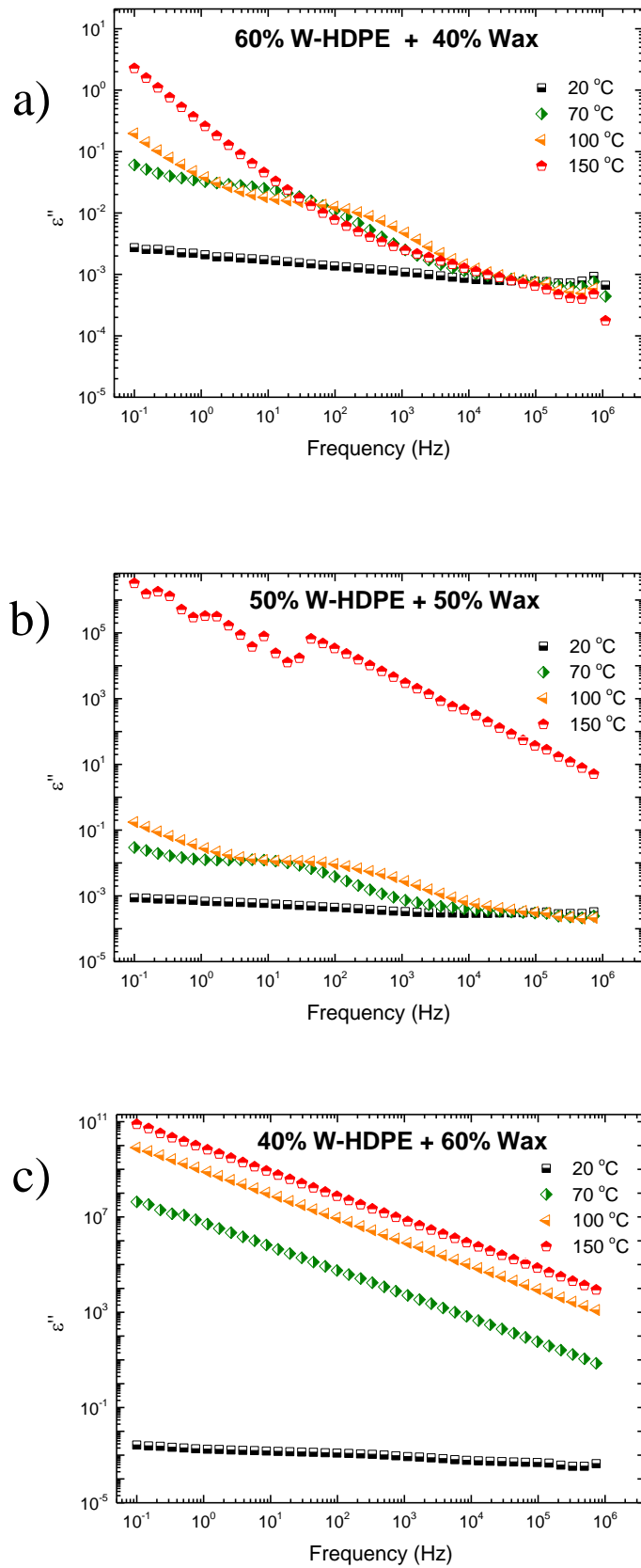


Figure 26: Dielectric loss vs different frequency values for W-HDPE/PW, wt/wt, (a) 60/40 (b) 50/50 (c) 40/60 blends

At intermediate frequencies the dipoles move but have not completed their movement before the field changes direction and they must realign with the changed field. Thus, the time taken for the dipoles in HDPE to return to their original random orientation (relaxation time) occurs exponentially. Also, it was observed from the results that with increase in temperature, the relaxation time for waste HDPE slightly decreased. Hence, this shift in relaxation time altered the dielectric loss values at varied frequency.

Similarly, in the case of blends with added paraffin as shown in Figure 26, the frequency at the maximum point of dielectric loss shifted to a greater value with increase in temperature. Interestingly, as the amount of paraffin increased from 40% to 60%, the dielectric loss was highly affected by the highest heating temperature of 150 °C. This may be due to the breaking of intermolecular forces between the polymer chains which in turn raised the thermal agitation. This increased the mobility of the molecules making the chains free to move in order to correspond with the changing electric field. As for electrical conductivity vs frequency plots, it was observed that at lower frequencies, and elevated temperatures, the electric conductivity in the composites increased due to a decrease in viscosity and an increase in ion mobility of the PCMs.

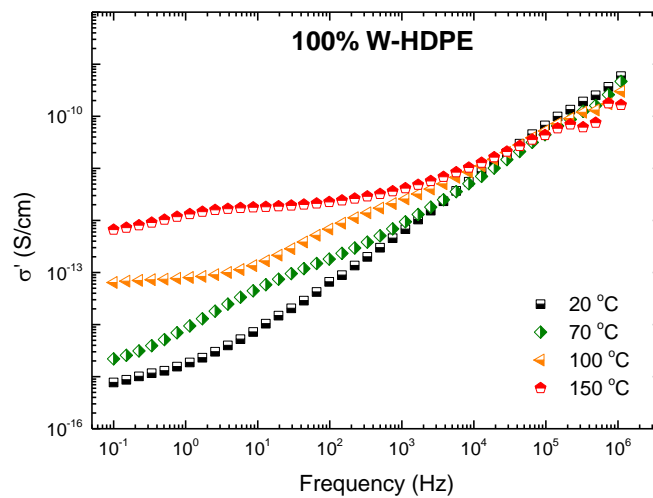


Figure 27: Electrical conductivity of waste HDPE vs frequency at elevated temperatures

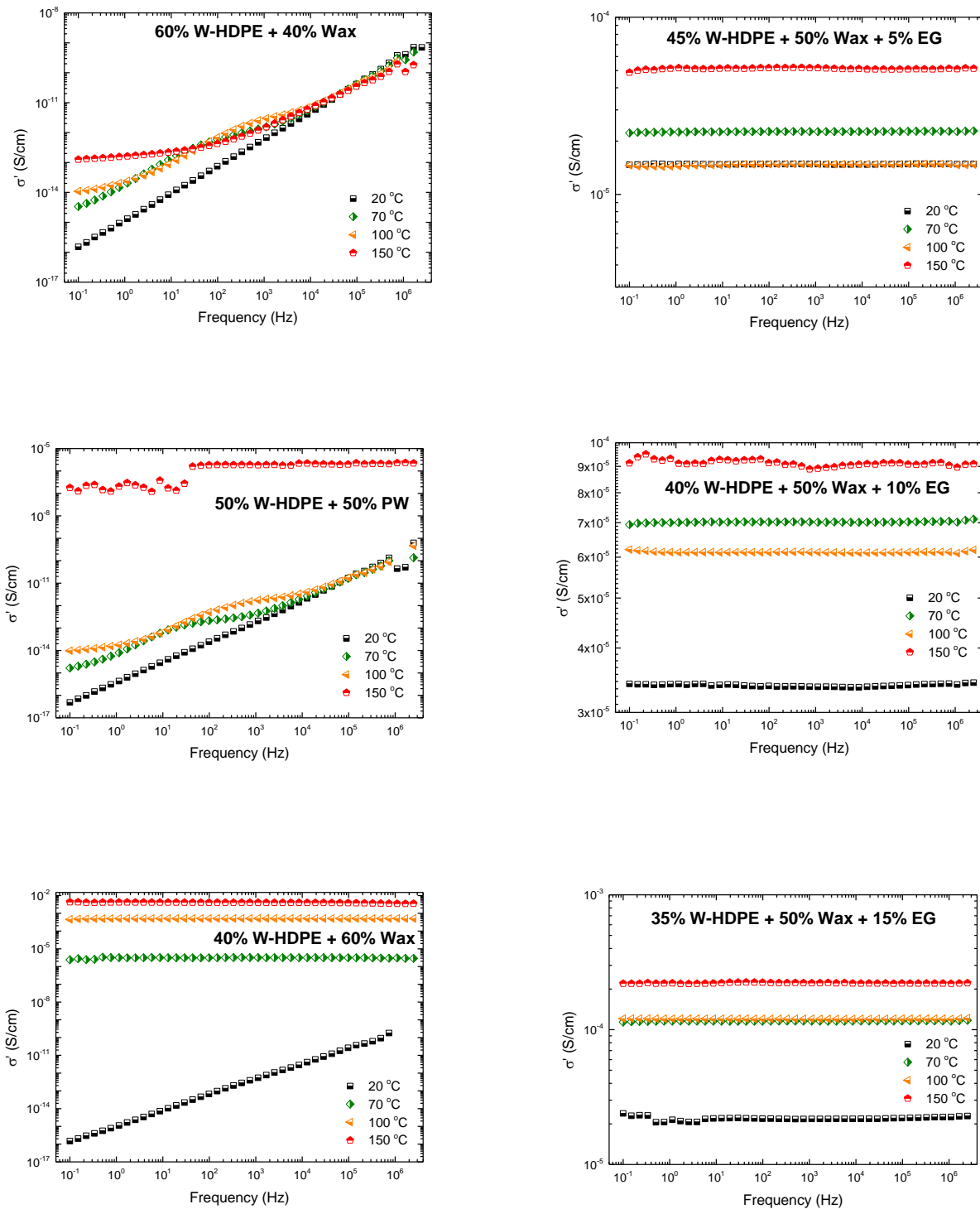
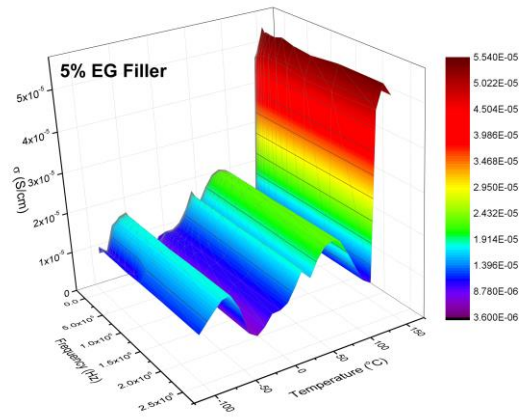


Figure 28: Electrical conductivity vs different frequency values for PCMs

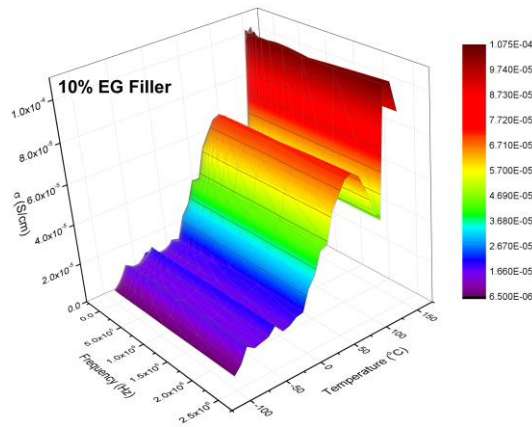
As noted from the plots in Figure 28, there is a clear difference in electrical conductivity values between the PCMs of added EG and the ones without the filler. The W-HDPE/wax blends with 40% and 50% paraffin, a normal behavior at room temperature was shown with a deviating increase as frequency increased. However, as temperature was raised from 20 °C to 70 °C, the melting point of paraffin wax was already due, and so a noticeable change in the trend was shown. This may be as a result of released paraffin from the PCM blend which actually caused the occurrence of relaxation phenomena. When the maximum amount of wax was added (60 wt%), at temperatures of 70 °C and greater, an unexpected trend line was observed. This could be the result of an unexpected aspect influencing the result: leakage of paraffin wax during the raise in temperature has most probably occurred, causing the PCM material to change its dimensions (thickness and diameter). This may be the reason of the rapid increase in the 40/60 blend's electrical conductivity value reaching almost  $10^{-2}$  S/cm. Nevertheless, when portions of expanded graphite were added to the PCMs, the trend was more clear showing the highest electrical conductivity value for 15% EG in the PCM.

As a way to confirm the positive effect of the filler to the whole composite PCM, Figure 29 shows 3-D plots of electrical conductivity versus frequency with respect of change in temperature for the materials with EG. It was concluded that the addition of EG made the material more stable at higher temperatures. And significantly reduced the peak fluctuations (as in Figure 29.a and Figure 29.b) as a result of inhibited leakage of paraffin wax out of the PCM material. Figure 29.c showed a much smoother trend due to the high amount of filler which also confirms an enhanced stability of the PCM.

a)



b)



c)

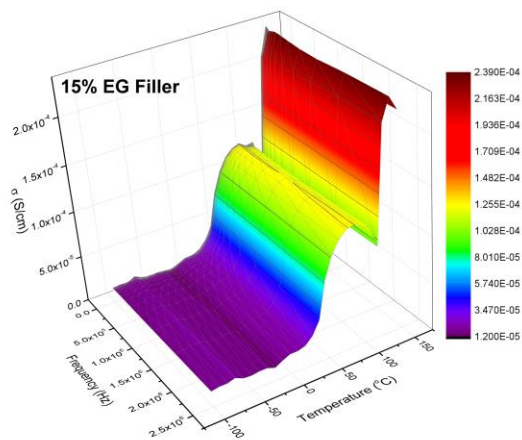


Figure 29: 3-D plots of electrical conductivity vs frequency with respect to change in temperature: a) 45/50/5 b)40/50/10 c) 35/50/15

#### 4.6 Mechanical properties of PCMs

Mechanical properties are summarized in Table 13. The Young modulus (E), stress at break ( $\sigma$ ), and strain at break ( $\epsilon$ ) were obtained along with their standard deviations.

Table 13: Mechanical properties obtained tensile measurement

Sample W-HDPE/Wax/EG	Young modulus		Stress at break		Strain	
	E (MPa)	SD	$\sigma$ (MPa)	SD	$\epsilon$ (%)	SD
100-0-0	809	34	20.3	6.6	659	288
60-40-0	419	33	13.7	1.4	1285	144
50-50-0	356	25	9.14	0.72	1203	114
40-60-0	297	36	6.08	0.26	1109	95
45-50-5	435	19	4.53	0.68	15.3	4.9
40-50-10	518	54	5.88	0.26	7.96	1.78
35-50-15	624	46	5.82	0.32	4.63	0.39

HDPE is an inherently very ductile material with high elongation at break, strength and relatively high Young modulus. This behavior is significantly changed when additives such as paraffin wax and expanded graphite are added. Firstly, the presence of soft, waxy material having low deformability, toughness and strength significantly decreases all these parameters of HDPE. This is because paraffin behaved as a plasticizer. This lead to a decrease in strain at break from 1285% to 1109% (when adding 40% to 60% of wax, respectively). Similarly, the strength of the blends decreased with increasing portions of paraffin wax up to 60 wt%. This may be due to the decrease in the orientation hardening of HDPE. Similarly, soft wax chains move more freely in the blend than chains of HDPE themselves which reduces the transferring of the stress applied across the whole blend resulting in the decrease in young modulus.

However, when EG was added to the composite PCMs, much higher stress was required for the fracture to take place at lower elongation. Thus, the EG particles influenced the overall materials mechanical behavior. The PCMs became harder and brittle which caused slipping to occur at lower strain percentages. This behavior was caused by the reinforcing effect of graphite particles. This is shown in Figure 30 and Figure 31.

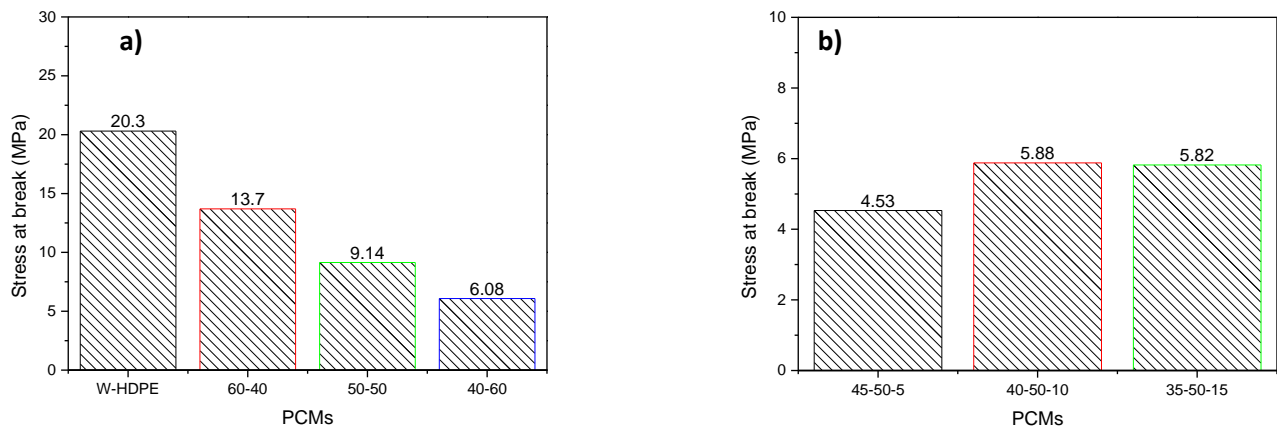


Figure 30: Stress at break for PCM blends with no filler (a) and added EG filler (b)

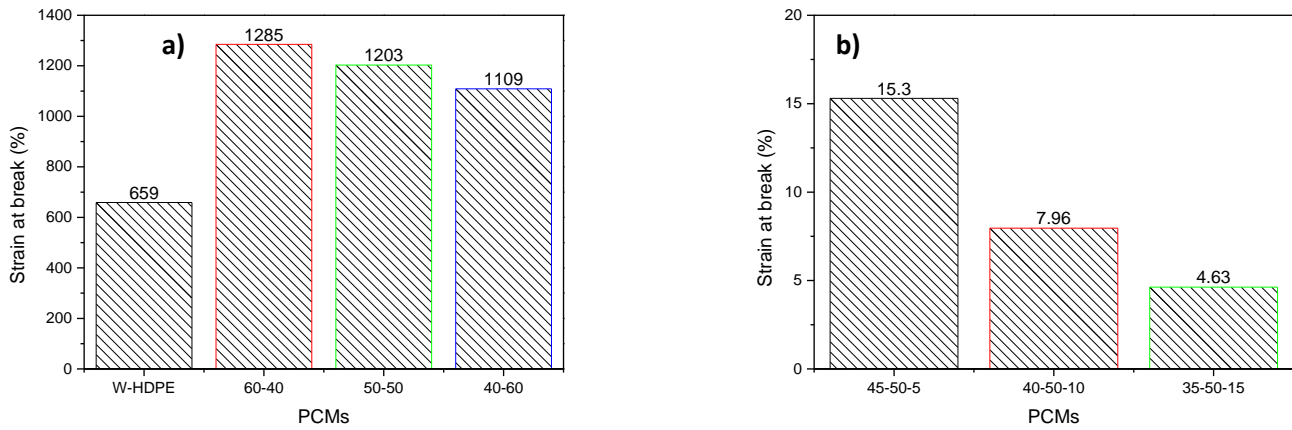


Figure 31: Strain at break for PCM blends with no filler (a) and added EG filler (b)



Elasticity is directly related to the uniform increase in separation between atoms of the PCMs. Graphite offers noticeable reinforcement to the PCMs that are mainly due to its stiffness [106] and partially due to the interfacial interaction between graphite and the polymer. This relation is shown in Figure 32.

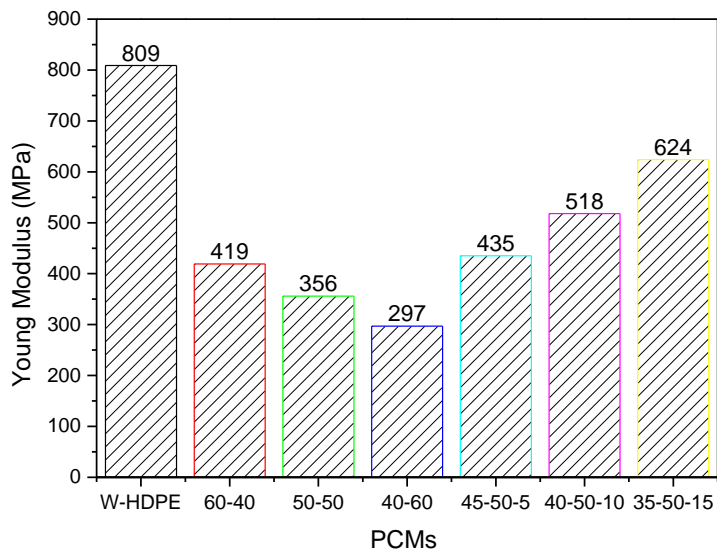


Figure 32: Young Modulus for all PCMs

## Chapter 5. CONCLUSIONS

Heat absorbers based on Phase Change Materials (PCM-HA) created from recycled high-density polyethylene, paraffin wax and expanded graphite were prepared and studied in this thesis. The main focus was to deal with their thermophysical properties, mechanical properties and electrical properties. The materials were artificially aged at selected conditions (temperature, UV irradiation, humidity) to characterize their long term behavior. It was found that paraffin wax blended with recycled HDPE and expanded graphite seemed to be good candidates for preparation of PCMs for different applications, such as thermal energy storage systems. The prepared PCMs were tested through long term artificial aging up to 100 days. This type of characterization was rarely reported in literature. Thus, the obtained results conveyed valuable benefits.

A Strong effect of aging on the final properties was found. The samples without the presence of graphite were cracked after 10 -20 days of UV exposure. The positive influence of expanded graphite was demonstrated also in this case. Samples mixed with EG did not lose their mechanical integrity and compactness even after 100 days-long aging. Degradation behavior of samples was analyzed using FTIR spectroscopy. In addition, the materials showed a high ability to absorb and release almost 70 J/g of heat energy. Addition of EG into the PCMs brought a lot of advantages. Firstly, it improved thermal conductivity of PCMs which in turn increased the rate of heat transfer. Secondly, EG also significantly reduced leakage of paraffin from the system when heated up to the melting point of the wax; this was confirmed by the long term leakage test. Further, dielectric behavior of PCMs was explored. Addition of EG to the materials confirmed the increase in electrical conductivity.

Generally, it was concluded that the use of PCM-HA would not only embrace utilization of recycled polyethylene products, but would also take part in direct energy savings and reduce energy consumption. In some countries, this may also lead to significant money savings. This is one of many attractive benefits of our PCM-HA system.

## **Chapter 6. RECOMMENDATIONS & FUTURE OUTLOOK**

The prepared phase change material heat absorbers (PCM-HA) with effective portions of expanded graphite can be majorly employed as a heat storage agent in building infrastructure; such as inner walls of buildings, ceilings, and even floors. For instance, our tested materials can be used as raw heat absorber elements that can be employed in the inner walls of the buildings.

The integration of such effective heat absorbers into the wall, ceilings, and even floors of buildings would majorly result in great savings in energy consumption. It is important to point out that for the purpose of lowering indoor air temperature swing, the suitable melting temperature of PCM should roughly be equal to the average indoor air temperature of regular sunny days. This allows the storage of a large amount of heat in a relatively small volume.

Taking into consideration the local climate here in the GCC region, the concept of utilizing local waste polyethylene materials, and employing them as raw elements in the processing of effective heat absorbers, such as our prepared PCM-HA, is considered to be a very operative way of directly employing recycled polyethylene in more advanced and multifunctional applications that best suit the local and international needs.

The future market demand is expected to significantly increase especially for heating and cooling technologies. This shows the high importance of considering our prepared PCM-HA in industrial processing; in order to meet the local and global demands of comfort cooling in bioclimatic buildings with high efficiency and lower technological expenses.

Simply, if this PCM-HA was wisely incorporated into the inner walls or blocks of the buildings, it would definitely result in saving a good amount of wasted energy generated from other heating and cooling facilities. This would attract more consumers in the future and may possibly become of greater demand.

An eco-friendly and safe material, such as our PCM, would best serve the local and international needs. The improved energy storage properties of the prepared PCM-HA are expected to greatly assist in reducing the expenses of generating electricity. Basically, the idea of PCM-HA production is thought of as an exclusive production that features the utilization of local recycled GCC plastic products that is of high demand both locally and internationally. The plastic process of making PCM-HA mainly involves advanced knowledge in the areas of materials processing and sustainable energy utilization that both are crucial when considering to enlarge the production scale under the direct support and sponsor of reputable Petrochemical and Plastics industries available here in GCC region.

The main part of making this PCM-HA process real, is optimizing the whole production scale of such special materials. A few factors to take into consideration during the optimization of PCM-HA product are proposed as follows:

1. Optimization of extrusion temperature heating and flow-rate to assure homogeneous mixing of all elements; especially when larger quantities of major elements are used.
2. Negligible suppressing for leakage of phase change materials with presence of required conductive fillers suitable for our applications in bioclimatic buildings
3. Highly compatibility of material that majority depends on the actual process methodology being followed all the way from mixing of raw elements to the actual shaping of material
4. Depending on the desired application, the incorporated phase change materials must be chosen based on the practical range of melting temperature

After assuring all main factors listed above, this highly advanced PCM-HA process can then be turned into a larger scale suitable for use in industrial factories that are specialized in extensive production of polymeric materials with very special thermal characteristics. Figure 33 shows the prospective features of the produced heat absorbers based on phase change materials and waste polyethylene.

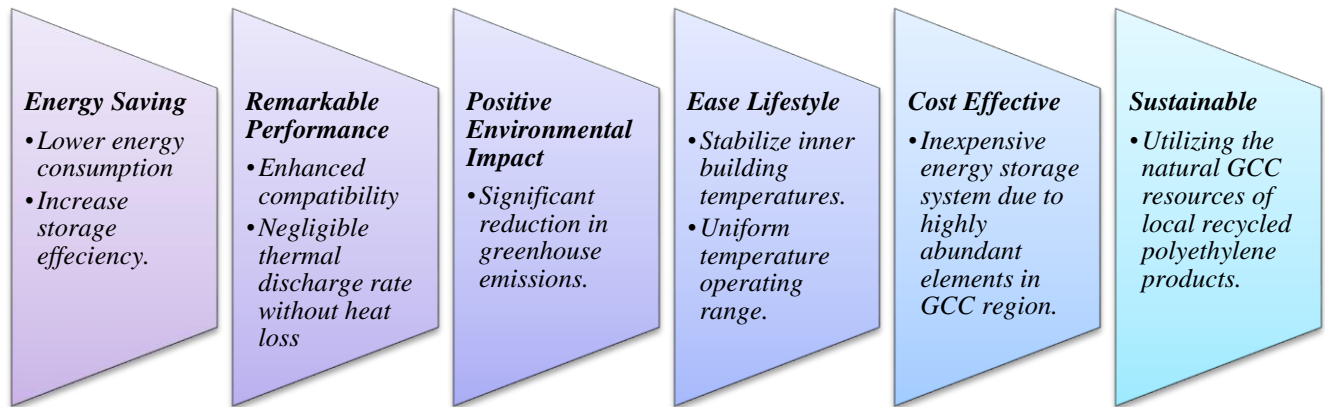


Figure 33: Prospective features of PCM-HA

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