Synthesis and Characterization of Phase Change Materials for Thermal Energy Storage Applications

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A thesis submitted to the National University of Sciences and Technology, Islamabad,

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Supervisor: Dr. Majid Ali

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U.S Pakistan Center for Advanced Studies in Energy

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DEDICATION

I dedicate my thesis to my beloved parents, siblings, and friends for their affection and support during my studies. Especially to my mother for always believing in me, praying for me, and giving me courage.

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LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

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DOMESTIC HOT WATER	DHW
EUTECTIC POINT	E.P
EUTECTIC PHASE CHANGE MATERIALS	EPCMS
FOURIER TRANSFORM INFRARED SPECTROSCOPY	FT-IR
LATENT HEAT	L.H
LATENT HEAT THERMAL ENERGY STORAGE	LHTES
MELTING TEMPERATURE	M.T
ONSET MELTING TEMPERATURE	TO
PEAK MELTING TEMPERATURE	TP
PEAK END MELTING TEMPERATURE	TE
PHASE CHANGE MATERIALS	PCMS
PALMITIC ACID	PA
POLYETHYLENE GLYCOL 2000	PEG2K
POLYETHYLENE GLYCOL 4000	PEG4K
POLYETHYLENE GLYCOL 6000	PEG6K
STEARIC ACID	SA
SPECIFIC HEAT CAPACITY	CP
SOLAR SPACE HEATING	SSH
THERMAL ENERGY STORAGE	TES
THERMAL ENERGY STORAGE SYSTEMS TESS	TESS

ABSTRACT

Eutectic phase change materials (EPCMs) based on fatty acids-polyethylene glycol are developed for low temperature thermal energy storage application. Four distinct eutectic PCMs (PA-PEG2K, PA-PEG4K, SA-PEG2K, and SA-PEG4K) are prepared through melt blending followed by ultra-sonication. Thermal properties such as melting temperature, latent heat, and eutectic composition of the PCMs are calculated using the Schrader equation. The chemical structure of the prepared eutectic PCMs is analyzed using Fourier Transform Infrared Spectroscopy. Thermal properties are also experimentally determined using a Differential Scanning Calorimeter and the prepared eutectic PCMs exhibit melting temperature ranging from 46.4°C to 54.7°C. The latent heat of prepared eutectic PCMs falls between 185.89 J/g and 188.33 J/g, and specific heat capacity in liquidus ranges from 2.2 $J\cdot g^{-1}\cdot °C^{-1}$ to 2.4 $J\cdot g^{-1}\cdot °C^{-1}$ whereas, specific heat capacity in solidus ranges from 1.6 $J\cdot g^{-1}\cdot °C^{-1}$ to 1.8 $J\cdot g^{-1}\cdot °C^{-1}$. It is evident from the TGA that these developed fatty acid-polyethylene glycols based binary eutectic combinations exhibit promising thermal stability. However, the results from DTC indicated that the thermal conductivity of EPCMS lies in the range of 0.347W/mK to 0.423W/mK. These eutectic PCMs have promising characteristics for low to moderate temperature thermal energy storage applications such as solar thermal space heating and domestic water heating systems.

Keywords: *Thermal energy storage, Eutectic phase change materials, Fatty acids, Polymers*

CHAPTER 1: INTRODUCTION

1.1 Energy

The advancement of technology has led to a rise in global energy demands. Consequently, there is a growing need to focus on sustainable energy sources due to the depletion of fossil fuels and the pressing challenge of climate change [1,2]. Solar energy stands out as a highly promising renewable energy source for capturing thermal energy without negatively impacting the environment. However, its intermittent nature presents a significant obstacle to its seamless integration into energy systems.

Electricity and natural gas serve as essential energy sources for district heating needs, encompassing both space and water heating applications. The energy crises in Pakistan have taken a substantial toll on both the residential and industrial sectors [3]. Pakistan, situated in an area with some of the world's most abundant solar insolation, boasts significant solar resources ideal for harnessing solar thermal energy.

Decarbonizing the energy sector involves the integration of renewable energy sources into existing systems, alongside the incorporation of various thermal energy storage systems with a remarkable round-trip efficiency exceeding 96% [4,5]. These thermal systems serve as a solution to mitigate the intermittency of solar energy, ultimately leading to a substantial reduction in greenhouse gas emissions and a significant decrease in reliance on fossil fuels. This transition also enhances the utilization of solar energy, ensuring the supply of affordable and environmentally friendly energy to end-users [6,7]. The integration of thermal energy storage (TES) systems with solar space and water heating applications reduces dependency on gas or electric heating units, which, in turn, lowers consumer utility bills. Embracing TES in conjunction with renewables enhances the proportion of renewable energy resources in everyday life, resulting in positive impacts on both the environment and the economy.

1.2 Thermal Energy Storage

Numerous techniques are available for energy storage, but one of the widely adopted methods is thermal energy storage [8]. A significant abundance of thermal energy sources, including geothermal and solar, is at our disposal. Additionally, waste heat generated by various processes offers another substantial source of thermal energy. These resources inspire the exploration of ways to harness this energy. Thermal energy storage methods can be broadly classified into two categories: physical and chemical storage methods [9]. In the past few decades, LHS has garnered attention due to its dependable performance, a diverse range of available materials, and other notable performance indicators, as illustrated in Figure 1.1.

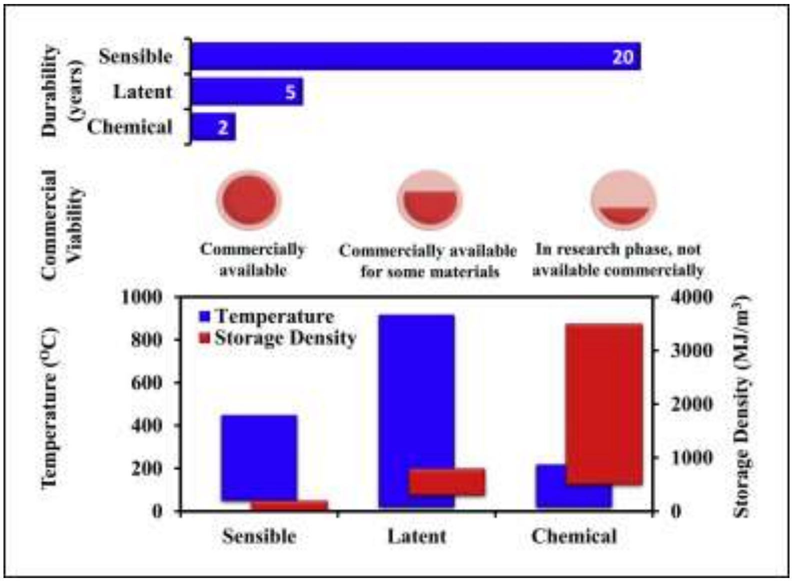

Figure 1. 1: Comparison of Thermal Energy Storage Types [9]

1.2.1 Sensible Heat Storage

Sensible heat storage is a type of thermal energy storage in which heat is stored by adjusting the medium's temperature. A variety of substances, such as water, air, oil, rock, bricks, concrete, or sand, can be used as storage media. Among these options, water and rock beds are the most frequently employed materials for sensible heat storage. The quantity of stored energy depends on factors such as the specific heat capacity, temperature increase, and the mass of the medium [10].

1.2.2 Latent Heat Storage

Latent heat is another type of thermal energy that is linked to the significant absorption and release of heat that takes place at a constant temperature during the storage medium's phase shift process. The mass of the medium and the specific latent heat have a direct correlation with the amount of this energy. [10]. Compared to sensible heat storage, latent heat storage has benefits, primarily due to its higher energy density. This method is particularly suitable for storing energy with minimal temperature variations, often applied in domestic hot water systems [11].

1.2.3 Thermochemical Energy Storage

Thermochemical energy refers to the amount of thermal energy stored and released through reversible endothermic and exothermic chemical reactions. It has the highest energy density among the three types [12].

1.3 Phase Change Materials (PCMs)

Materials with the ability to store latent heat are referred to as Phase Change Materials (PCMs). As the source temperature increases, PCMs undergo phase changes at a constant temperature, breaking chemical bonds and storing latent heat [9], as demonstrated in Figure 1.2.

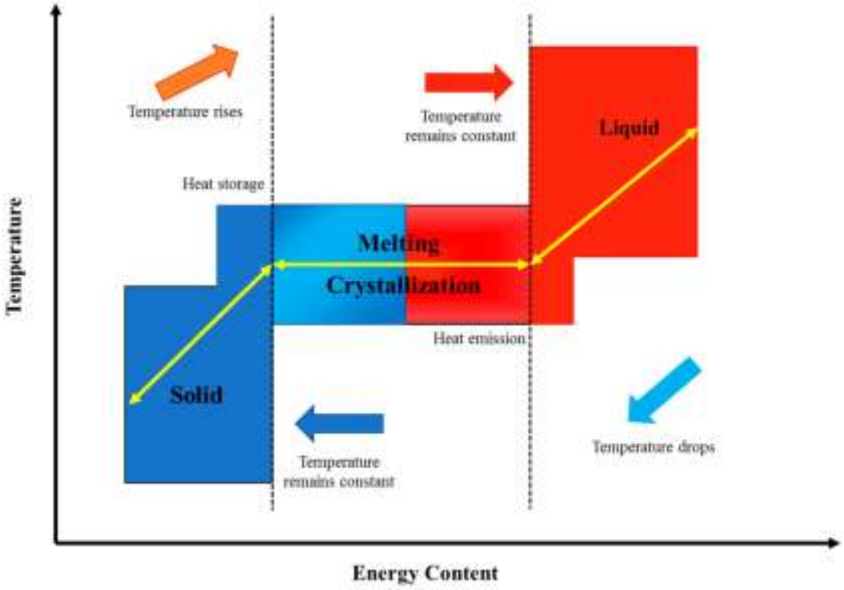

Figure 1. 2: Phase Changing Phenomenon

These substances are utilized to capture thermal energy from renewable sources for subsequent use. While they can store and release a significant amount of latent heat, they exhibit low thermal conductivity. **Figure 1.3** displays various types of Phase Change Materials, but this section specifically delves into solid-liquid PCMs, including organic, inorganic, and eutectic PCMs [9].

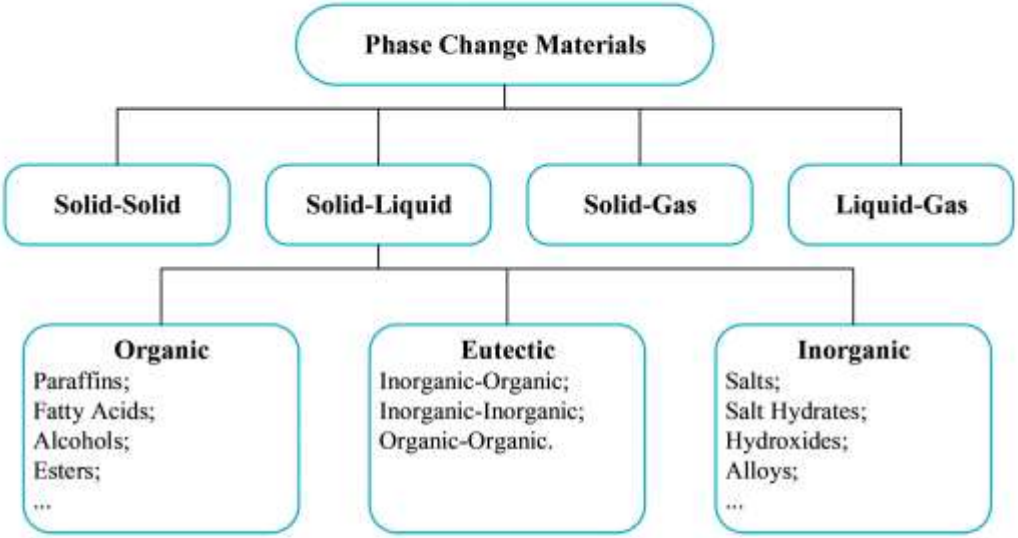

Figure 1. 3: Classification of PCMs [14]

PCMs have the potential to be applied in various fields, including thermal batteries, solar thermal power plants, space heating/cooling, smart textiles, buildings, the food industry, spacecraft thermal control, concentrated solar power plants, and more, as depicted in **Figure 1.4.** However, the limited thermal conductivity of PCMs can pose restrictions on these applications.

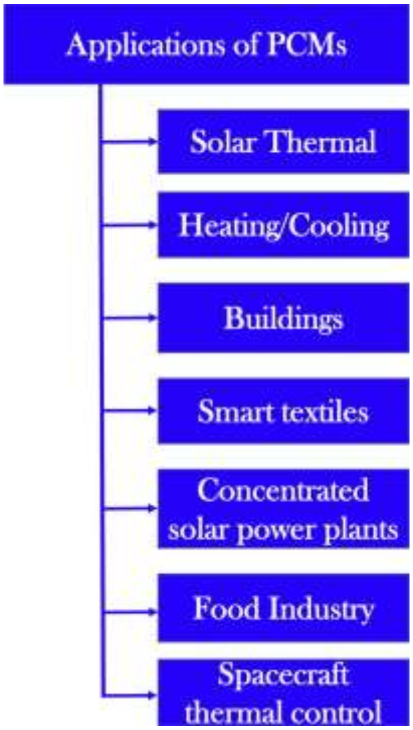

Figure 1. 4: PCMs Applications [9]

1.4 Motivation

Thermal energy storage research is active due to increased energy demand and addressing renewable energy intermittency. Combining LHTES with solar thermal collectors contributes to the global goal of reducing temperature rise and decarbonizing energy consumption [15].

Materials like organic PCMs and their mixtures, such as fatty acids and paraffin compounds, are a good option for combining thermal energy storage (TES) with solar heating systems. These substances show promise for various uses due to their ability to store a lot of energy. Designing effective materials and systems for TES with high energy capacity is crucial, and the scientific community is paying a lot of attention to it.

The thermophysical characteristics, including the melting temperature and latent heat, of organic EPCMs are investigated as potential options for long-term heat storage (LHTES) [14,15].

The advantages of these solid-liquid PCMs highlights their suitability for applications requiring low to moderate temperatures [18]:

- Readily accessible
- Environmentally friendly and bio-based
- Minimal supercooling
- Uniform melting
- Compatible with construction materials
- Dependable

Within the category of organic PCMs, fatty acids stand out for their affordability [17–20] and excellent chemical and thermal stability. They are also biodegradable, with a melting temperature well-suited for low to moderate temperature applications in long-term heat storage (LHS) [21–26]. These applications include thermal control in buildings, regulating temperature in textiles, and district water heating (DWH) [27,28].

Specialized engineered materials known as EPCMs can be created by combining specific mass ratios of organic, inorganic, or a combination of both types of PCMs [21,29,30]. Accordingly, nine distinct EPCMs based on fatty acids have been developed to cater to low to moderate temperature applications based on specific requirements.

1.5 Research Statement

The prediction of thermophysical properties and the determination of the eutectic point of eutectic PCMs have not been extensively studied. Additionally, there are discrepancies in the experimentally determined thermophysical properties, such as L.H and M.T, found in the literature [31,32]. Accurate thermophysical properties are essential for designing appropriate LHTES systems to efficiently utilize the technology [35]. This study provides theoretical and experimental insights into the development of eutectic PCMs, and it also examines the effect of the number of components on the M.T, L.H, and specific heat capacity.

Different fatty acids namely palmitic acid (PA), stearic acid (SA), myristic acid (MA), polyethylene glycol 2000 (PEG2K), polyethylene glycol 4000 (PEG4K) and polyethylene glycol 6000 (PEG6K) are considered to develop EPCMs having high latent heat of fusion.

1.6 Objectives of Research

The following are the objective of this work:

- To predict the thermophysical properties and eutectic point of eutectic PCMs
- Selecting the suitable Phase Change Materials (PCMs) to develop a series of organic EPCMs and determine the thermophysical properties from Schrader Equation.
- Thermal stability and chemical characterization of EPCMs are determined through TGA and FT-IR.
- Analysis of thermophysical properties (melting temperature, latent heat, and specific heat capacity) of Phase Change Materials (PCMs) using Differential Scanning Calorimetry (DSC).

1.7 Thesis Outlines

The thesis begins with Chapter 1: Introduction, providing an overview of TES, phase change materials, their working principles, and the research objectives focused on eutectic PCMs.

Chapter 2: Literature Review covers the classification, properties, and selection criteria of PCMs, with a focus on eutectic PCMs and the charging/discharging processes of LHTES systems.

Chapter 3: Methodology and Characterization Methods explains the synthesis and testing of eutectic PCMs, detailing the experimental techniques and characterization methods used to evaluate thermal properties.

Chapter 4: Experimental outlines the materials, procedures, and setup used in the study to test the synthesized eutectic PCMs within a thermal storage system.

Chapter 5: Results and Discussion presents the findings, analyzing the performance of the eutectic PCMs in energy storage and comparing them with theoretical data.

Chapter 6: Conclusion and Future Recommendations summarizes the research outcomes and suggests future directions for improving eutectic PCM synthesis and LHTES applications.

1.8 Flow Chart

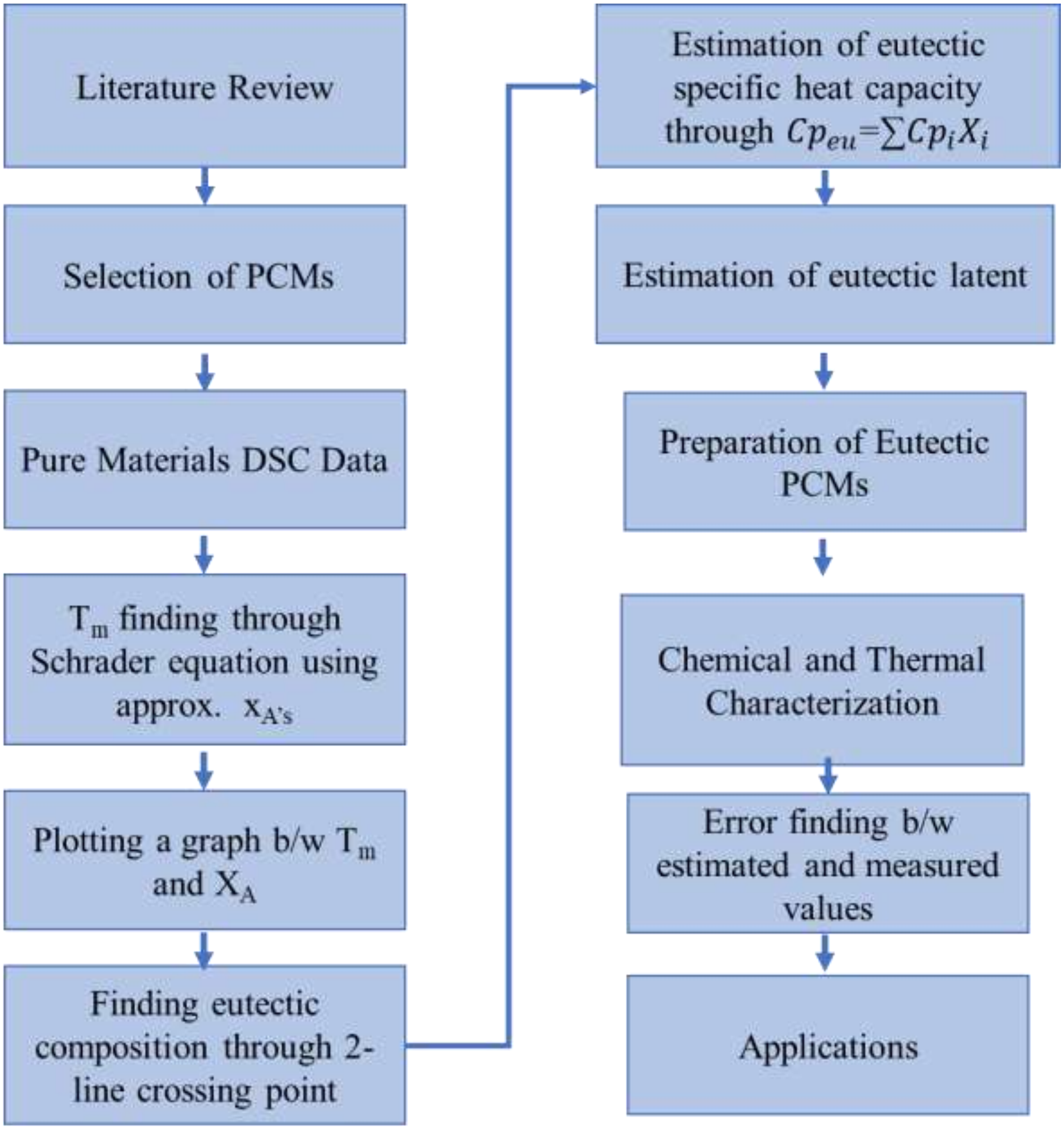

Figure 1. 5: Thesis flow chart

CHAPTER 2: LITERATURE REVIEW

2.1 Classification of Phase Change Materials

Based on phase transformation mode, PCMs are often categorized as; Solid-Solid, Solid-Gas, Liquid-Gas, and Solid-liquid PCMs [36]. Solid-solid PCMs have low latent heat during phase transition, while both Solid-Gas and Liquid-Gas PCMs are frequently avoided in LHTES systems due to the considerable changes in volume that occur during their phase transitions [37]. Whereas, due to high energy storage density and a wide working temperature range for TES applications, Solid-liquid PCMs are well-known [38]. They are further classified as shown in **Figure 2.1**. Organic PCMs such as; paraffin, non-paraffin, and their eutectics have extensively been used in the literature [15,37] However, the thermal properties of PCMs are critical for their potential applications. Among all organic PCMs fatty acids are the most widely used PCMs. Some properties of fatty acids including; high thermochemical stability, non-toxic, biodegradable, and an appropriate operating temperature range for low to moderate-temperature applications made them attractive [17,19,22].

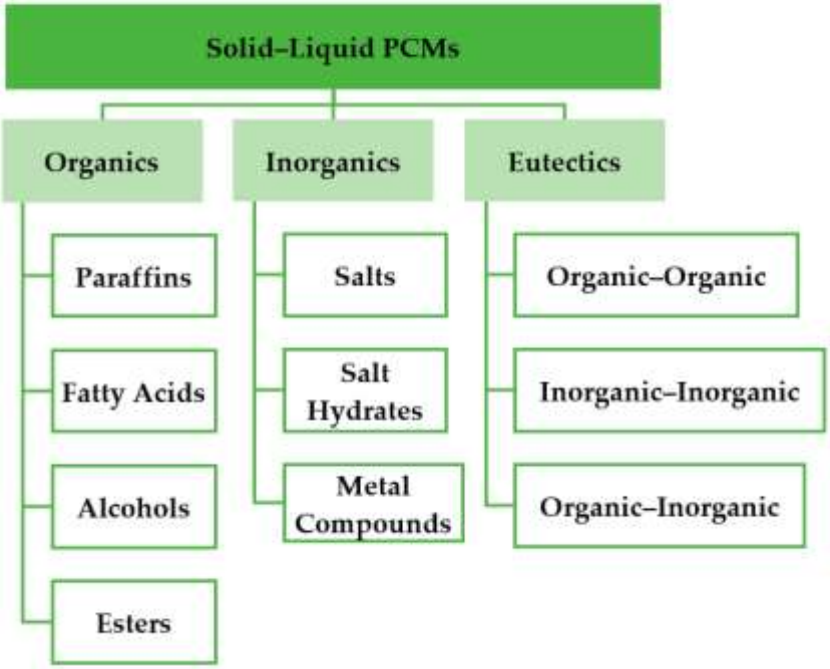

Figure 2. 1: Classification of Solid-Liquid PCMs

2.2 Phase Transition Temperature

According to the phase transition temperature, PCMs are categorized into low temperature PCMs, medium temperature PCMs and high temperature PCMs. Hoshi et al.[40] classified PCMs with melting points below 220°C as low temperature PCMs, whereas, medium temperature PCMs having melting points between 220 and 420°C and those with melting values over 420 °C as high-temperature materials. However, the melting points of few organic compounds [18],[41],[42],[43] are shown in Figure 2.2 (a-c). Since their melting temperatures falls in the range of 100-200°C, Organic PCMs involving Paraffin, fatty acids, polyalcohol's, polymeric materials like PEG (polyethylene Glycol) and sugar alcohols like D-threitol, Erythritol, D-mannitol, and pentaerythritol are typically taken into consideration for low temperature applications [44]. However, melting temperatures for the majority of the organic compounds are lower than 80 °C. Whereas, among the chosen organic materials, high-density polyethylene (HDPE) has the highest melting point, which is 150°C. Organic EPCMs fall into the low temperature PCMs group. Although, the melting points of few inorganic materials [45],[41],[46],[47],[48] are shown in Figure 2.3 (a-c). While the melting temperature for most salt hydrates are lower than 220°C. However, the use of these inorganic salts, such as metal carbonates, chlorides, sulphates, fluorides, and nitrates, as PCMs for high-temperature TES applications needing operating temperatures over 500 °C is widespread [47]. Even though the melting temperatures of a few different eutectic mixes are shown in Figure 2.4 (a-c) from ambient temperature up to about 770 °C [18],[46],[47],[48],[49]. Whereas, the melting points of metal alloys and inorganic eutectics are remarkably high, as can be easily seen, making them perfect for concentrating solar power (CSP) applications. Figure 2.4 illustrates the importance of eutectic aluminum alloys for high-temperature TES systems.

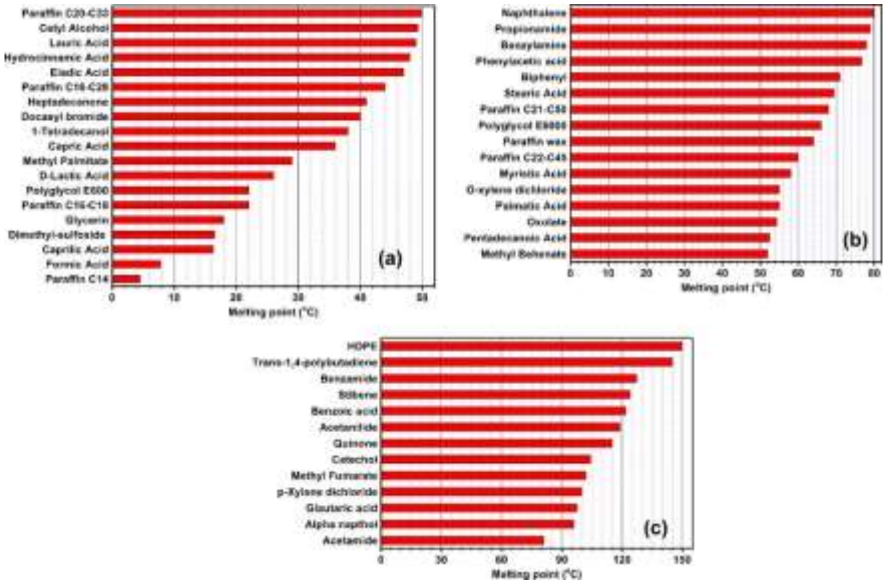

Figure 2. 2: Melting temperatures of selected organic PCMs (a) below 50°C (b) between 50°C to 80°C (c) above 80°C for TES [9]

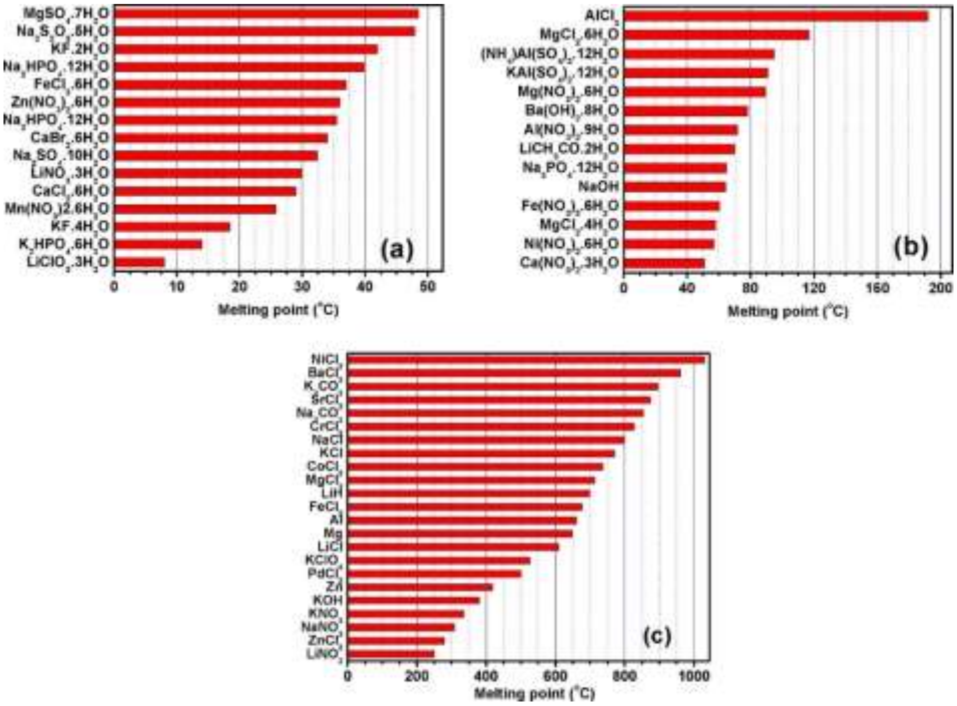

Figure 2. 3: Melting temperatures of selected inorganic PCMs (a) below 50°C (b) between 50°C to 80°C (c) above 80°C for TES [9]

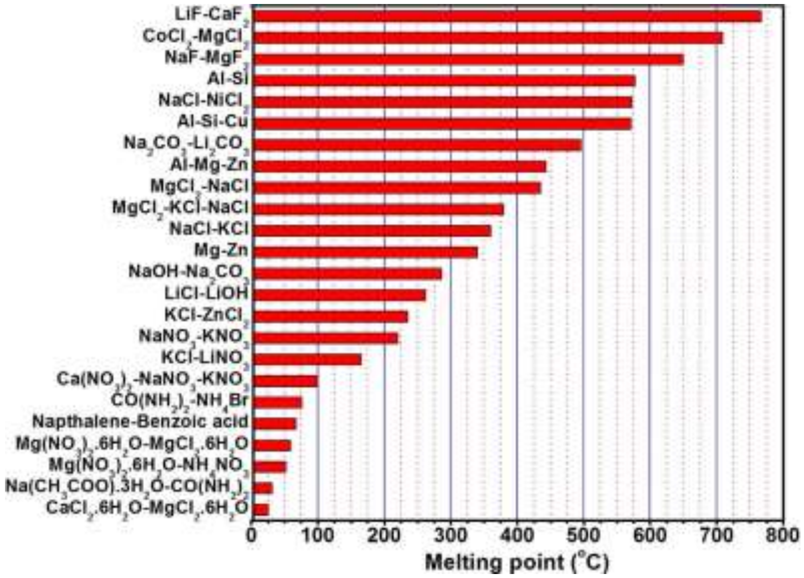

Figure 2. 4: Melting temperatures of selected eutectic PCMs for TES [9]

2.3 Properties of Phase Change Materials for Thermal Energy Storage

Most Important thermal properties of PCMs are; M.T, L.H, Cp, thermal stability [50] and thermal conductivity [51].

According to Chu et al. [52] energy storage systems is important since renewable energy sources are intermittent in nature. These resources are unable to completely fulfil the supply and demand chain. It is critical to propose an effective way to store energy for real-world applications.

Numerous investigations on organic PCMs (fatty acids) and their eutectics as potential LHTES candidates have been carried out [22,23]. Hassan et al.[37]. examined the thermal properties of Stearic acid (SA), having M. T in the range of 67-69 °C and L.H of fusion was 222.16 KJ.kg^{-1}. Whereas, the M. T range of Palmitic acid (PA) was 62-67°C with the L.H of fusion was 209.46 KJ.kg^{-1}. However, in the case of eutectic PCM (eutectic composition of SA/PA: 39/61), the melting temperature was dropped to 52.5-55.1°C, and L.H of fusion was reduced to 181-182.4

KJ.kg^{-1} which reflects that prepared eutectic PCMs would be suitable for SSH and DHW applications. Additionally, Ke et al.[54]. also examined the thermal characteristics of SA and PA. Where the latent heat of SA was 222.8- 226.7 KJ.kg^{-1} and the M. T was in the range of 67.06-68.96 °C which was similar to the data reported by Hassan et al. [37]. Furthermore, PA also shows almost a similar melting temperature (60.38-62.11°C) and L.H of fusion (212.1-214.6 KJ/kg). When the eutectic of SA/PA was prepared with the eutectic composition of 37.01/62.99, the temperature was reduced to 53.45-53.69°C, and latent heat is decreased to 204.2-204.7 KJ.kg^{-1}.

Zhou et al. [55]. also prepared EPCMs for TES by using Lauric Acid (LA) and PA. It was observed that the M. T and L.H of PA remained in a similar range (58.9-64°C, 185.4-212.1 KJ.kg^{-1} respectively). However, the M. T of LA was 42.4-44°C with L.H of 174.9-186.4 KJ.kg^{-1}. Whereas, the prepared eutectic of LA/PA (69.8/30.2) reduced the M. T from 42.4-64°C to 34.60-37.80°C with decreased L.H from 174.9-212.1 KJ.kg^{-1} to 154.8-164 KJ.kg^{-1}. The thermal properties of SA and Myristic acid (MA) were investigated by Sari et al. [56]. It was found that the M. T and L.H of SA (67.80°C,198.9 KJ.kg^{-1} respectively) remained the same. However, the M. T of MA was 52.32 °C with a L.H of 182.6 KJ/kg. Whereas, the eutectic of MA/SA (64/36) reduced the melting temperature from 52.32-67.80°C to 44.10°C with decreased latent heat from 182.6- 198.9 KJ.kg^{-1} to 182.4 KJ.kg^{-1}.

Kou et al. [57] investigated the thermal properties of Polyethylene glycol (PEG-2K and PEG-4K). The M. T and L.H of PEG-2K were 50.77°C and 165.43 KJ.kg^{-1} respectively. Whereas, the melting temperature of PEG4K was 55.95°C and latent heat was 173.62 KJ.kg^{-1}. Additionally, Jia et.al. [58] also examined the M.T and L.H of PEG-2K which was 52.5°C and 154.1 KJ.kg^{-1}respectively. Furthermore, Fang et al. [59] also show almost the same melting temperature

(55.3°C) and L.H (186.7 $KJ.kg^{-1}$) of PEG-4K. The open-source literature reveals that the M.T of PEG-2K lies in the range between 50-53°C while for PEG-4K its 55-58 °C.

By performing a thermal characterization on myristic and palmitic acids after 1500 melt/freeze cycles, Sharma et al. [60] investigated their thermal stability. According to Cai et al. [61], the melting point of fatty acid eutectic mixtures was determined to be 35–53°C. Thermal properties of PCMs are listed in Table 2.1, 2.2 and 2.3.

Table 2. 1: Thermal Properties of Organic PCMs used for Thermal Energy Storage.

Materials	**Melting Temperature**	**Latent Heat of fusion**	**Specific Heat Capacity** (C$_p$)		**Density**	**Ref**
	(T$_m$)	**(ΔH$_m$)**	**C$_{ps}$**	**C$_{pl}$**	**(ρ_s)**	
	(°C)	**(kJ/kg)**	**(kJ/kg K)**	**(kJ/kg K)**	**(kg/m^3)**	
Formic acid	8	277	1.00	1.17	1227	[44]
Acetic acid	17	192	1.33	2.04	1214	[62]
Lauric acid	44	212	2.02	2.15	1007	[62]
Stearic acid	54	157	1.76	2.27	940	[63],[19]
Palmitic acid	61	222	1.69	2.20	989	[64]
Paraffin wax	0-90	150-250	3.00	2.00	880-950	[48]
Acetamide	82	260	2.00	3.00	1160	[65]
Oxalic acid	105	356	1.62	2.73	1900	[66]
Urea	134	250	1.80	2.11	1320	[67]
Maleic acid	141	385	1.17	2.08	1590	[68]
Adipic acid	152	275	1.87	2.72	1360	[69]
Erythritol	117	340	2.25	2.61	1450	[70]
Phthalic anhydride	131	160	1.85	2.20	1530	[71]
2-Chlorobenzoic acid	142	164	1.30	1.60	1544	[72]
Capric acid	32	156	1.91	2.11	1004	[73]
d-mannitol	165	300	1.31	2.36	1490	[74]
Hydroquinone	172	258	1.59	1.64	1300	[75]
HDPE	130	255	2.60	2.15	952	[36]

Table 2. 2: Thermal Properties of Inorganic PCMs used for Thermal Energy Storage.

Materials	**Melting Temperature**	**Latent Heat of fusion**	**Specific Heat Capacity** (C_p)		**Density**	**Ref**
	(T_m)	**(ΔH_m)**	**C_{ps}**	**C_{pl}**	**(ρ_s)**	
	(°C)	**(kJ/kg)**	**(kJ/kg K)**	**(kJ/kg K)**	**(kg/m^3)**	
Calcium chloride hexahydrate	30	125	1.42	2.20	1710	[9,13,17, 47]
Sodium sulphate decahydrate	32	180	1.93	2.80	1485	[13,17,47]
Sodium thiosulfate pentahydrate	462	210	1.46	2.39	1666	[1,13, 48]
Sodium acetate trihydrate	58	266	1.68	2.37	1450	[13,49,50]
Barium hydroxide octahydrate	78	280	1.34	2.44	2180	[13,51]
Magnesium nitrate hexahydrate	89	140	2.50	3.10	1640	[13,17,52]
Oxalic acid dihydrate	105	264	2.11	2.89	1653	[70]
Magnesium chloride hexahydrate	117	150	2.00	2.40	1570	[13,52]

Table 2. 3: Properties of Eutectic PCMs for Thermal Energy Storage.

Eutectic PCMs	Eutectic type	Eutectic Composition	Melting Temperature	Latent heat of fusion	Application areas	Ref
		(wt.%)	(°C)	(KJ/Kg)		
SA-PA	Binary	36.8/63.2	55	180	-	[21]
SA-PA	Binary	39/61	55.1	181	Domestic water heating, solar space heating	[37]
SA-PA	Binary	37.01/62.9	56.2	204.7	-	[54]
MA-SA	Binary	64/36	44.1	182.4	Low temperature solar heating	[23]
LA-MA	Binary	66/34	34.2	166.8	Low Temperature solar heating	[7, 53]
LA-PA	Binary	69/31	35.2	166.3	-	[23]
CA-LA	Binary	64/36	18.5	162.9	Solar Passive heating & cooling	[82]
CA-MA	Binary	73/27	21.7	165.22	Solar Passive heating & cooling	[82]
CA-MA	Binary	78/22	20.5	153	Passive cooling in buildings	[50]
CA-LA-SA	Ternary	30/60/10	16.4	174.9	Low temperature TES	[83]
CA-PA-SA	Ternary	80/10/10	19.8	154.1	-	[83]
LA-MA-SA	Ternary	57.5/34.3/8.2	29.4	-140	Building heating/cooling	[84]
SA-PA-PT68	Ternary	43.92/28.08/28	52.1	167.9	Domestic water heating	[37]
SA-PA-LA-MA	Quaternary	6.76/12.57/55.24/25.4	29.64	151.9	Temperature regulation and insulation textiles	[54]
SA-PA-LA-PT68	Quaternary	14.04/21.96/54/10	30.0	157.9	Thermoregulating textiles	[37]
CA-LA-MA-PA-SA	Quinary	50.7/31.2/10.3/5.1/2.7	17.64	132.8	Human thermal comfortability	[54]

2.4 Selection Criteria

The selection of an appropriate PCM for a certain application is a difficult task with a variety of factors that need to be considered. The lack of thermophysical property data for the majority of PCMs complicates the selection procedure even further.

The fundamental requirement of a suitable PCMs for a specific application is that its melting temperature falls within the TES storage system's intended operating temperature range. PCMs with high latent heat values are preferred due to their high energy storage densities (MJ. m^{-3}) [41, 83,84]. A PCM's thermal conductivity should be more than 0.2 W/m. K, PCMs with higher heat capacities and thermal conductivities improve the LHTES system's storage capacity [87]. Other desirable characteristics are minimal super cooling, low vapor pressure, coherent melting behavior, cyclic reliability, and a less corrosive PCM [86–88].

Based on market research and the availability of PCM, "Palmitic acid, stearic acid, myristic acid, polyethylene glycol 2000, polyethylene glycol 4000, and polyethylene glycol 6000'' were chosen for the experimental study on eutectic PCMs at the National University of Sciences and Technology, Islamabad, Pakistan.

2.5 Eutectic Phase Change Materials

Special substances known as Eutectic PCMs (EPCMs) are created by mixing specific components in precise mass ratio [37]. EPCMs are divided into three categories based on the type of their constituents: organic [36, 58, 89–91] inorganic [92,93] and organic-inorganic eutectics [39,94,95]. EPCMs can be binary, ternary, quaternary, or quinary mixtures [37]. Figure 2.5 depicts the operational temperature range of the EPCMs that have been developed [98].

Figure 2. 5: Melting Temperature range of fatty acids based EPCMs

Kant et al. [99] developed ternary eutectic systems using fatty acids and found that their melting temperature ranges from 14 to 21°C. In a separate study, Ke [100] utilized a predictive methodology to create various Eutectic Phase Change Materials (EPCMs) based on fatty acids, analyzing their thermophysical properties.

CHAPTER 3: METHODOLOGY & CHARACTERIZATION METHODS

The selection of PCM for developing eutectic phase change materials (EPCMs) focuses on thermo-physical properties such as high latent heat, energy density, and melting point. Additionally, it is crucial to consider kinetic, physical, and chemical properties, as well as factors like availability, reliability, and adaptability.

The framework of the study for EPCM development integrates mathematical models to determine eutectic compositions and predict their thermo-physical properties across various combinations of materials.

Nine EPCMs were synthesized using the melt blending method [84]. FT-IR was employed to analyze the chemical structure of the eutectic PCMs. Additionally, DSC and TGA [101] were utilized to experimentally measure the thermo-physical properties and thermal stability of these EPCMs. The acquired data provide essential insights for integrating EPCMs into LHTES.

3.1 Thermal Characterization

3.1.1 Differential Scanning Calorimeter (DSC) Analysis

Differential scanning calorimetry (DSC250, TA-Instruments) is employed to evaluate the phase transition behaviours and specific heat capacity of the prepared EPCMs. The instrument has an accuracy of ± 0.1 °C and is operated with a scanning rate of 10°C/min under a constant flow rate of Nitrogen at 50 ml/min. The scanning temperature range for both heating and cooling cycles is set between 0 and 90 °C. Temperature and heat flow calibrations of DSC are carried out with indium and sapphire, respectively. Each

EPCMs sample, weighing between 5 and 8 mg, are put in T-zero Aluminium pans and sealed with T-zero lids to perform thermal analysis in DSC.

Figure 3. 1: DSC- 250 (TA Instruments) apparatus

3.1.2 Thermal Gravimetric Analysis (TGA)

The thermal stability of the eutectic PCMs is evaluated using a TGA 5500 instrument from TA Instruments, USA. Prior to reaching its breakdown temperature, the furnace underwent nitrogen gas purging to prevent any undesired reactions. A sample weighing 10 mg was placed on a pan inside the furnace, and the eutectic sample was subjected to heating between 25°C and 300°C at a rate of 10 °C/min. Throughout the temperature variation, changes in sample weight were continuously recorded.

Figure 3. 2: TGA 5500 (TA Instruments) apparatus

3.1.3 Thermal Conductivity (DTC) Analysis

Thermal conductivity of the pure PCMs and prepared EPCMs was measured using DTC 300, TA Instruments, USA with an accuracy of ± 3%. The guarded heat flow test method is used by this equipment and testing is performed as per ASTM-E1530.

Figure 3. 3: DTC-300 Thermal Conductivity Meter (TA Instruments) Apparatus

3.2 Chemical Structure Characterization

3.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The chemical structure of the synthesized eutectic mixtures is examined using Fourier Transform Infrared Spectroscopy (FT-IR, Agilent Cary 630), with spectra recorded in the range of 5000 to 400 cm^{-1}. By analyzing the absorption spectra of electromagnetic radiation within the frequency range of 4000 to 400 cm^{-1}, it becomes possible to identify organic compounds, as these frequencies correspond to the vibrations of chemical bonds in organic materials.

Figure 3. 4: The Cary 630 FTIR Spectrometer

CHAPTER 4: EXPERIMENTAL

4.1 Materials

Pristine materials are used for the preparation of the EPCMs without further purification in this study and their thermal properties are enlisted in **Table 4.1.** The examined fatty acids are neither toxic, flammable, or corrosive. The thermal properties of pure materials are also determined through DSC. The weight of pure materials for preparation of the EPCMs is measured using (AS-220.R2, RADWAG) weight balance having an accuracy of ± 0.2mg.

Table 4. 1: Thermal characteristics of the fatty acids used to prepare the eutectic combinations.

Samples/ Materials	CAS number	Supplier	Purity	Molecular weight	Melting point	Specific heat capacity		Latent heat of fusion
						At 70-80°C Cp_{liquid}	At 20-30°C Cp_{solid}	
			(%)	(g/mol)	(°C)	(J/g· °C)	(J/g· °C)	(J/g)
Polyethylene Glycol 2K	25322-68-3	Sigma Aldrich	97	2000	49.4	2.1	1.5	182.9
Polyethylene Glycol 4K	25322-68-3	Sigma Aldrich	97	4000	56.0	2.2	1.6	198.0
Polyethylene Glycol 6K	25322-68-3	Sigma Aldrich		6000	59.1	-	-	200.3
Palmitic Acid	57-11-4	Sigma Aldrich	95	256.42	61.3	2.6	1.9	214.2
Stearic Acid	57-11-4	Sigma Aldrich	95	284.48	53.5	2.3	1.8	197.9
Myristic Acid	544-63-8	Alfa Aesar	99.2	228.37	53.2	2.3	1.7	192.0

4.2 Determination of Eutectic mass ratios

Two approaches are typically used to determine the eutectic composition (X_{eu}) referred to as the eutectic point: the proportioning test and the prediction method [37]. In the proportioning test, a series of specimen with various mass ratios, such as components

A-B (90-10%), *A-B* (80-20%), *A-B* (70-30%), and so forth are prepared, eutectic point is determined by comparing heat flow patterns from DSC of all prepared mixtures with varying quantities of the components. The prediction method identifies the optimum mass ratios for eutectic mixtures by generating phase diagrams for binary mixtures. The phase diagrams are generated by plotting the mass fraction of each component in the eutectic combination against temperature, acquired from the Schrader equation [102].

In the ongoing research, EPCMs are created using mass ratios determined through theoretical calculations, aiming to minimize costs associated with preparation and characterization of 32 EPCMs compared to the proportioning method. The Schrader equation [101–103] formulated for a binary EPCM consisting of component A and component B, is applied in this context.

$$T_m = [\frac{1}{T_{o,A}} - \frac{R.lnX_A}{\Delta H_{m,A}}]^{-1} \qquad (1)$$

$$T_m = [\frac{1}{T_{o,B}} - \frac{R.lnX_B}{\Delta H_{m,B}}]^{-1} \qquad (2)$$

where T_m is the melting point of eutectic mixture in K, $T_{o,A}$ and $T_{o,B}$ are the onset melting point in K, X_A, and X_B are the mole fractions, and $H_{m,A}$ and $H_{m,B}$ is molar L.H in kJ. kmol^{-1}, of constituent A and, B respectively. Whereas, R is a real gas constant, 8.314 kJ. kmol^{-1}. K^{-1}.

Cp for the liquid and solid phase of the pure fatty acids and polymers used in this study is given in Table. 1. The Cp of the eutectic mixture is calculated by considering Equation 3 for its liquid and solid phase [98,104].

$$Cp_{eu} = \Sigma X_i Cp_i \qquad (3)$$

where Cp_{eu} stands for the specific heat capacity of the eutectic mixture and Cp_i for the specific heat capacity of individual component *i*, both expressed in kJ.kg^{-1}.C^{-1}. X_i is the mole fraction of component *i* in the eutectic mixture.

Another significant thermal characteristic of PCMs is melting enthalpy. Equation 4 is used to calculate the melting enthalpy of fatty acids-polymers based EPCM [100].

$$H_{eu} = T_{eu}\Sigma[X_i.\frac{H_i}{T_i} + \left\{X_i(Cp_{li} - Cp_{si}).\frac{lnT_{eu}}{T_I}\right\}] \qquad (4)$$

where H_{eu} is the melting enthalpy of eutectic mixture in kJ.mol^{-1}, and T_{eu} is the eutectic mixture's melting temperature in K, which was calculated using the Schrader equation. H_i is the melting enthalpy of constituent i in kJ.mol^{-1}, and X_i is the mole fraction of constituent i. The melting temperature of component i in the eutectic mixture is represented by T_i, while the specific heat capacity of its liquid and solid phase is represented by Cp_{li} and Cp_{si}, respectively, in kJ.kg^{-1}.C^{-1}.

4.3 Preparation of EPCMs

The eutectic PCMs are prepared using two step method; melt blending followed by ultra-sonication [84]. The stepwise description is represented in Figure 4.1. To prepare, 20 g of eutectic mixture initially, measured amount of the respective fatty acids and polymers are added in a beaker. The eutectic composition of each binary combination is predetermined using Schrader equation [37]. Primarily, the pristine materials are combined in a beaker and heated for 60mins at constant temperature of 70°C using a water bath, as shown in Figure 4.1. After uniform melting of the materials in the beaker, the mixture is stirred for 45mins at 600rpms. Homogenization of the mixture is achieved through ultra-sonication for 15mins interval. After sonication, the homogenous eutectic mixture is progressively cooled to room temperature for uniform solidification. A similar method is used to prepare other eutectic combinations.

Figure 4. 1: Schematic of Eutectic PCMs preparation.

CHAPTER 5: RESULTS & DISCUSSION

5.1 Development of Eutectic PCMs

5.1.1 Phase Diagrams

Phase diagrams are created based on the results of the Schrader equation for eutectic phase change materials (EPCMs) to determine their eutectic mass ratios and melting temperatures, as depicted in **Figures 5.1-5.9.**

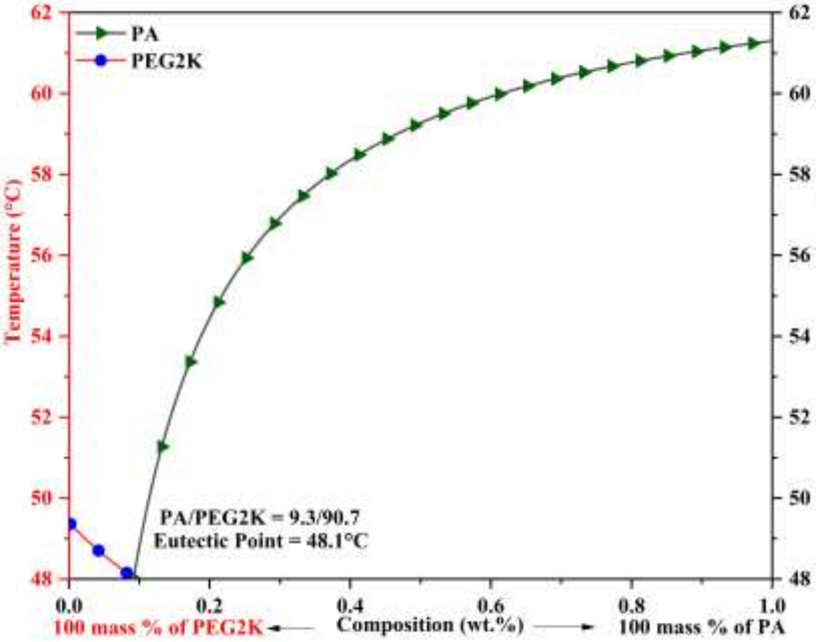

Figure 5. 1: Phase Diagram of PA-PEG2K

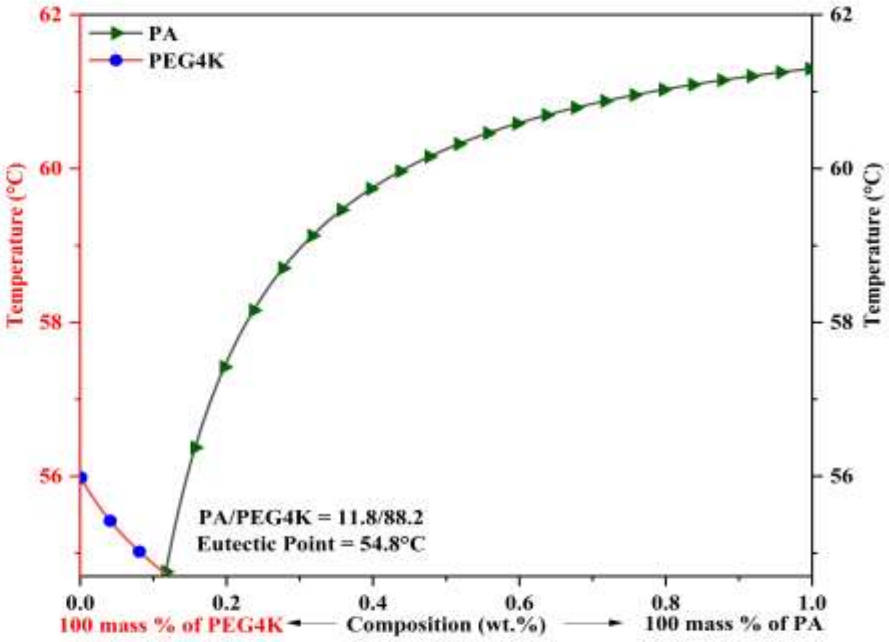

Figure 5. 2: Phase Diagram of PA-PEG4K

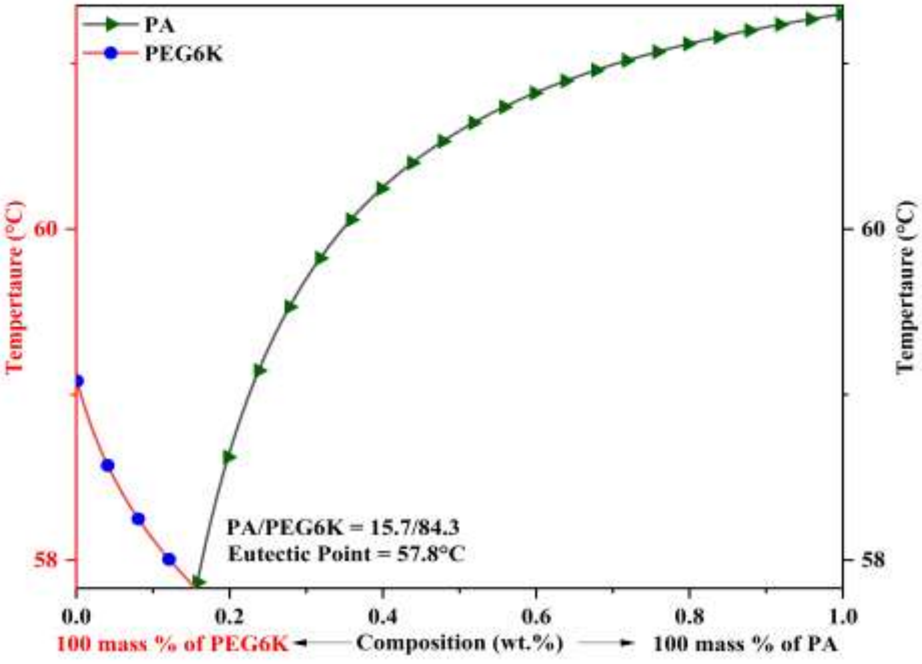

Figure 5. 3: Phase Diagram of PA-PEG6K

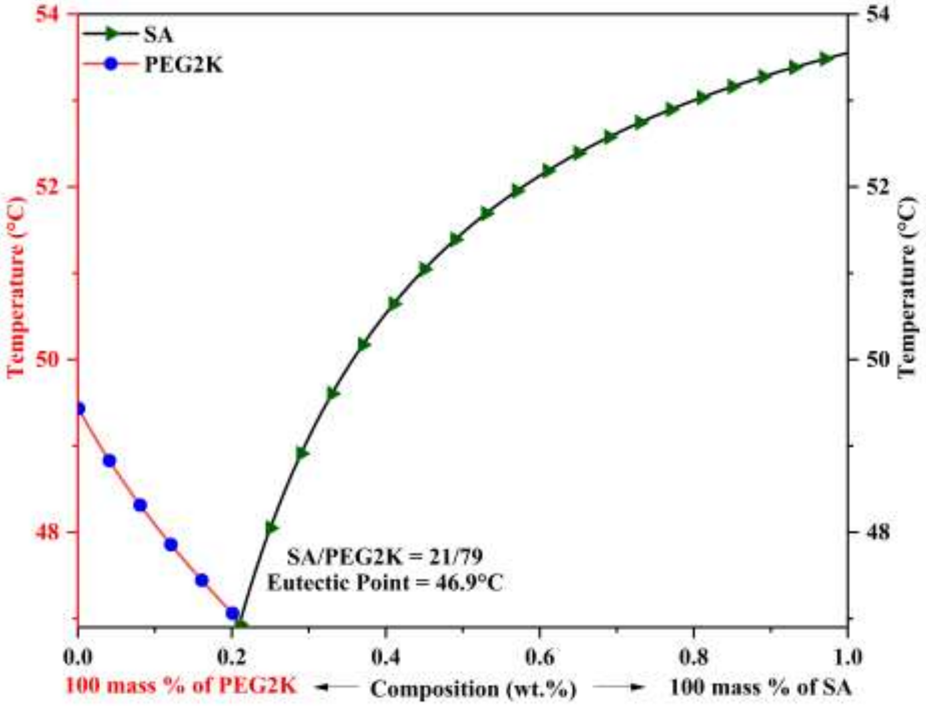

Figure 5. 4: Phase Diagram of SA-PEG2K

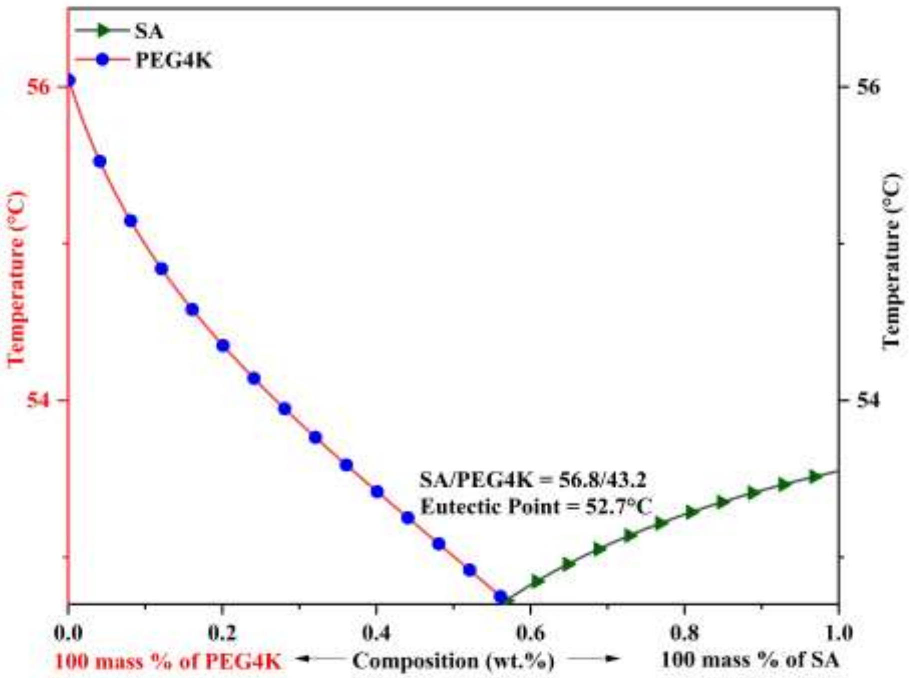

Figure 5. 5: Phase Diagram of SA-PEG4K

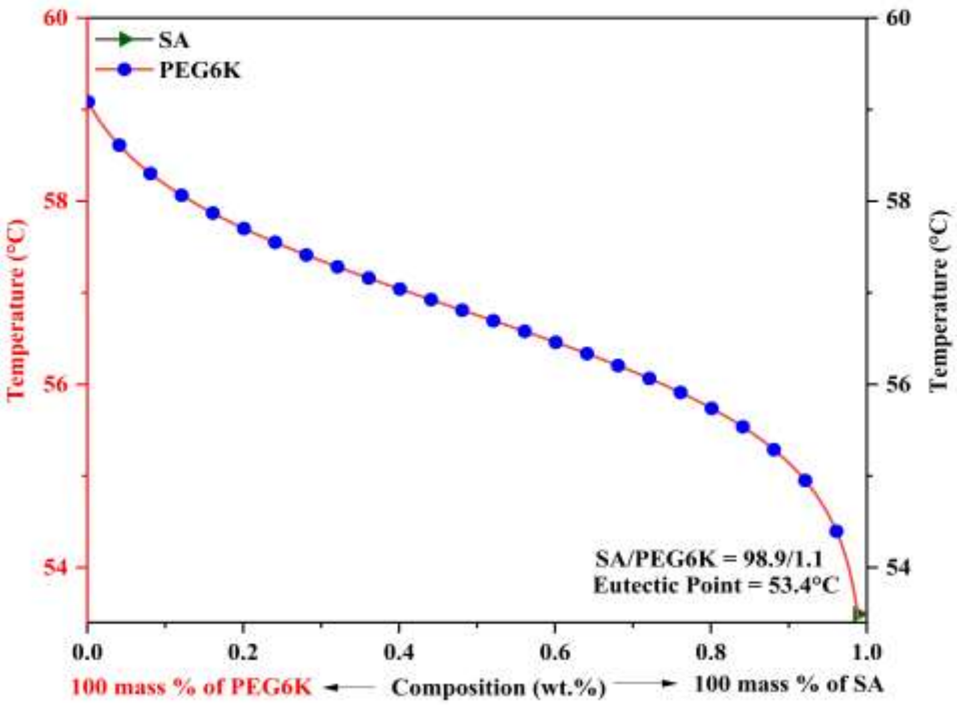

Figure 5. 6: Phase Diagram of SA-PEG6K

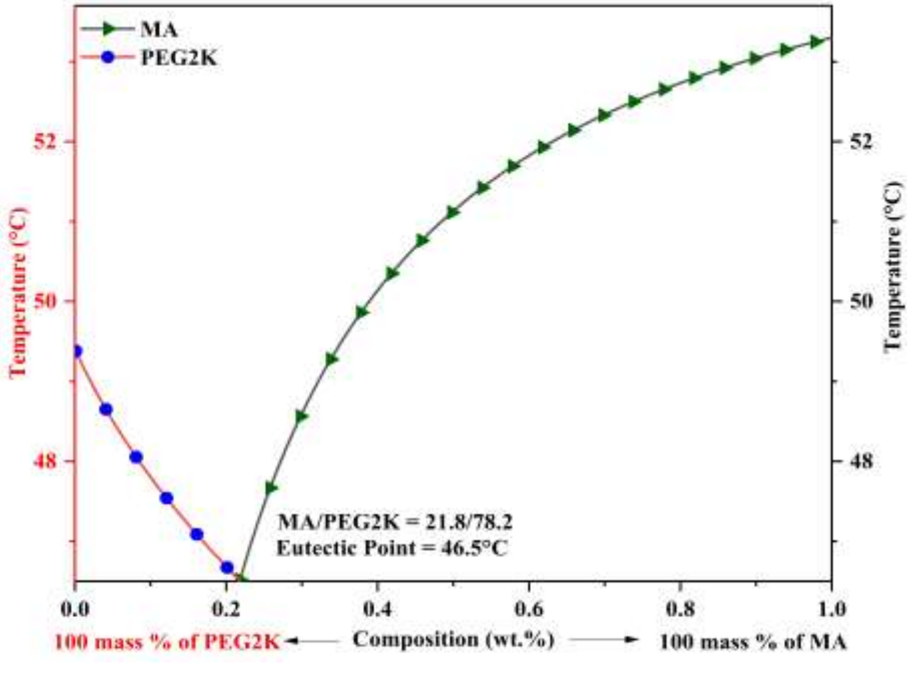

Figure 5. 7: Phase Diagram of MA-PEG2K

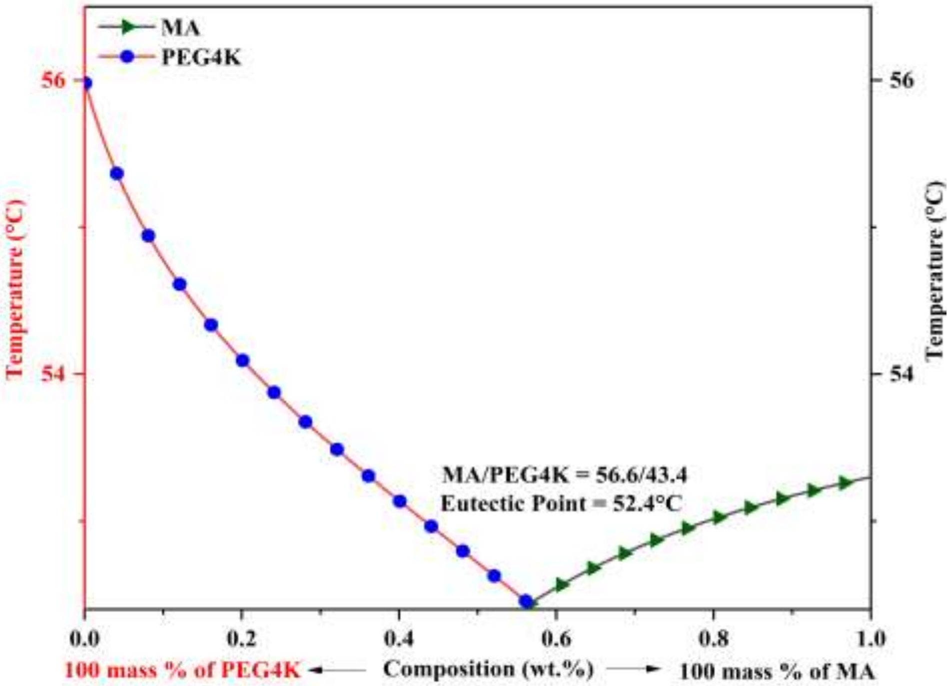

Figure 5. 8: Phase Diagram of MA-PEG4K

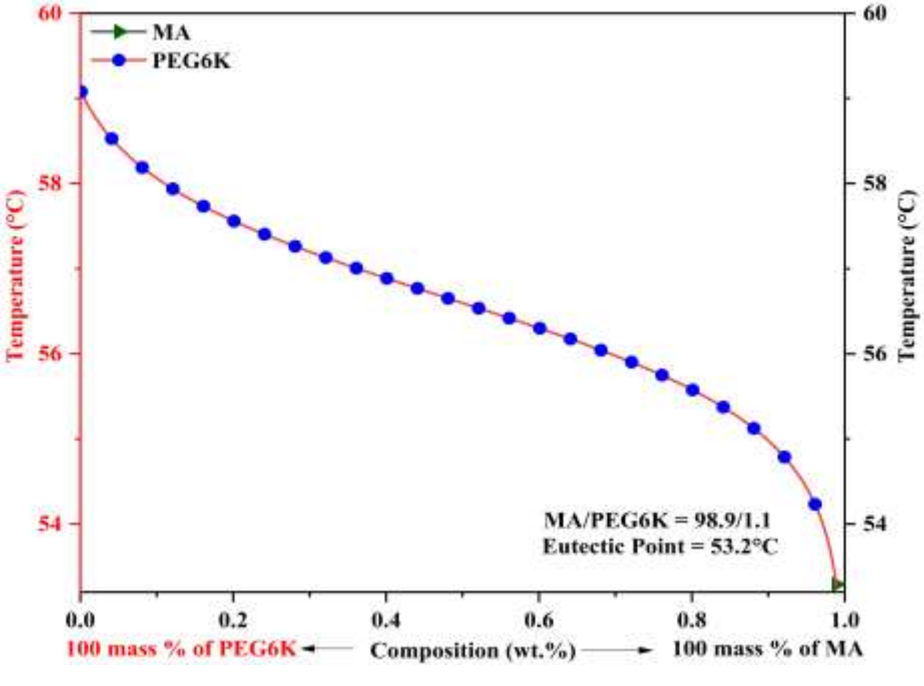

Figure 5. 9: Phase Diagram of MA-PEG6K

Examining the phase diagrams (refer to Figures 5.1-5.9), we can see that the melting temperature of EPCMs is lower than that of the individual components listed in Table 4.1. We figure out the composition and melting temperature of EPCMs by examining their specific phase diagrams. **Table 5.1** summarizes the properties of EPCMs determined through theoretical calculations.

Table 5. 1: Theoretical eutectic point derived from phase diagrams and predicted thermal properties of binary EPCMs.

EPCMs	Eutectic composition	Eutectic point	Specific Heat Capacity (C_p)		L.H of fusion
			At 70-80°C	At 20-30°C	
			$C_{pliquid}$	C_{psolid}	
	(wt.%)	(°C)	(J/g. °C)	(J/g. °C)	(J/g)
PA-PEG2K	9.3/90.7	48.1	2.3	1.6	169.5
PA-PEG4K	11.8/88.2	54.8	2.4	1.8	189.0
PA-PEG6K	15.7/84.3	57.8	-	-	-
SA-PEG2K	21.0/79.0	46.9	2.2	1.6	170.3
SA-PEG4K	56.8/43.2	52.7	2.2	1.7	194.0
SA-PEG6K	98.9/1.1	53.4	-	-	-
MA-PEG2K	21.8/78.2	46.5	-	-	-
MA-PEG4K	56.6/43.4	52.4	-	-	-
MA-PEG6K	98.9/1.1	53.2	-	-	-

9 samples are prepared using the calculated mass proportions. The thermal analysis of these prepared EPCMs is conducted using DSC, and the thermal properties determined through experiments are analyzed in subsection 5.1.4. Among other binary eutectic PCMs considered in this study, the calculated eutectic point of PA-PEG6K is highest, i.e. 57.8°C. This is because of the larger molecular weight of PEG6K.

5.1.2 Fourier Transform Infrared Spectroscopy Analysis

The chemical composition of prepared eutectic combinations is analyzed using FT-IR. The acquired FT-IR spectra of pure materials PA, PEG2K, SA, PEG4K, MA, PEG6K and eutectic combinations of PA-PEG2K, PA-PEG4K, PA-PEG6K, SA-PEG2K, SA-PEG4K, SA-PEG6K, MA-PEG2K, MA-PEG4K and MA-PEG6K is given in **Figure 5.10-5.18.** It reveals a recurring pattern in the eutectic spectra, and each spectrum's fingerprint region, located in the bottom-right spot, produces a distinct pattern that corresponds to a specific category of organic molecules. The peaks found at 2910, 2847, 2914, 2848, 2880, 2874, 2843 and 2882cm^{-1} in the pure PA, PEG2K, SA, PEG4K, MA, PEG6K spectra exhibit the symmetrical and asymmetrical vibrations of the C-H group, respectively. Whereas, the bending vibrations of C=O are denoted by a prominent peak at 1695 and 1689cm^{-1}. However, an occurrence of C-O is indicated by the peaks at 1291, 1298, 1281, 1236, 1279, 1233, 1289, 1278 and 1239cm^{-1} and the stretched vibrations of the -OH bond seen in the peaks at 938, 940, 951, 953, 934 and 951cm^{-1}. While the peaks at 1096, 1062, 1094, 1056 and 1092cm^{-1} show the bending vibration of the C-N bond. The deformation vibrations of the –CH_3 groups are related to the medium absorbance peaks at 1464, 1419, 1465, 1428 and 1340, 1458, 1424 and 1339cm^{-1}. Whereas the minor peak at 726, 722, 721 and 839cm^{-1} denotes –CH_2 groups' rocking vibrations [107–109].

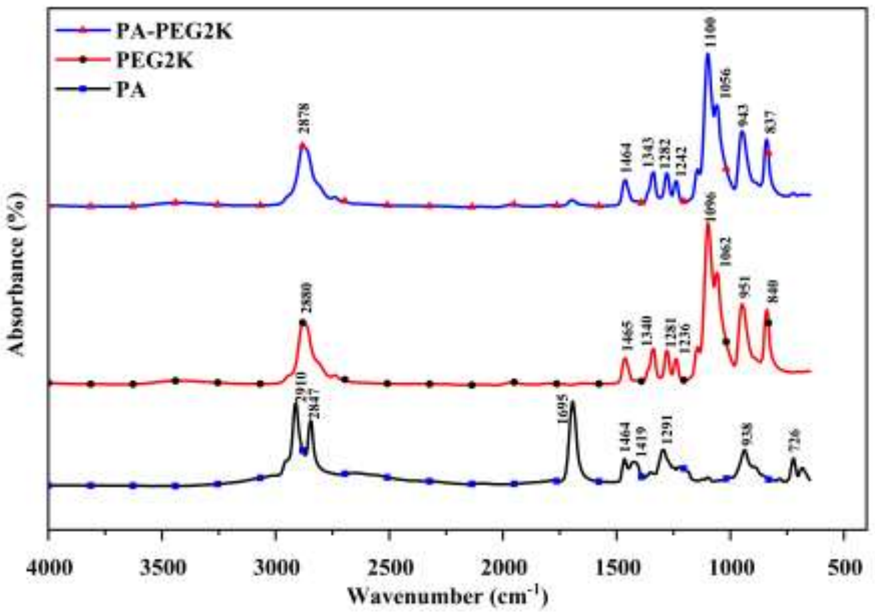

Figure 5. 10: FTIR spectra of pure PCMs (PA, PEG2K) and Eutectic combination (PA-PEG2K)

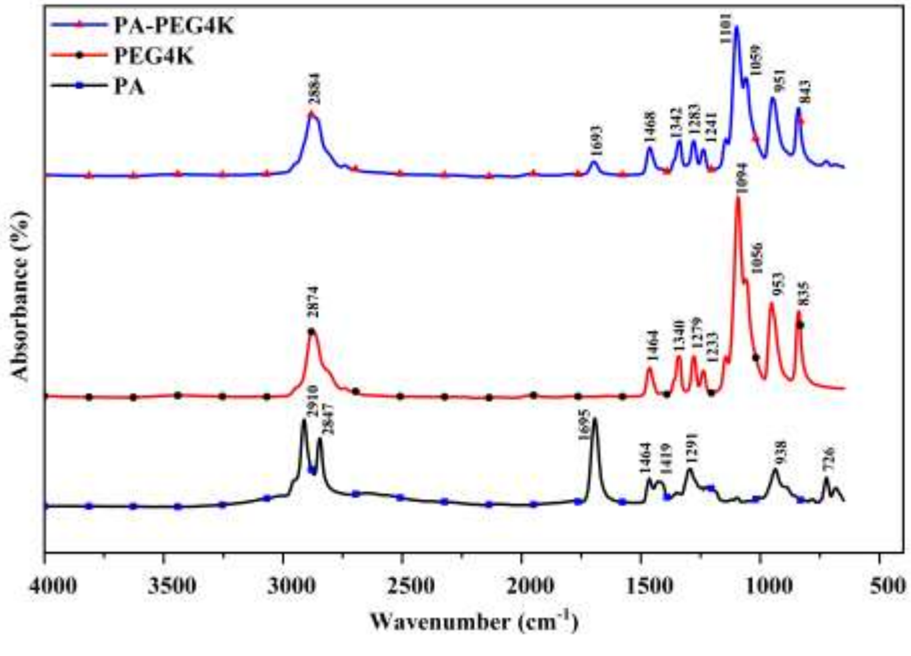

Figure 5. 11: FTIR spectra of pure PCMs (PA, PEG4K) and Eutectic combination (PA-PEG4K)

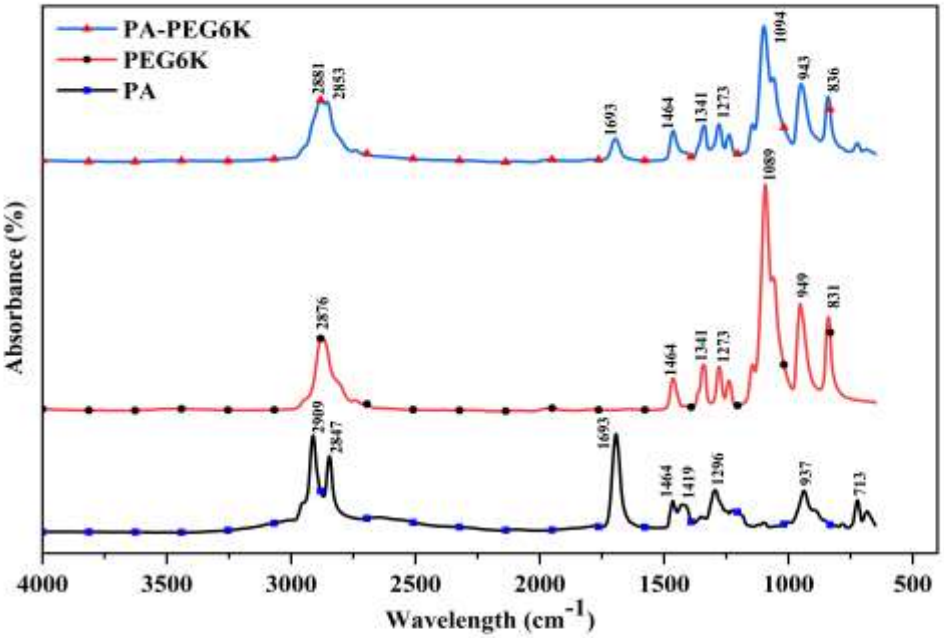

Figure 5. 12: FTIR spectra of pure PCMs (PA, PEG6K) and Eutectic combination (PA-PEG6K)

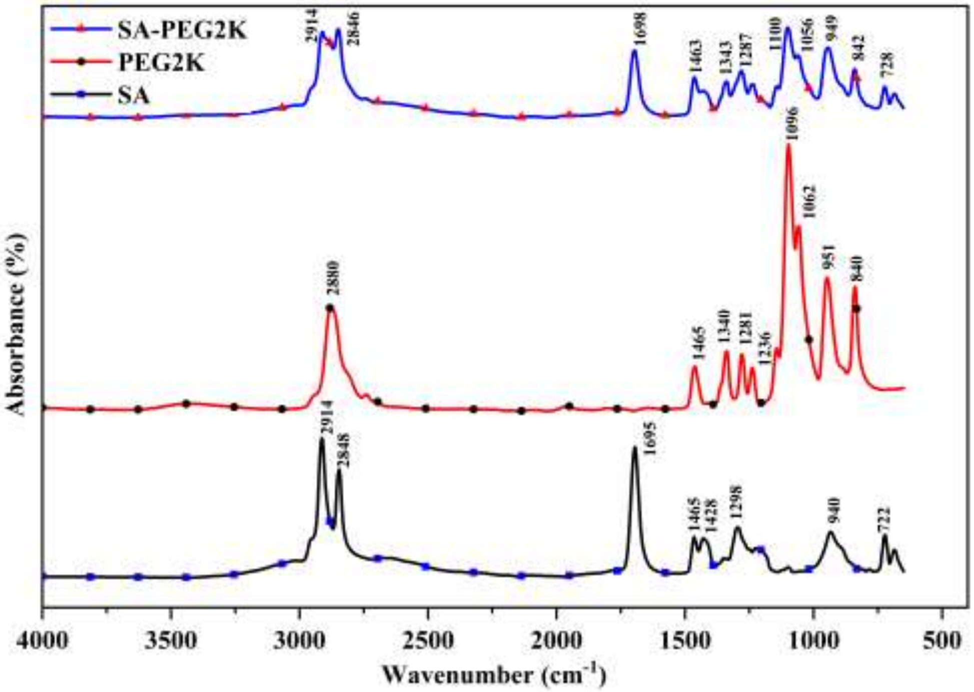

Figure 5. 13: FTIR spectra of pure PCMs (SA, PEG2K) and Eutectic combination (SA-PEG2K)

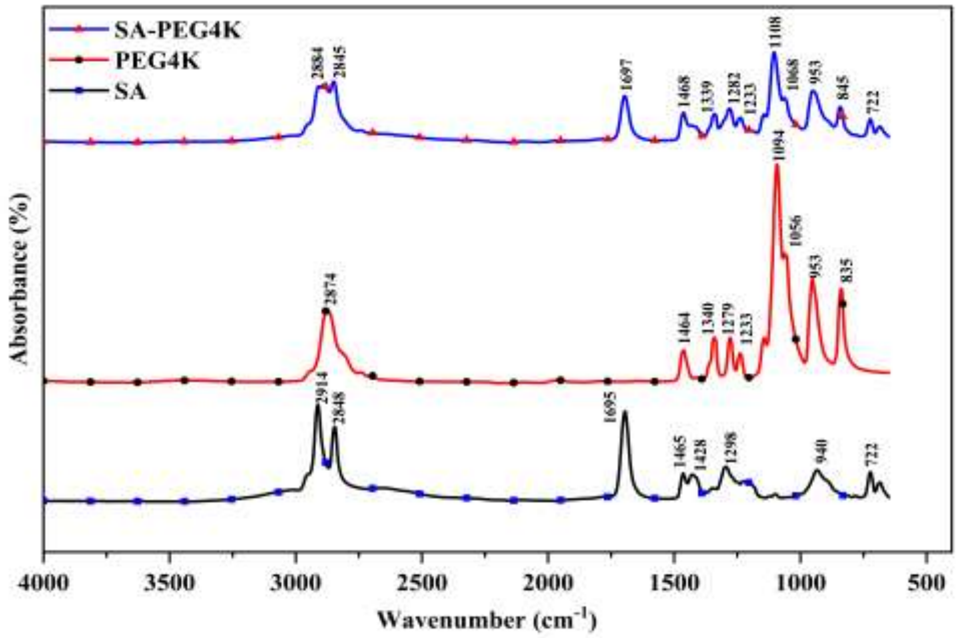

Figure 5. 14: FTIR spectra of pure PCMs (SA, PEG4K) and Eutectic combination (SA-PEG4K)

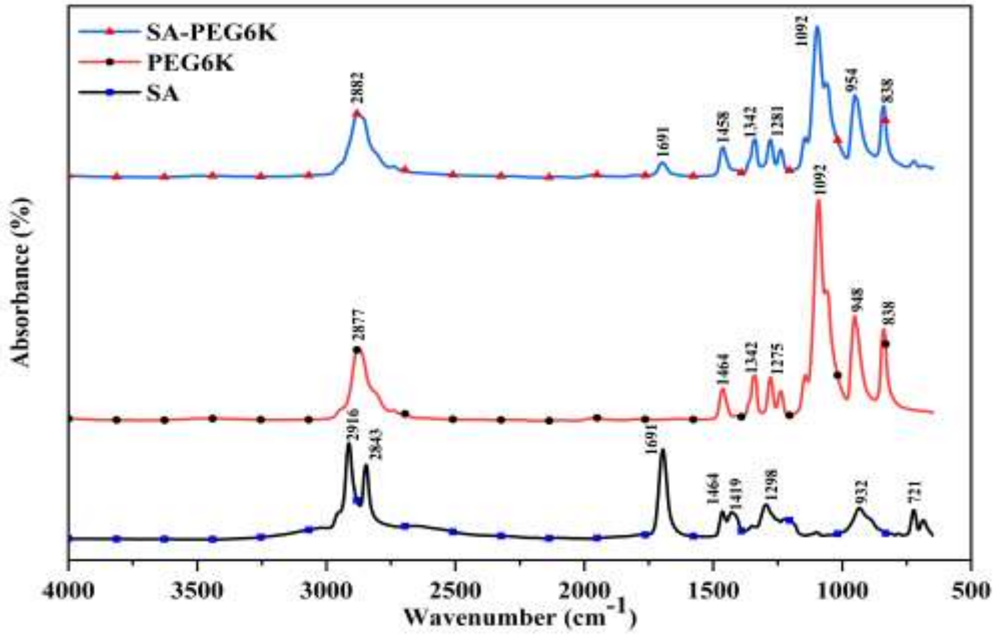

Figure 5. 15: FTIR spectra of pure PCMs (SA, PEG6K) and Eutectic combination (SA-PEG6K)

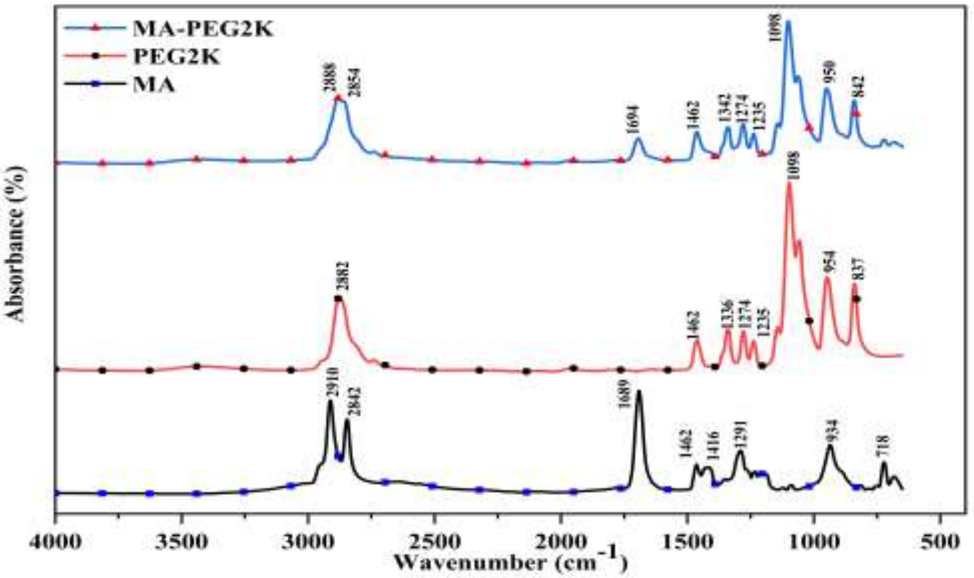

Figure 5. 16: FTIR spectra of pure PCMs (MA, PEG2K) and Eutectic combination (MA-PEG2K)

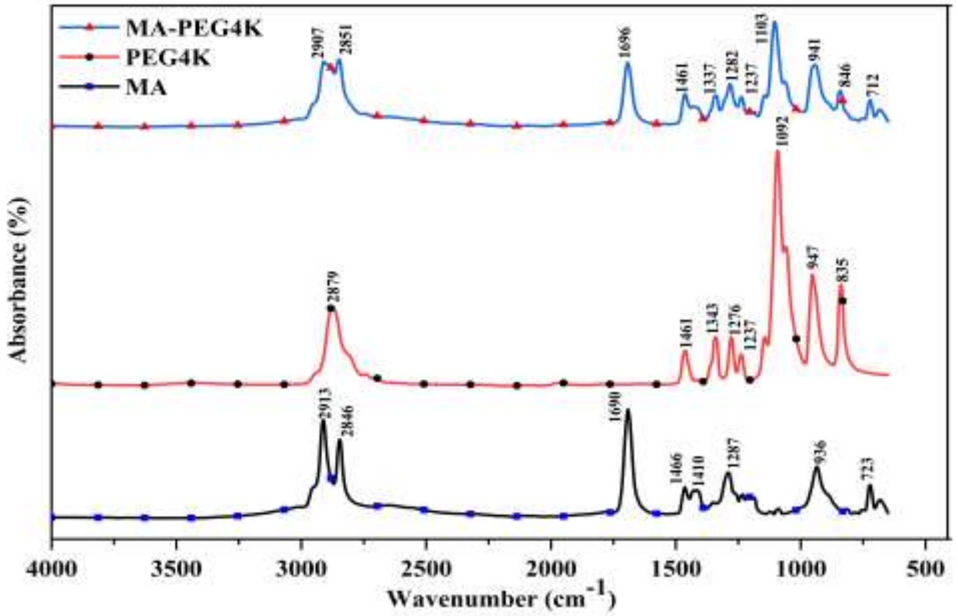

Figure 5. 17: FTIR spectra of pure PCMs (MA, PEG4K) and Eutectic combination (MA-PEG4K)

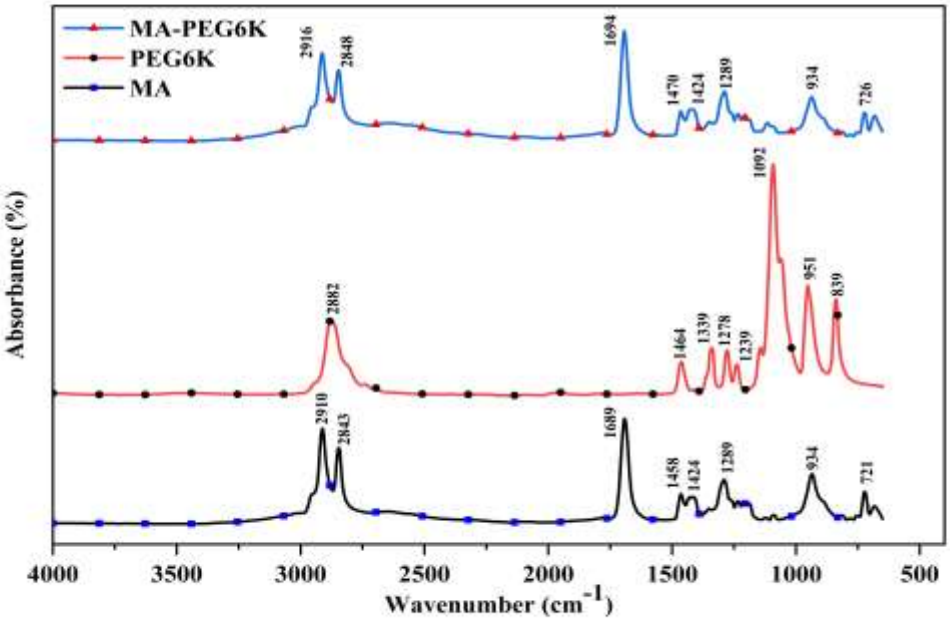

Figure 5. 18: FTIR spectra of pure PCMs (MA, PEG6K) and Eutectic combination (MA-PEG6K)

However, in the case of eutectic PA-PEG2K, PA-PEG4K, PA-PEG6K, SA-PEG2K, SA-PEG4K, SA-PEG6K, MA-PEG2K, MA-PEG4K and MA-PEG6K, the absorption peaks at 2878, 2884, 2881, 2853, 2914, 2846, 2845, 2882, 2888, 2854, 2907, 2851, 2916, and 2848cm^{-1} reflect symmetrical and asymmetrical vibrations of the C-H groups. On the other hand, the vibrations caused by stretching of C=O are indicated by an elevated peak at 1693, and 1694cm^{-1}. The medium absorption peak between 1464, 1468, 1463, 1458, 1462, 1461, 1470, and 1424cm^{-1} represents the deformation vibrations of the -CH_3 groups, whereas the –CH_2 groups' rocking vibrations are represented by the weak absorbance peak at 728, 722, 712, and 726cm^{-1}. The peak at 1282, 1242, 1283, 1241, 1273, 1287, 1233, 1274, 1235, 1237, and 1289cm^{-1} shows the presence of C-O, while the peak at 943, 951, 949, 953, 954, 950, 941, and 934cm^{-1} may show the bending vibrations of the -OH bond. The vibration of the C-N bond can be seen at 1100, 1101, 1094, 1056, 1108, 1068, 1092, 1098, and 1103cm^{-1}. Although, no additional peak is seen in the spectrum, demonstrating that the eutectic constituents does not interact chemically and no other product is produced during the formation of EPCM [37].

5.1.3 Differential Scanning Calorimeter Analysis

The melting peaks for pure materials (PA, SA, MA, PEG2K, PEG4K, and PEG6K) based on the DSC results are illustrated in **Figures 5.19-5.33.** The melting temperature of PA, SA, MA, PEG2K, PEG4K and PEG6K is 61.3, 53.5, 53.2, 49.4, 56.0 and 59.1°C, respectively, whereas, the L.H of fusion is 214.27, 197.92, 192.05, 182.92, 198.01, and 200.35J/g, respectively. It is evident that the melting temperature of the pure material are in line with the literature [110–112] which validates the accuracy of equipment and purity of PA, SA, MA, PEG2K, PEG4K and PEG6K used in this study.

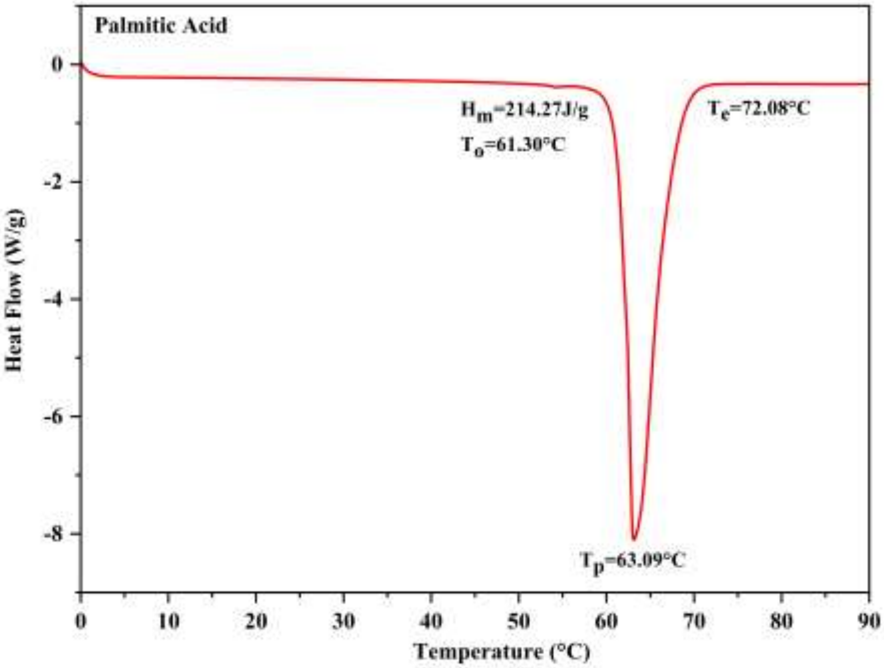

Figure 5. 19: Heat flow curves of PA

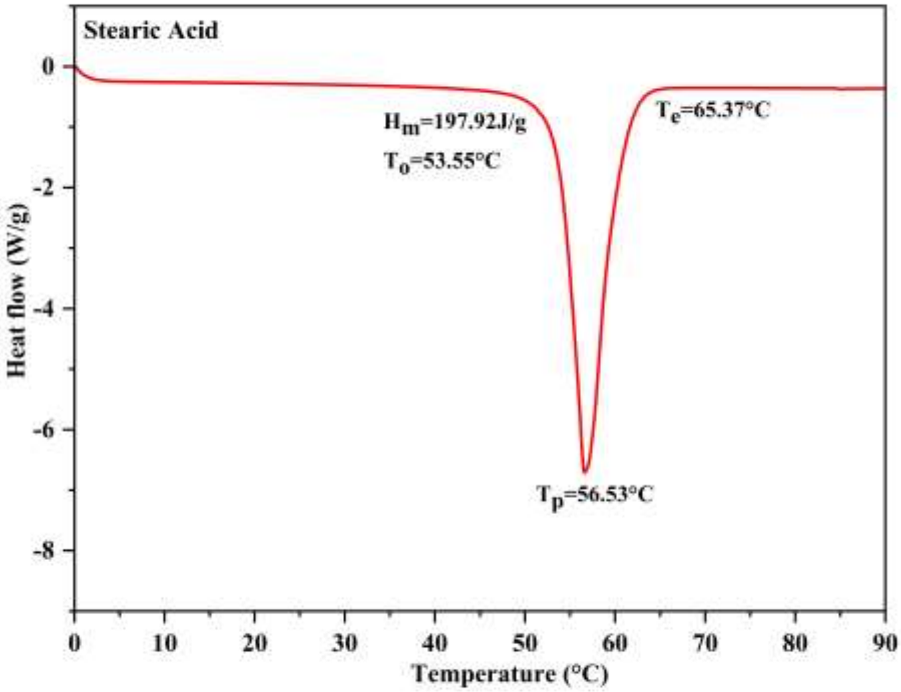

Figure 5. 20: Heat Flow Curve of SA

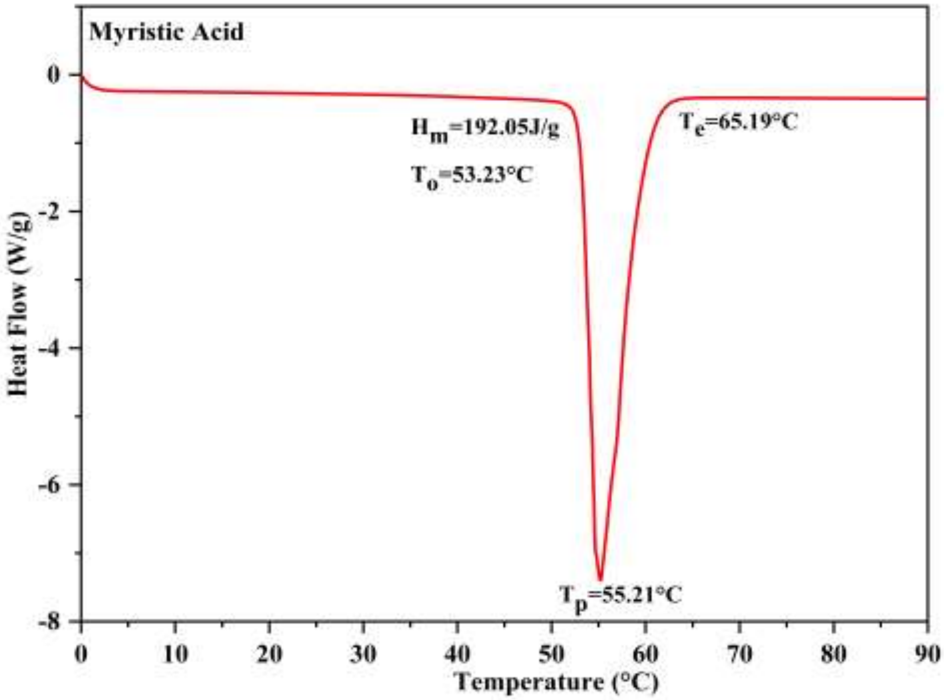

Figure 5. 21: Heat Flow Curve of MA

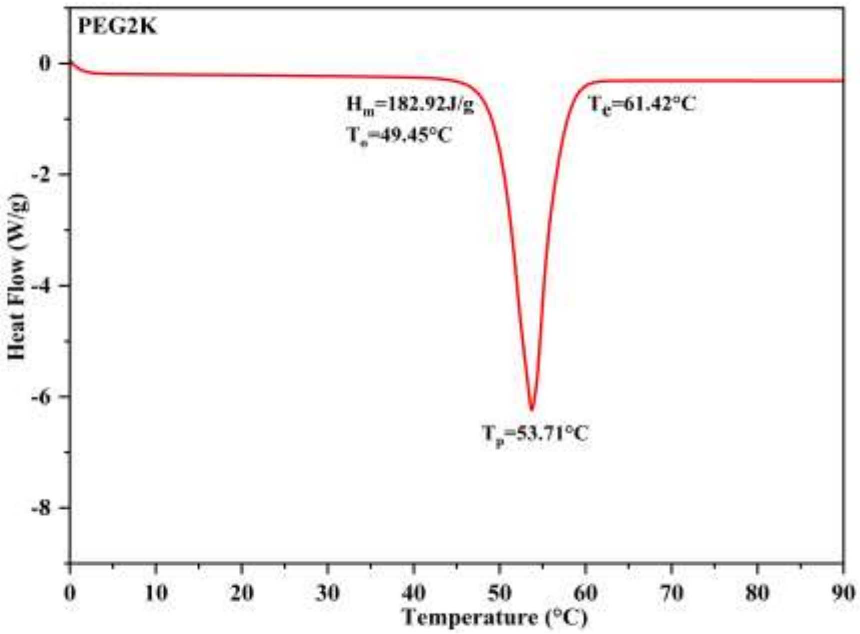

Figure 5. 22: Heat Flow Curve of PEG2K

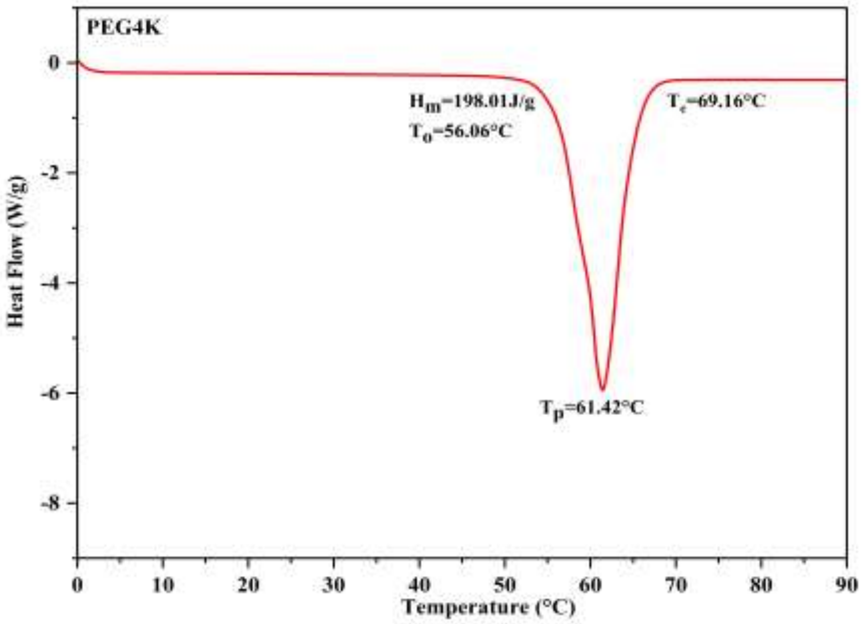

Figure 5. 23: Heat Flow Curve of PEG4K

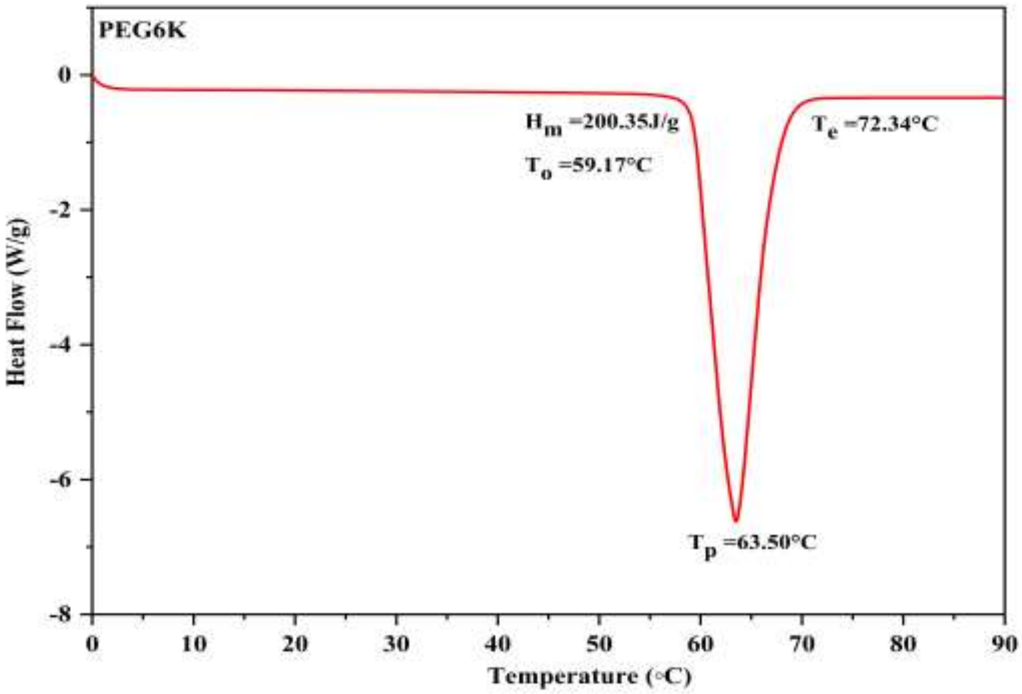

Figure 5. 24: Heat Flow Curve of PEG6K

The DSC-derived melting curves of the eutectic combinations: PA-PEG2K, PA-PEG4K, PA-PEG6K, SA-PEG2K, SA-PEG4K, SA-PEG6K, MA-PEG2K, MA-PEG4K and MA-PEG6K are given in **Figures 5.25-5.33**. Thermal properties of eutectic materials determined from DSC are given in **Table 5.2**, which reveals that PA-PEG2K, PA-PEG4K, PA-PEG6K, SA-PEG2K, SA-PEG4K, SA-PEG6K, MA-PEG2K, MA-PEG4K and MA-PEG6K melt at 46.4, 54.7, 55.5, 46.4, 52.0, 51.9, 43.0, 49.6, and 53.1°C respectively and solidify at 32.4, 37.0, 36.1, 45.4, 51.8, 52.2, 29.3, 48.8, 51.4°C, respectively. However, the L.H of fusion for the melting lies in the range of 185.8-215.7J/g, while for solidification it ranges from 109.3-216.9J/g.

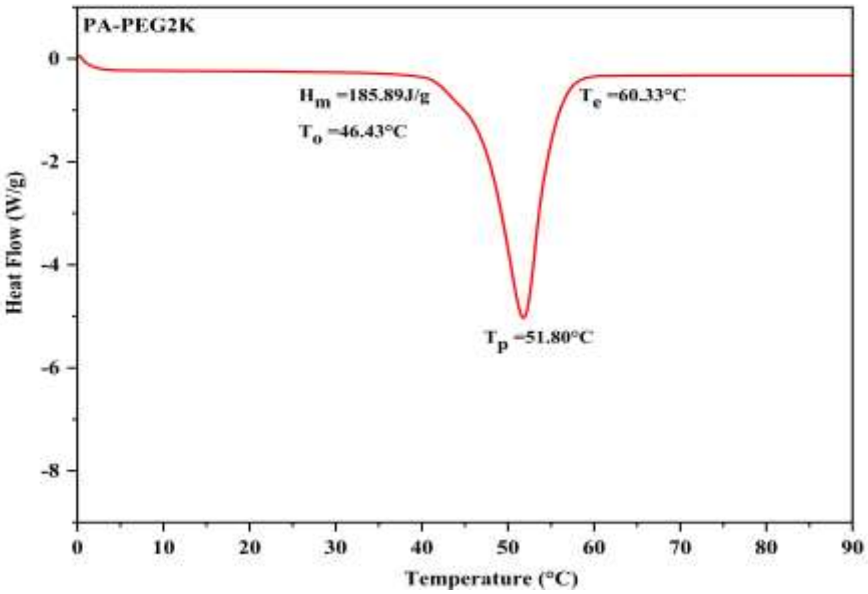

Figure 5. 25: Heat Flow Curve of PA-PEG2K

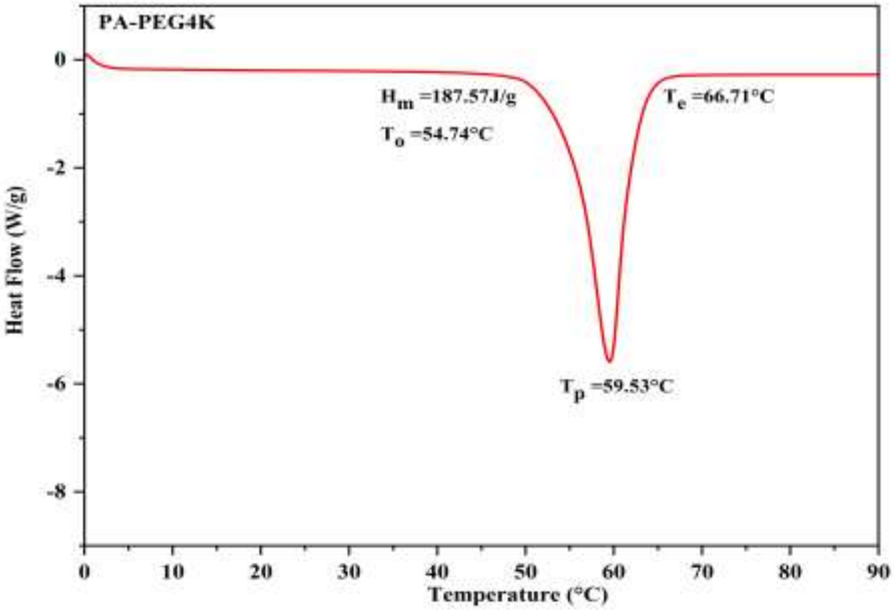

Figure 5. 26: Heat Flow Curve of PA-PEG4K

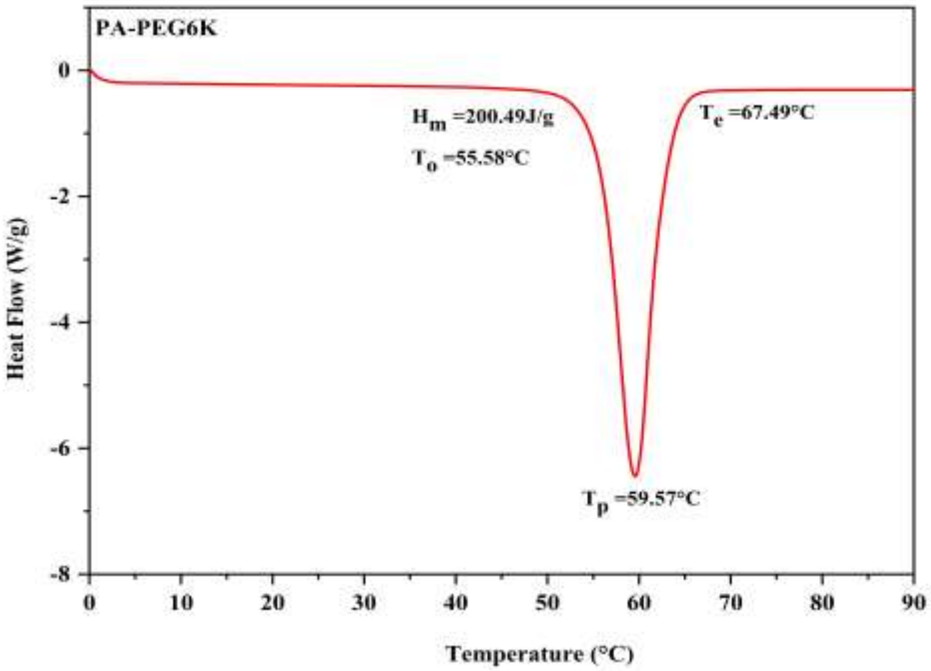

Figure 5. 27: Heat Flow Curve of PA-PEG6K

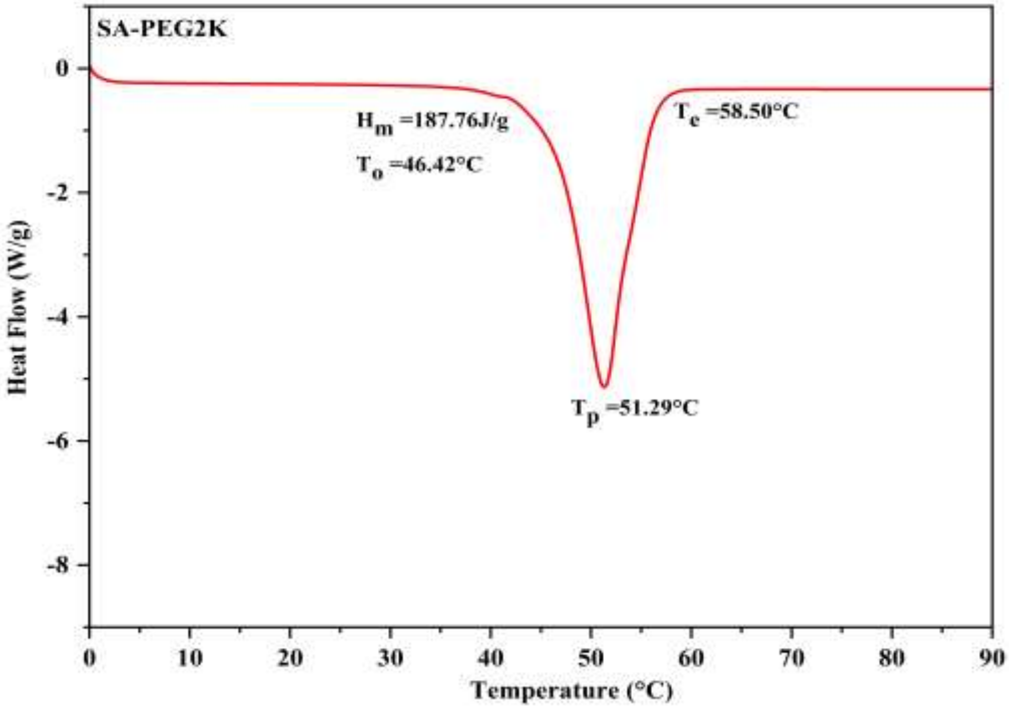

Figure 5. 28: Heat Flow Curve of SA-PEG2K

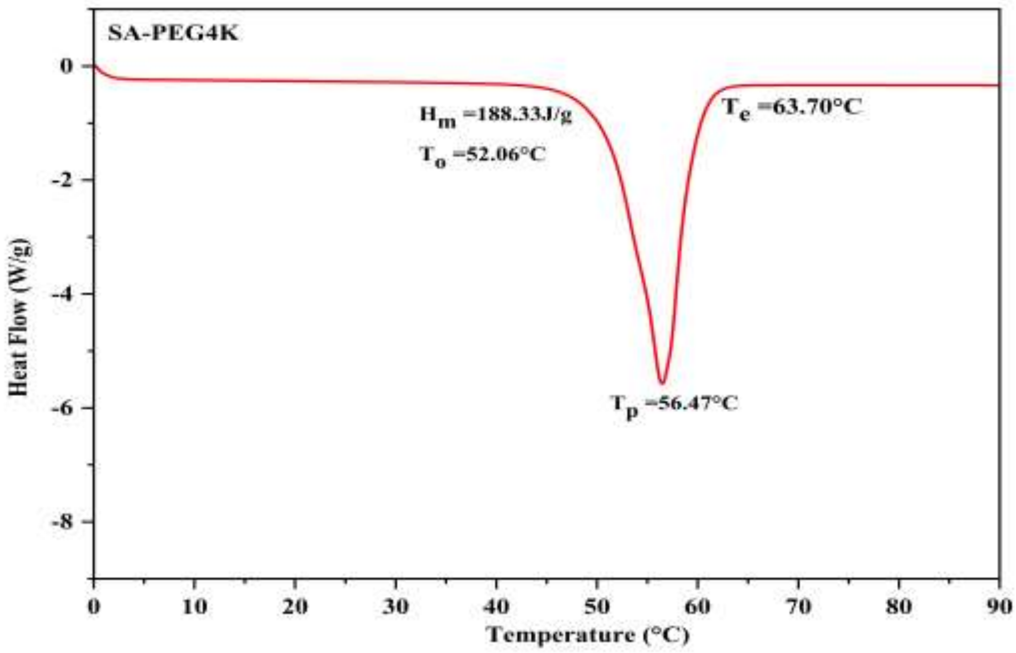

Figure 5. 29: Heat Flow Curve of SA-PEG4K

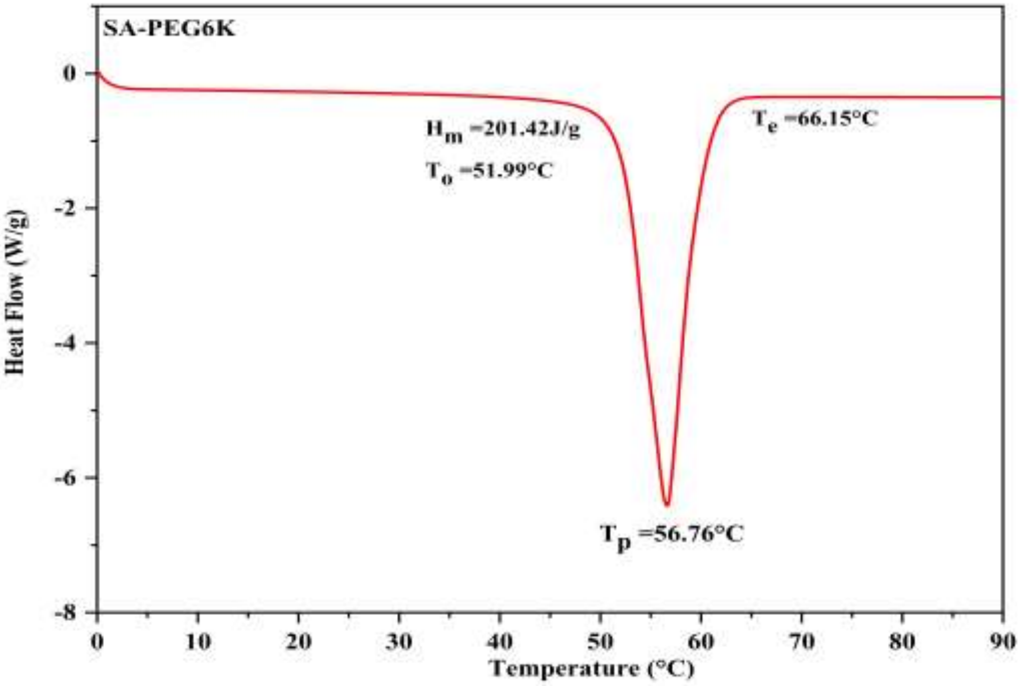

Figure 5. 30: Heat Flow Curve of SA-PEG6K

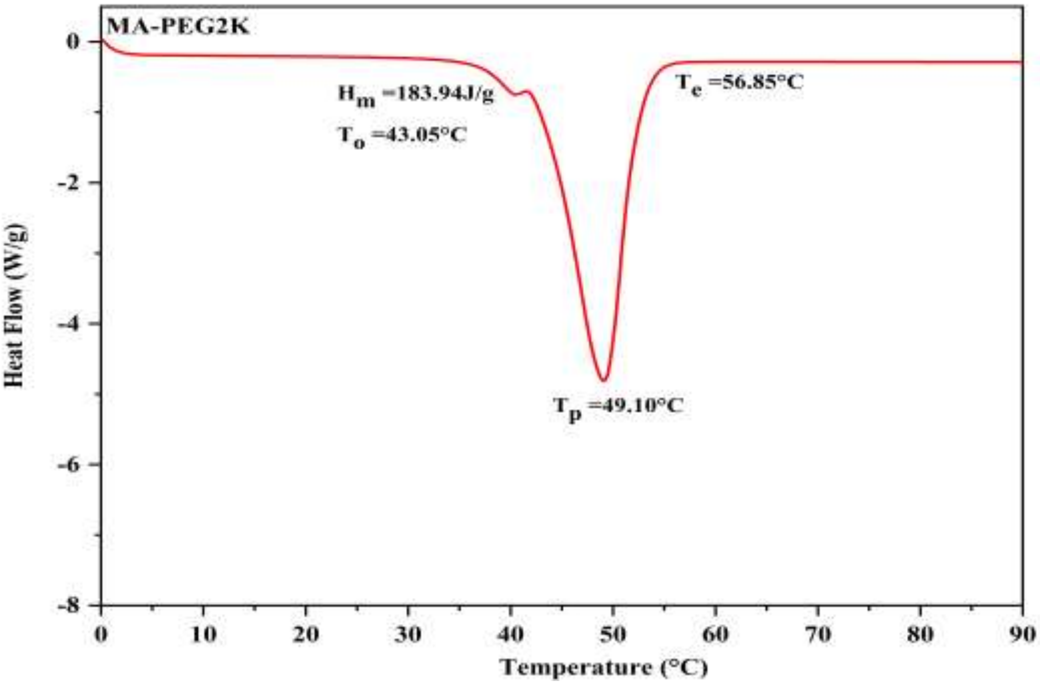

Figure 5. 31: Heat Flow Curve of MA-PEG2K

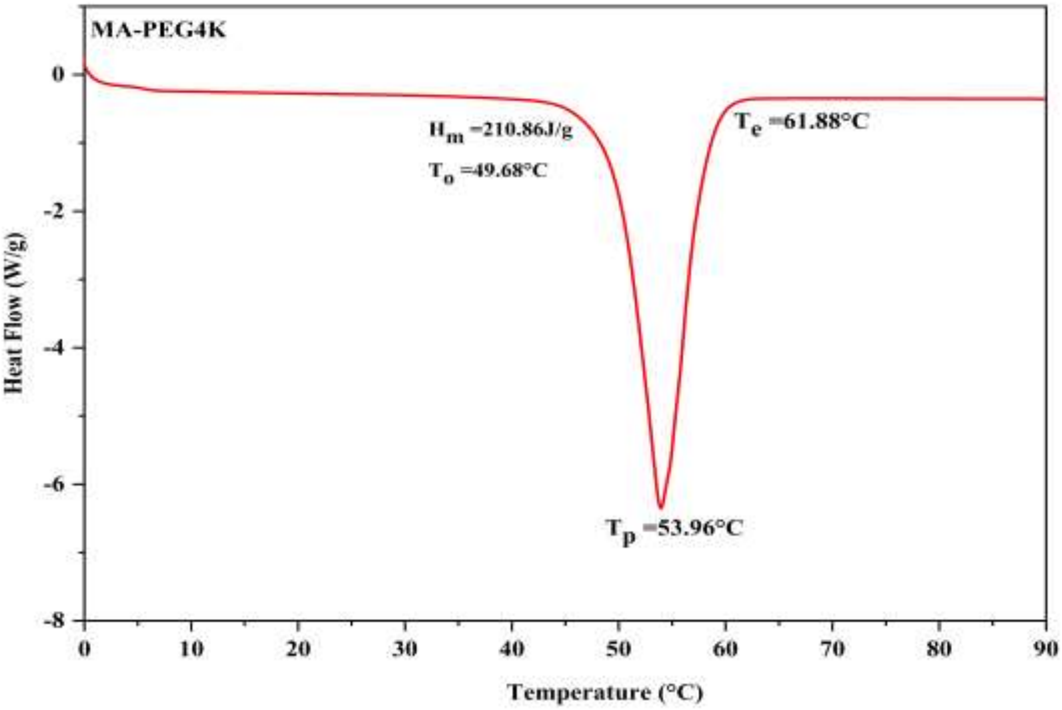

Figure 5. 32: Heat Flow Curve of MA-PEG4K

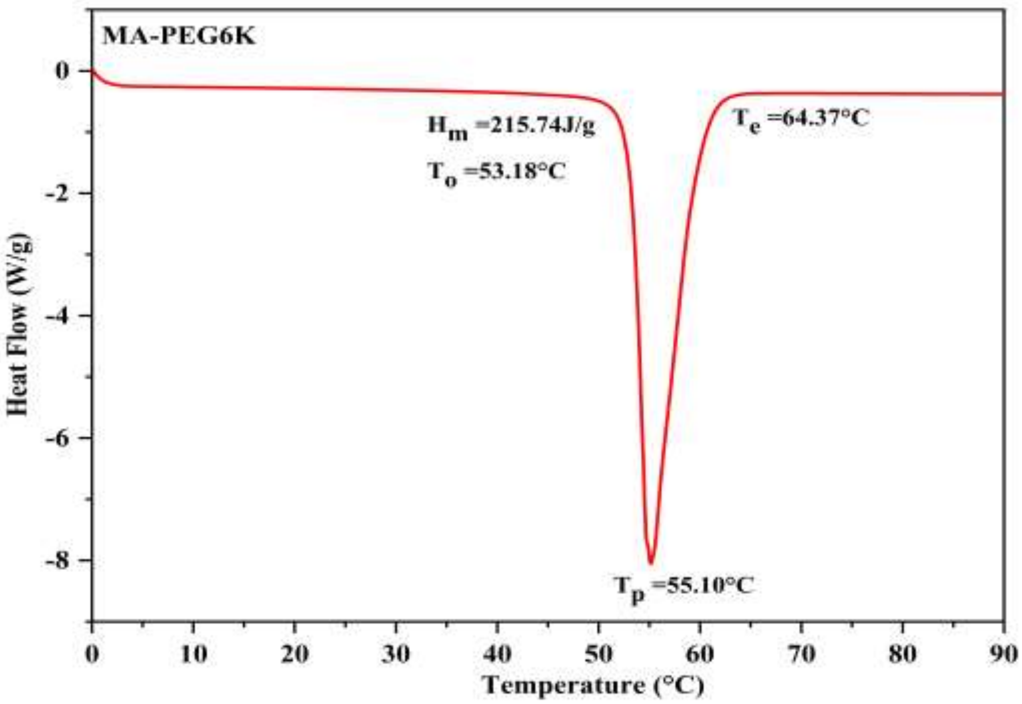

Figure 5. 33: Heat Flow Curve of MA-PEG6K

Table 5. 2: Thermal characteristics of EPCMs as determined by DSC.

EPCMs	Eutectic Composition	Melting				Solidification			
		T_o	T_p	T_e	L.H of fusion	T_o	T_p	T_e	L.H of fusion
	(wt.%)	(°C)	(°C)	(°C)	(J/g)	(°C)	(°C)	(°C)	(J/g)
PA-PEG2K	9.30/90.7	46.4	51.8	60.3	185.8	32.4	28.2	17.8	171.2
PA-PEG4K	11.8/88.2	54.7	59.5	66.7	187.5	37.0	35.0	20.0	166.0
PA-PEG6K	15.7/84.3	55.5	59.5	67.4	200.4	36.1	33.0	23.2	138.3
SA-PEG2K	21.0/79.0	46.4	51.2	58.5	187.7	45.4	43.4	16.9	175.0
SA-PEG4K	56.8/43.2	52.0	56.4	63.7	188.3	51.8	49.7	18.4	176.3
SA-PEG6K	98.9/1.1	51.9	56.7	66.1	201.4	52.2	50.7	33.7	196.3
MA-PEG2K	21.8/78.2	43.0	49.1	56.8	183.9	29.3	26.8	11.2	109.3
MA-PEG4K	56.6/43.4	49.6	53.9	61.8	210.8	48.8	48.7	35.0	201.2
MA-PEG6K	98.9/1.1	53.1	55.1	64.3	215.7	51.4	50.9	35.7	216.9

A comparison of predicted and measured thermal characteristics of eutectic PCMs is presented in **Table 5.3.** Although the predicted thermal characteristics agree with the measured values. However, the relative difference of 7.5% might be due to the impurities in the PCMs. An absolute difference of 3.5°C is present in the predicted and measured M.T of MA-PEG2K.

Table 5. 3: Comparison of predicted and measured thermal characteristics of eutectic PCMs.

Eutectic PCMs	Predicted M. T	Measured M. T	Absolute Difference in M. T	Relative Difference in M. T	Predicted L.H of fusion	Measured L.H of fusion	Absolute Difference in L.H	Relative Difference in L.H
	(°C)	(°C)	(°C)	(%)	(J/g)	(J/g)		(%)
PA-PEG2K	48.1	46.4	1.7	3.5	169.5	185.8	16.3	9.6
PA-PEG4K	54.8	54.7	0.1	0.1	189.0	187.5	1.5	0.7
PA-PEG6K	57.8	55.5	2.3	3.9	198.7	200.4	1.7	0.8
SA-PEG2K	46.9	46.4	0.5	1.0	170.3	187.7	17.4	10.2
SA-PEG4K	52.7	52.0	0.7	1.3	194.3	188.3	6	3.0
SA-PEG6K	53.4	51.9	1.5	2.8	197.5	201.4	3.9	1.9
MA-PEG2K	46.5	43.0	3.5	7.5	165.9	183.9	18.0	10.8
MA-PEG4K	52.4	49.6	2.8	5.3	188.9	210.8	21.9	11.5
MA-PEG6K	53.2	53.1	0.1	0.1	192.0	215.7	23.7	12.3

5.1.3 Specific Heat Capacity Analysis

Cp relates to other thermophysical characteristics, such as thermal diffusivity, and is an essential property for designing the storage capacity of LHTES systems. Due to the restricted availability of this data, design engineers are forced to rely on discrete assumptions and assumed values, which can have a detrimental effect on the LHTES system's performance [37].

Measured Cp values of pure PCMs and prepared EPCMs are shown in **Figure 5.34 (a-b).** However, the initial abrupt rise in the Cp value of pure PCMs demonstrates heat absorption and a subsequent phase transition from solid to liquid during the melting cycle.

However, this tendency has been seen due to molecular collisions' rise in kinetic energy [37].

In both phases, Cp values of pure PCMs (PA, SA, PEG2K and PEG4K) represented in **Figure 5.34(a)** are in line with the literature [19,63-64]. In addition, Cp values of eutectic PCMs (PA-PEG2K, PA-PEG4K, SA-PEG2K and SA-PEG4K) for solid phase are 1.6, 1.8, 1.6 and 1.7 J/g.°C respectively . While, for liquid phase the Cp values are 2.3, 2.4, 2.2 and 2.2 J/g.°C (shown in **Figure 5.34(b)**). It is observed that Cp values drastically rise during the phase transformation, since the Cp deals with sensible heat, therefore, it is not taken into account during the phase transition of PCMs. However, compared to the liquid phase, the solid phase exhibits a stronger increase in the Cp with increasing temperature due to the molecules' limited motion and comparatively low entropy in solids [37].

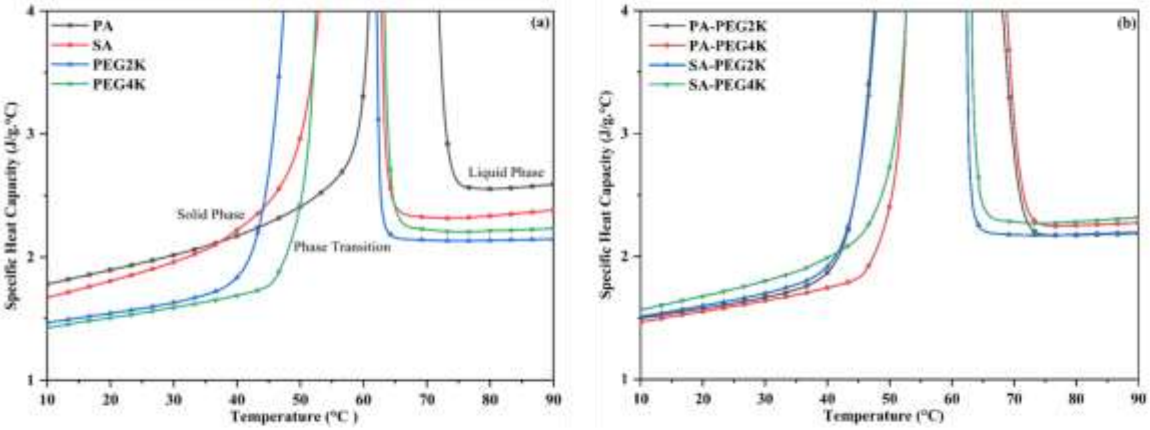

Figure 5. 34: (a) Specific Heat Capacity of Pure PCMs(b) Specific Heat Capacity of EPCMs

5.1.4 Thermal Gravimetric Analysis

The TGA findings reveal a decline in weight with rising temperature, as depicted in **Figure 5.35-Figure 5.37.** The eutectic samples were heated at a rate of 10°C per minute, ranging from 25 to 300°C. **Figure 5.35-5.37** shows that the eutectic samples remain intact, with minimal weight loss noticeable when the temperature is below 195°C. This suggests a high level of stability for EPCMs within the operational temperature range. EPCMs began to degrade at about 200°C and initial loss was mostly due to the evaporation of the

PCMs. The rate of weight loss increased rapidly above 210°C. The weight losses of the EPCMs at temperatures of 296°C, 296.5°C, 297°C, and 295.6°C were 9.6%, 10.9%, 15.5%, 19.0%, 51.1%, 97.0%, 21.1%, 58.7%, and 97.8% respectively. About 300°C was the point at which the EPCMs completely degraded; at this temperature, 90.4%, 89.1%, 84.5%, 81.0%, 48.9%, 3.0%, 78.9%, 41.3%, and 2.2% of the residue remained.

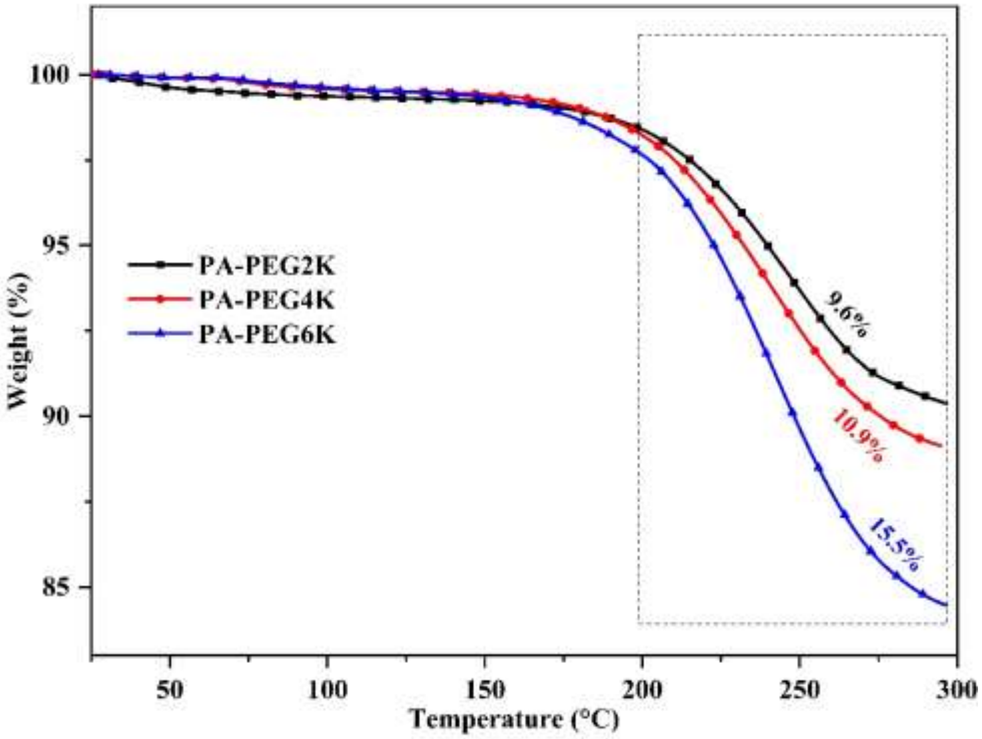

Figure 5. 35: TGA of PA-PEG2K, PA-PEG4K, and PA-PEG6K

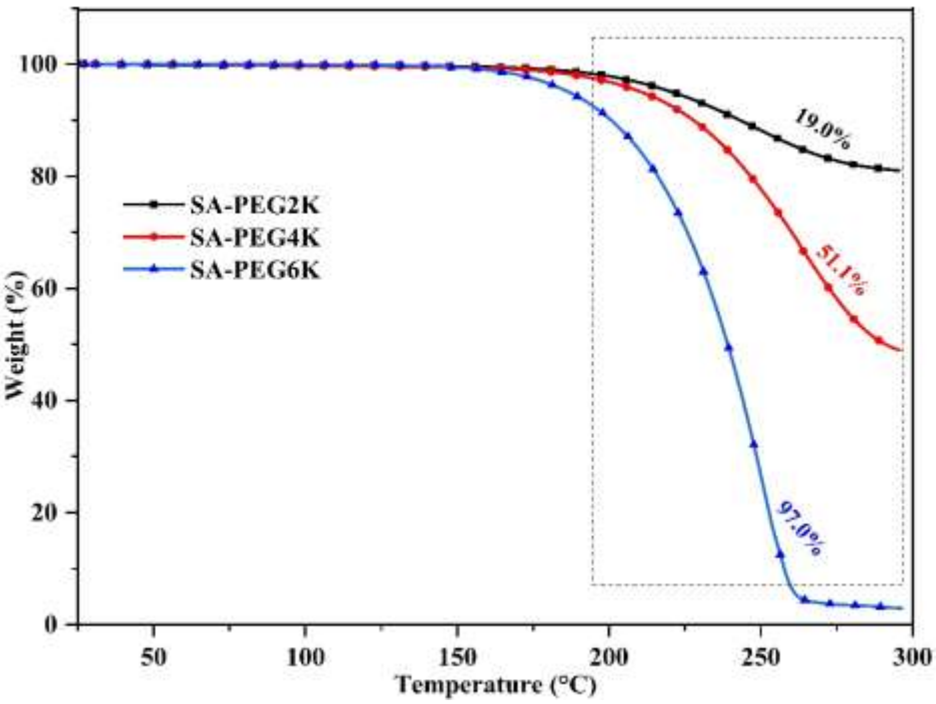

Figure 5. 36: TGA of SA-PEG2K, SA-PEG4K, and SA-PEG6K

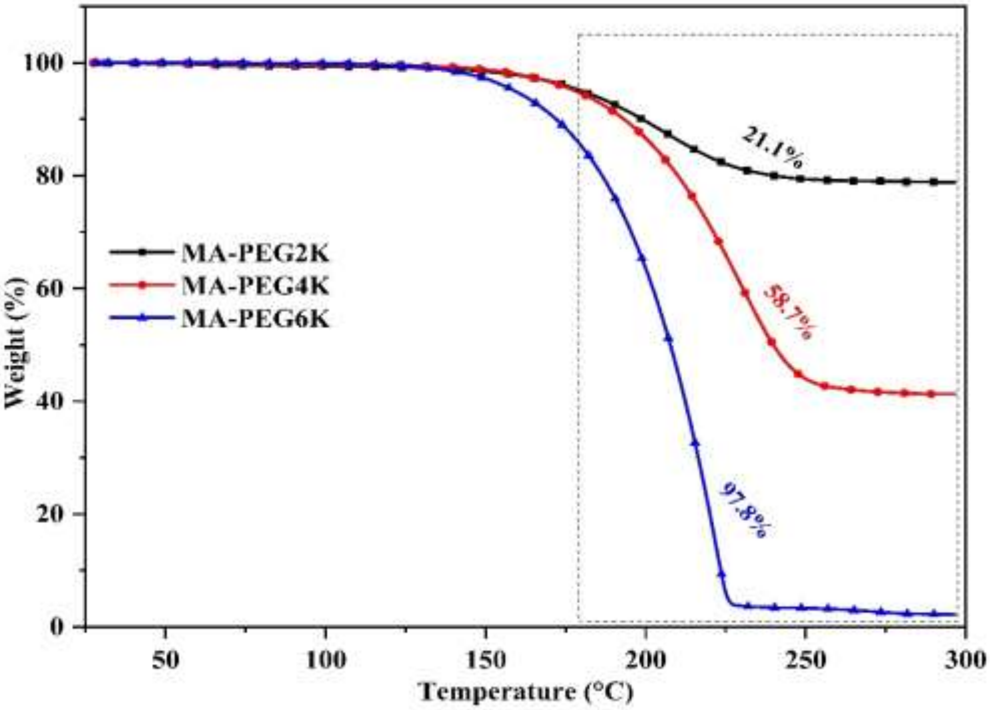

Figure 5. 37: TGA of MA-PEG2K, MA-PEG4K, and MA-PEG6K

Table 5. 4: Thermal Stability of EPCMs as determined by TGA.

Materials	Temperature Range (°C)			Weight Loss (%)	Residue Left (%)
	Overall	1st Stage	2nd Stage		
PA/PEG2K	25-300	187.9	296.0	9.6	90.4
PA/PEG4K	25-300	178.3	296.5	10.9	89.1
PA/PEG6K	25-300	179.5	294.6	15.5	84.5
SA/PEG2K	25-300	297.0	297.0	19.0	81.0
SA/PEG4K	25-300	295.6	295.6	51.1	48.9
SA/PEG6K	25-300	188.8	262.8	97.0	3.0
MA/PEG2K	25-300	160.1	246.9	21.1	78.9
MA/PEG4K	25-300	165.9	251.9	58.7	41.3
MA/PEG6K	25-300	161.2	226.7	97.8	2.2

5.1.5 Thermal Conductivity Analysis (DTC)

PCMs absorb or release heat during melting or solidification. However, when the PCM melts and solidifies, the rate at which thermal energy is stored and released is determined by its thermal conductivity [113]. Whereas, pure PCMs have low thermal conductivity, which restricts their applications and lowers the rate at which heat may be stored and released. A PCM with higher thermal conductivity speeds up heat transmission during the melting and solidification processes and reduces the time required for these processes. [113]

Measured thermal conductivity values of pure and EPCMs are shown in **Figure.5.38**. The thermal conductivity of pure materials (PA, SA, PEG2K and PEG4K) is 0.367, 0.325, 0.390 and 0.463W/mK respectively. Whereas the thermal conductivity of EPCMs (PA-PEG2K, PA-PEG4K, SA-PEG2K and SA-PEG4K) is 0.423, 0.389, 0.347, and 0.350W/mK. The results revealed that the thermal conductivity of binary eutectic PA-PEG2K increased from 0.367W/mK for PA and 0.390W/mK for PEG2K to 0.423W/mK. Whereas, in the case of PA-PEG4K, SA-PEG2K and SA-PEG4K, the enhancement in thermal conductivity is slightly lower than pure PEG2K and PEG4K, but higher than pure PA and SA.

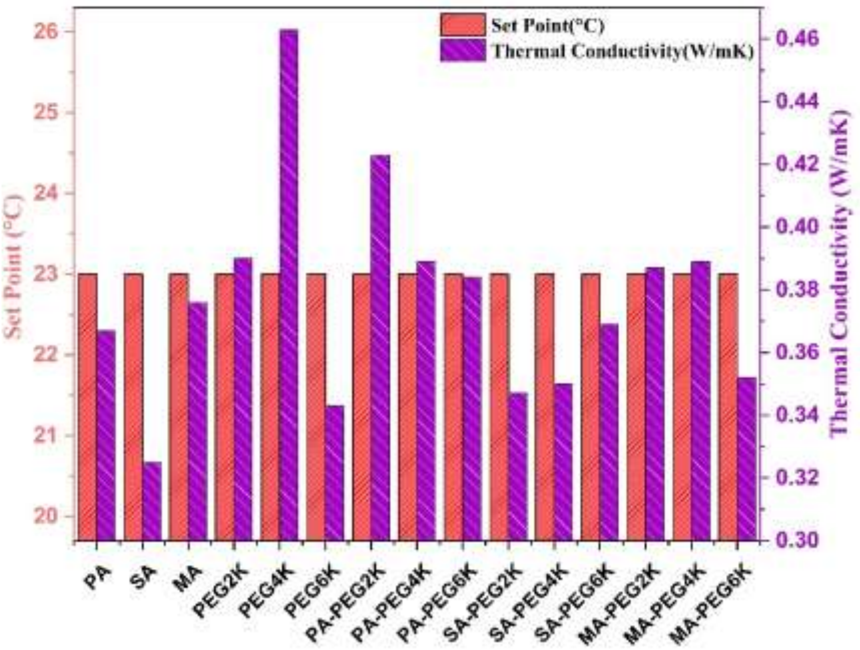

Figure 5. 38: Thermal Conductivity of EPCMs

The comparison of calculated and observed thermal conductivity of EPCMs is presented in **Table.5.5.** Although the calculated thermal conductivity aligns with the experimental values. However, the relative difference of 13.7% might be due to the impurities in the PCMs.

Table 5. 5: Comparison of predicted and measured thermal Conducivity of EPCMs.

Materials	Predicted Thermal Conductivity	Measured Thermal Conductivity	Absolute Difference	Relative Difference
	(W/mk)	(W/mK)	(W/mK)	(%)
PA/PEG2K	0.387	0.423	0.036	9.3
PA/PEG4K	0.451	0.389	0.062	13.7
PA/PEG6K	0.381	0.384	0.003	0.7
SA/PEG2K	0.376	0.347	0.029	7.7
SA/PEG4K	0.384	0.350	0.034	8.8
SA/PEG6K	0.325	0.369	0.044	13.5
MA/PEG2K	0.386	0.387	0.001	0.2
MA/PEG4K	0.413	0.389	0.024	5.8
MA/PEG6K	0.376	0.352	0.024	6.3

5.1.6 Performance Characteristics Analysis

The performance characteristics of the prepared fatty acids-polymers based EPCMs in this study are compared with the litearture as given in **Table 5.6.** When compared to other EPCMs described in the literature, binary fatty acids-polymers EPCMs have the most promising thermal properties.

Table 5. 6: Comparison of performance characteristics of EPCMs.

Eutectic PCMs	Composition	Thermal characteristics		Application Areas	Ref
		M.T	L.H of fusion		
	(wt.%)	(°C)	(J/g)		
SA-PA	37.01/62.9	56.2	204.7	DHW, SSH	[54]
SA-PA	36.8/63.2	55.0	180	DHW, SSH	[21]
PA-PEG6K	15.7/84.3	55.5	200.4	DHW,SSH	This study
SA-PEG6K	98.9/1.1	51.9	201.4	DHW,SSH	This study
MA-PEG6K	98.9/1.1	53.1	215.7	DHW,SSH	This study
PA-PEG4K	11.8/88.2	54.7	187.5	DHW, SSH	This study
SA-PEG4K	56.8/43.2	52.0	188.3	DHW, SSH	This study
MA-PEG4K	56.6/43.4	49.6	210.8	DHW	This study
PA-PEG2K	9.3/90.7	46.4	185.8	DHW	This study
SA-PEG2K	21.0/79.0	46.4	187.7	DHW	This study
MA-PEG2K	21.8/78.2	43.0	183.9	DHW	This Study

As shown in **Figure 5.39(a),** the M.T of prepared EPCMs: PA-PEG2K, PA-PEG4K, PA-PEG6K, SA-PEG2K, SA-PEG4K, SA-PEG6K, MA-PEG2K, MA-PEG4K and MA-PEG6K ranges from 43.0 to 55.5°C and their melting enthalpy ranges from 183.9 to 215.7J/g making them appropriate for applications such as DHW and SSH. However, Cp of EPCMS in liquid phase ranges from 2.2 to 2.4 $J\cdot g^{-1}\cdot °C^{-1}$ and for solid phase it ranges from 1.6 to 1.8 $J\cdot g^{-1}\cdot °C^{-1}$, as shown in **Figure 5.39(b).** The developed eutectic PCMs are applicable in TESS, incorporating renewable energy sources like solar energy for effective operation.

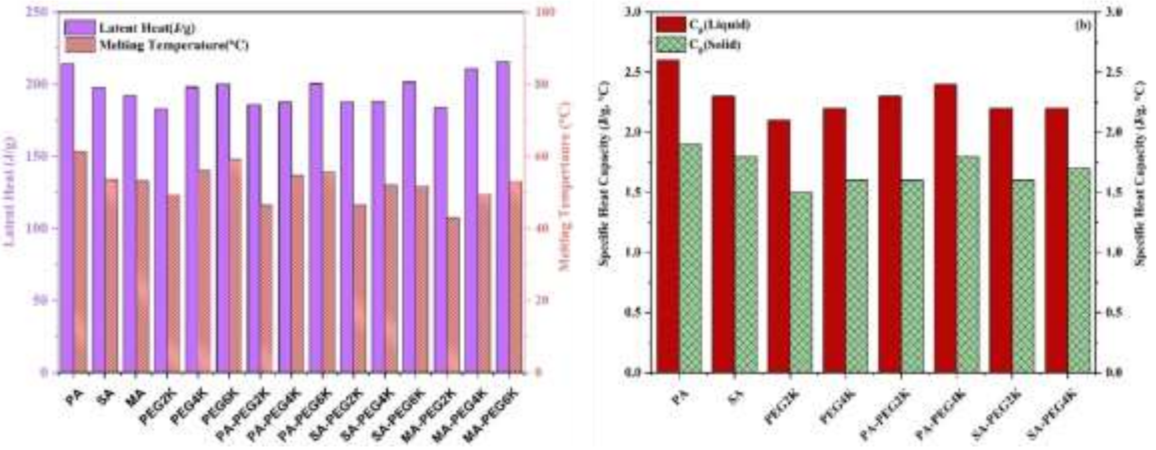

Figure 5. 39: Fatty acid-polymers based PCMs and EPCMs (a) Melting Temperature and Latent heat (b) Specific Heat Capacity

CHAPTER 6: CONCLUSION & FUTURE RECOMMENDATIONS

6.1 Conclusion

This research aims to develop EPCMs using a combination of fatty acids and polymers to address the needs of thermal energy storage applications. Specifically, palmitic acid, stearic acid, myristic acid, polyethylene glycol 2K, polyethylene glycol 4K and polyethylene glycol 6K have been employed. Nine eutectic PCMs PA-PEG2K, PA-PEG4K, PA-PEG6K, SA-PEG2K, SA-PEG4K, SA-PEG6K, MA-PEG2K, MA-PEG4K, and MA-PEG6K were prepared. Key findings include:

- **Melting Points:** The EPCMs exhibited melting points between 43.0°C and 55.5°C.
- **Latent Heat:** The latent heat of fusion ranged from 183.9 J/g to 215.7 J/g.
- PA-PEG4K and MA-PEG6K showed minimal deviation (0.1%) between predicted and measured melting temperatures.
- **High Latent Heat:** PA-PEG4K and MA-PEG6K had latent heats of 187.5 J/g and 215.7 J/g, respectively.
- FTIR analysis confirmed no significant chemical changes in the structure of the pure PCMs.
- **Thermal Stability:** TGA results showed promising thermal stability for the binary eutectic combinations.
- **Thermal Conductivity:**
    - PA-PEG2K showed an enhanced thermal conductivity of 0.423 W/m·K, compared to 0.367 W/m·K for PA and 0.390 W/m·K for PEG2K.

    - Thermal conductivity improvements for PA-PEG4K, SA-PEG2K, and SA-PEG4K were lower than pure PEG2K and PEG4K but higher than pure PA and SA.
- **Applications:** Given their attributes, these EPCMs exhibit commendable thermal energy storage properties, making them suitable for applications such as solar thermal space heating, domestic water heating systems, and thermal management in building structures..

6.2 Future Recommendations

An examination of the thermal stability of Enhanced Phase Change Materials (EPCMs) is essential for determining the operational safety threshold temperature of PCMs. The incorporation of various nanomaterial additives can augment the thermal conductivity of EPCMs. Structural analysis of the nanomaterial addition in EPCMs, utilizing techniques such as SEM, XRD, and FT-IR, can provide insights into its impact on thermophysical properties. These EPCMs may be integrated into experimental setups to assess operational capabilities, including response time and other performance indicators. Furthermore, the development of multicomponent EPCMs can be pursued, using the identified EPCMs as parent materials, resulting in enhanced operating windows concerning onset melting and end-set melting temperatures. Additionally, research on the corrosion resistance of materials commonly considered for Thermal Energy Storage (TES) tank construction can contribute valuable insights.

Thermal energy storage using PCMs holds great promise for addressing energy fluctuation problems and improving energy efficiency in various applications, including passive building and cold thermal energy storage. Future recommendations for the use of PCMs in TESS include continued research and development to enhance the thermal properties and stability of PCMs, as well as their compatibility with different applications. Additionally, efforts to optimize the integration of PCM-based TESS in buildings and cooling applications, and to overcome technical challenges, are crucial for the widespread adoption of this technology. PCMs for TES applications are the subject of ongoing research and special issues, which show an increasing interest and investment in this sector and emphasize the significance of additional developments and improvements in the use of PCMs for TES.

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LIST OF PUBLICATIONS

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View Submission View Reference Checking Results Send E-mail	POLYMER-24-2695	Development and Thermal Analysis of Fatty Acid/PEG based Binary Eutectic Phase Change Materials for Low Temperature Applications	Aug 26, 2024	Nov 24, 2024	Under Review