

REPUBLIC OF TÜRKİYE
YILDIZ TECHNICAL UNIVERSITY
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**DEVELOPMENT OF POLYMER-BASED
MICROCAPSULE REINFORCED COMPOSITE
MATERIAL**

Elmas KIRTAY

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Department of Chemistry

Program of Physical Chemistry

Supervisor

Prof. Dr. Tarık EREN

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A thesis submitted by Elmas KIRTAY in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE** is approved by the committee on 29.07.2024 in the Department of Chemistry, Program of Physical Chemistry.

Prof. Dr. Tarık EREN
Yıldız Technical University
Supervisor

Approved By the Examining Committee

Prof. Dr. Tarık EREN, Supervisor
Yıldız Technical University

Prof. Dr. Dolunay ŞAKAR DAŞDAN, Member
Yıldız Technical University

Assoc. Prof. Çağatay ELİBOL, Member
Turkish-German University

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Dedicated to my family

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LIST OF SYMBOLS

%	Percent
ΔH	Enthalpy
ΔH_{fus}	Heat of fusion substance
ΔT	Temperature difference between reference and sample
°C	Celsius Degree
cm	Centimeter
eV	Electronvolt
g	Gram
g/mol	Gram per mol
J/g	Joules per gram
K	Kelvin
K	Constant
kg	Kilogram
kJ/kg	Kilojoules per kilogram
M	Mass os substance
mbar	Millibar
mg	Milligram
ml	Milliliter
N	Normality
PPI	Pores Per Inch
q	Total change in heat energy
t	Testing Time
v/v	Volume per volume
W	Watt

LIST OF ABBREVIATIONS

AIBN	Azobisisobutyronitrile
CAS	Chemical Abstracts Service
CMC	Carboxymethyl Cellulose
C_p	Heat Capacity
CV	Coefficient of Variation
DSC	Differential Scanning Calorimetry
EPCM	Encapsulated Phase Change Material
FTIR	Fourier Transform Infrared Spectroscopy
LHTES	Latent Heat Thermal Energy Storage
MMA	Methyl methacrylate
M_n	Number Average Molecular Weight
OD	Octadecane
PCM	Phase Change Material
PDVB	Poly(divinylbenzene)
PEG	Polyethylene Glycol
PEGDA	Polyethylene Glycol Diacrylate
PMMA	Poly (methyl methacrylate)
PP	Polypropylene
SBIR	Small Business Innovation Research
T_c	Crystallization Temperature
T_d	Decomposition Temperature
TEM	Transmission Electron Microscope
TEOS	Tetraethyl Orthosilicate
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
T_m	Melting Temperature
XPS	X-ray Photoelectron Spectroscopy

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Development of Polymer-Based Microcapsule Reinforced Composite Material

Elmas KIRTAY

Department of Chemistry

Master of Science Thesis

Supervisor: Prof. Dr. Tarık EREN

The increasing global population, technological advancements, and the resulting rise in living standards have significantly boosted the global demand for energy. Consequently, energy storage and the use of renewable energy sources present many alternatives. Various methods can be employed to store different forms of energy. Studies in this field have highlighted the use of phase change materials (PCMs), which can store thermal energy and absorb or release large amounts of latent heat during phase transitions. However, issues such as thermal instability and the inability to maintain long-term properties pose challenges to the use of latent heat storage. To address these problems, research has focused on encapsulating PCMs or storing them within a container. In this thesis, polymethyl methacrylate-polyethylene glycol-based copolymers were synthesized, and commercial paraffin (commercial RT-28, RUBITHERM®) was encapsulated. After evaluating the encapsulation efficiency and heat storage capacity, a second layer coating was applied using (i) the Stöber process with silica, (ii) carboxymethyl cellulose (CMC), and (iii) a commercial silicate solution (Flexdub). The chemical structures of the obtained capsules were analyzed using FTIR, their thermal behaviors were assessed with TGA and DSC, and TEM was used to examine the surface morphology and microscopic structure, while XPS was employed for surface elemental analysis. The capsules were found to be stable at 100°C after 50 thermal cycles. It was observed

that particularly the double-layered PCM coated with the commercial silicate solution (Flexdub) remained stable at 140 °C. To investigate the behavior of double-layered capsules in an extruder line, a certain amount was added to a polypropylene matrix, and the phase change property of the obtained composite was analyzed.

Keywords: Phase change materials, thermal conductivity, copolymer, encapsulation.



Polimer Esaslı Mikro kapsül Takviyeli Kompozit Malzemenin Geliştirilmesi

Elmas KIRTAY

Kimya Anabilim Dalı
Yüksek Lisans Tezi

Danışman: Prof. Dr. Tarık EREN

Her geçen gün artan nüfus, teknolojik gelişmeler ve bunların beraberinde artan yaşam standartları tüm dünyada ihtiyaç duyulan enerji talebini arttırmaktadır. Bu nedenlerden dolayı enerji depolama ve yenilenebilir enerji kaynaklarının kullanımı iyi birer alternatiftir. Enerjinin farklı türleri çeşitli yöntemlerle depolanabilir. Bu alanda yapılan çalışmalar incelendiğinde faz değişim malzemelerinin (FDM'lerin) kullanıldığı görülmektedir. Bu malzemeler termal enerji depolayabilir ve faz değişim sürecinde büyük miktarda gizli ısıyı emebilir ve serbest bırakabilir. Ancak bu malzemelerin termal kararlılığı ve uzun süreli özelliğini koruyamaması gizli ısı depolamanın kullanımında karşılaşılan bazı sorunlardır. Bu sorunların çözümü için FDM'lerin kapsülleme veya bir konteyner içinde saklama şeklinde uygulaması üzerine çalışmalar yapıldığı görülmektedir. Tez çalışmasında polimetil metakrilat-polietilen glikol esaslı kopolimerler sentezlenmiş ve ticari parafin (ticari RT-28, RUBITHERM®) kapsüllenmiştir. Kapsülleme verimliliği ve ısı depolama kapasitesi değerlendirildikten sonra, (i) Stöber prosesi ile silika, (ii) karboksimetil selüloz (CMC) ve (iii) ticari silikat çözeltisi (Flexdub) ile ikinci bir katmanın kaplaması yapılmıştır. Elde edilen kapsüllerin kimyasal yapıları FTIR kullanılarak analiz edilmiş, termal davranışları TGA ve DSC ile değerlendirilmiş, yüzey morfolojisi ve mikroskobik yapısının incelenmesi için TEM, yüzey elementel analizi için XPS kullanılmıştır. Kapsüllerin 100 °C de ve 50 termal döngü sonrasında kararlı olduğu görülmüştür. Çift kaplama sonrası özellikle ticari silikat

Anahtar Kelimeler: Faz değişim malzemeleri, ısıl iletkenlik, kopolimer, kapsülleme.

1

INTRODUCTION

In the present day, humans require various forms of energy to fulfill fundamental needs such as food, clean water, transportation, and heating/cooling. With the continuous growth of the world's population, energy demand is rapidly increasing. To meet this demand, fossil fuels are commonly used. However, the limited natural sources of fossil fuels and their inability to meet the growing demand pose serious challenges in the energy sector.

Fossil fuels such as coal, oil, and natural gas have been fundamental sources of energy production for many years. However, their reserves are limited and are being depleted continuously. According to United Nations projections, the global population is expected to reach 9.2 billion by 2040. [1] Consequently, this will require supplying energy to an additional 1.9 billion people. The inadequacy of fossil fuel resources in the face of rising energy demand raises concerns about future energy security.

Moreover, the environmental impacts of fossil fuels cannot be ignored. The release of carbon dioxide and other greenhouse gases into the atmosphere contributes to adverse effects on climate change. This situation threatens the sustainability of energy production and environmental health.

To address these challenges, the use of energy storage and renewable energy sources has emerged as a significant alternative. Renewable energy sources, derived from natural resources such as solar, wind, hydroelectric, and geothermal sources, are unlimited and renewable. However, the variable nature of these sources necessitates the development of energy storage systems. Energy storage technologies play a critical role in stabilizing energy supply by storing energy generated from energy sources and meeting energy demand effectively.

1.1 Energy Storage Technologies

Population growth, urban expansion, and industrialization have led to an increasing primary energy consumption over the years, necessitating the development of

environmentally friendly, economical, and sustainable solutions. The practice of energy storage is not a new phenomenon. It is known that batteries have been used since the early 1800s.[2] On the other hand, applications of pumped hydroelectric energy storage in the United States date back to the 1930s. [3] Due to the demand for a dynamic, flexible, and clean grid, new generation energy storage projects have gained momentum. Worldwide efforts are underway to develop reliable, economical, efficient, and high-capacity energy storage solutions to utilize energy more effectively from various sources. Energy storage not only helps mitigate the intermittent nature of solar and wind energy but also enables rapid response to large fluctuations in demand, making the grid more responsive and potentially reducing the need for backup power plants.

Figure 1.1 classifies commonly applied energy storage techniques according to the type of energy. [4]

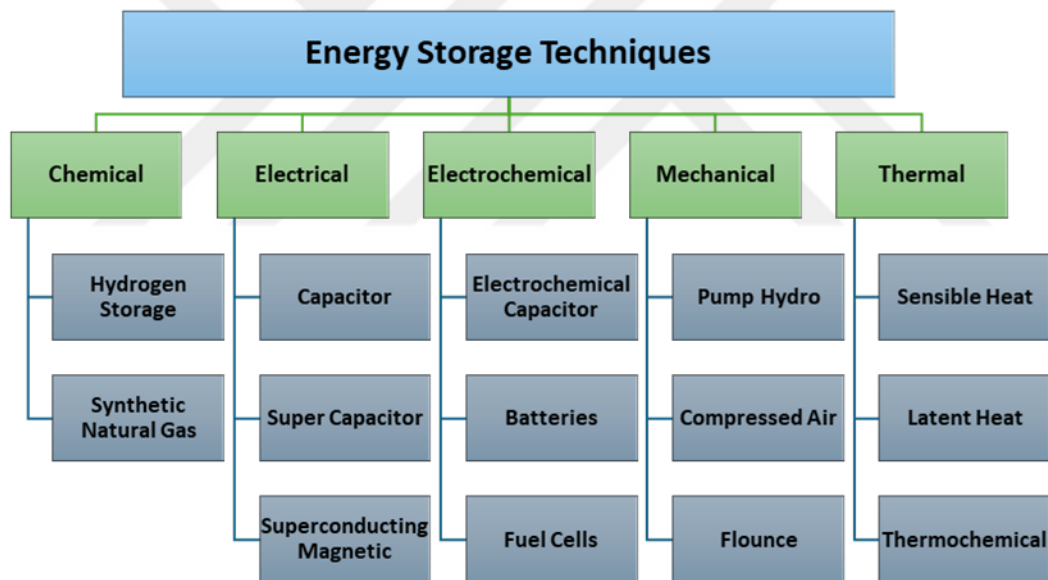


Figure 1.1 Commonly used energy storage techniques

There are various types of energy storage alternatives depending on the application type, the required needs, and economic conditions.

1.2 Thermal Energy Storage

In thermal energy storage techniques, thermal energy can be stored or reused through the material's temperature changes (sensible heat), phase transitions (latent heat), or thermochemical reactions. In sensible thermal energy storage, thermal

energy is stored or extracted by changing the temperature of a solid or liquid medium. Latent thermal energy storage utilizes the energy released or absorbed during phase change processes, such as solid-liquid or liquid-gas transitions. Heat of fusion is the amount of energy required to melt or freeze a substance at constant pressure. It is sometimes referred to as enthalpy of fusion or latent heat of fusion. Figure 1.2 shows the solid-liquid phase change of water. The heat of fusion of water at 0 °C must release 334 J/g energy to completely freeze and become ice. In addition, for 1g of ice to completely melt at 0 °C, it must absorb 334 J/g energy.

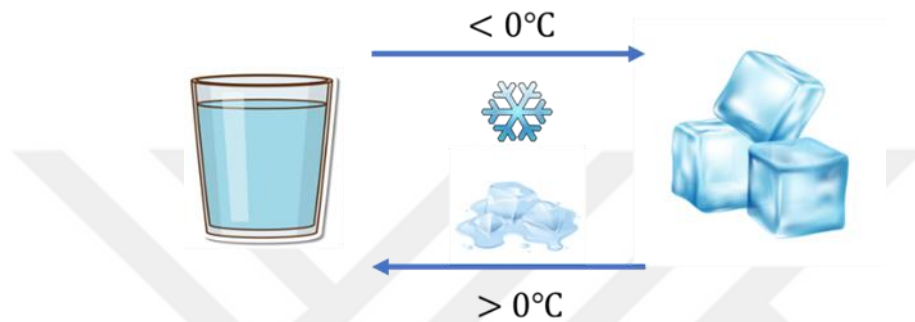


Figure 1.2 Solid-liquid phase change of water

The energy required to change the phase of a substance at its melting point is calculated from equation 1.1

$$q = m\Delta H_{fus} \quad (1.1)$$

q = Total change in heat energy (J)

ΔH_{fus} = Heat of fusion of substance (J/g)

m = Mass of substance (g)

Thermochemical storage techniques involve storing significant amounts of thermal energy through reversible endothermic or exothermic reactions, which are particularly advantageous for applications requiring long-term energy storage.

Sensible thermal energy storage is one of the oldest techniques, characterized by the lowest cost per unit of energy stored. In contrast, latent thermal energy storage systems provide higher energy storage density per unit volume compared to sensible storage.

Thermochemical energy storage systems store or release thermal energy through chemical reaction principles. $C + \text{heat} \rightleftharpoons A + B$ is one way to express the thermochemical storage reaction. In this process, A and B are reactants, while C is referred to as the thermochemical material. Matter A may consist of hydroxides, hydrates, carbonates, ammonia, or comparable chemicals, while Matter B may consist of such as water, hydrogen, carbon monoxide, ammonia. Although there are no phase limitations, A and B can be in any phase while C is usually either a solid or a liquid. Thermochemical thermal energy storage systems experience very little or no heat loss during the storage period compared to other thermal energy storage types, thus eliminating the need for insulation.[5] Consequently, they are suitable for long-term heat storage, such as seasonal storage. These systems have higher energy densities compared to phase change materials (PCMs) and sensible storage media. The higher energy density enables more compact energy storage, which is particularly advantageous in situations where space is limited.

Table 1.1 lists the different types of material possess energy storage density and charging reaction temperatures. Especially, these two parameters are highly important for thermochemical energy storage of the usage of materials.

Table 1.1 Potential materials to be used in thermochemical energy storage

Thermochemical Material (C)	Solid Reactant (A)	Working Fluid (B)	Energy Storage Density of Thermochemical Material (GJ/m ³)	Charging Reaction Temperature (°C)
MgSO ₄ ·7H ₂ O	MgSO ₄	7H ₂ O	2.8	122
FeCO ₃	FeO	CO ₂	2.6	180
Ca(OH) ₂	CaO	H ₂ O	1.9	479
Fe (OH) ₂	FeO	H ₂ O	2.2	150
CaCO ₃	CaO	CO ₂	3.3	837
CaSO ₂ ·H ₂ O	CaSO ₄	2H ₂ O	1.4	89

Although thermochemical thermal energy storage has a high energy storage density, its high costs have limited its commercial adoption.

In heating and cooling applications, one of the preferred methods for thermal energy storage is typically either sensible or latent thermal energy storage. The sensible thermal energy storage method involves storing or reusing energy by altering the temperature of the storage medium. The relationship between temperature and enthalpy for this method is depicted in Figure 1.3. In such applications, materials used are expected to have a high volumetric heat capacity ($C_v = \rho c_p$ (C_v : ($\text{J}/\text{m}^3 \cdot \text{K}$) ρ : Density of the material (kg/m^3) c_p : Specific heat capacity of the material ($\text{J}/\text{kg} \cdot \text{K}$)). In this method, if the mass of the storage material is increased, a large amount of energy can be stored. However, this increase in mass is a disadvantage for areas with limited space. Increasing the density and overall mass reduces the portability and flexibility of the system, thus limiting its usability.

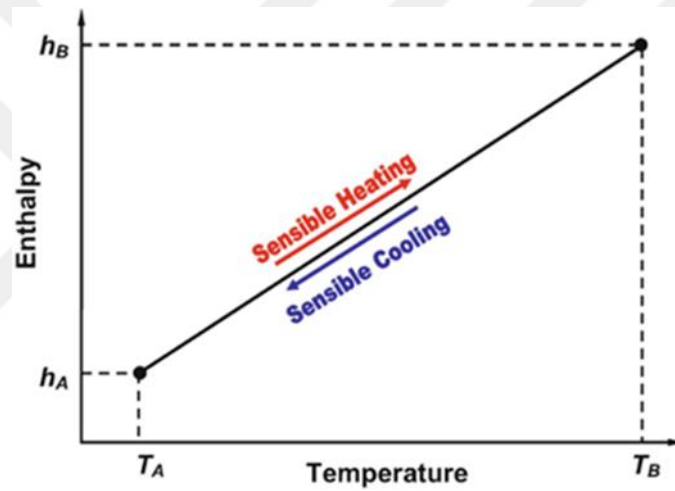


Figure 1.3 Temperature-enthalpy change for sensible thermal energy storage

The storage (or reuse) of large amounts of thermal energy in a limited volume can be effectively accomplished using the latent thermal energy storage method. This approach leverages the enthalpy change associated with the solid/liquid phase transition of the storage material, rather than relying on temperature changes. The temperature-enthalpy relationship for this method is illustrated in Figure 1.4

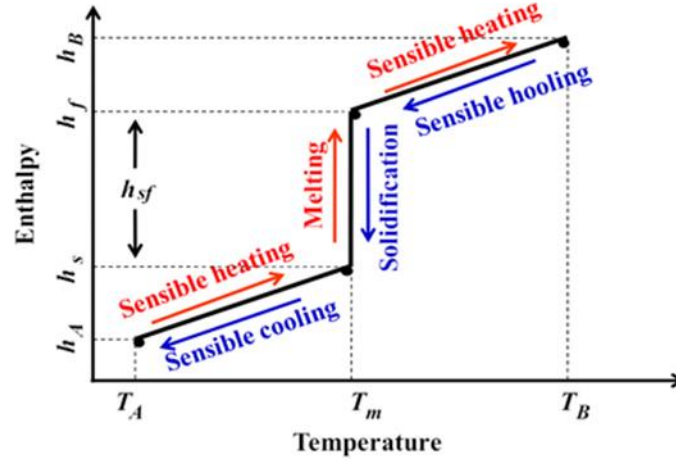


Figure 1.4 Diagram depicting the enthalpy-temperature relationship during latent heat storage

In this method, the energy stored (or reused) is directly proportional to the mass of the material and its latent heat of phase change. Utilizing materials with high latent heat of phase change in these systems enables the storage of a greater amount of thermal energy per unit volume compared to the sensible energy storage method. Since the materials used in latent thermal energy storage systems undergo phase changes, they are referred to as PCMs. A detailed explanation about the PCMs used in this field will be given and discussed in Chapter 2. In this thesis, a study was carried out on encapsulated PCMs with copolymers for latent heat storage.

1.3 Aim of Thesis

Thermal energy storage is of great importance in increasing energy efficiency and integrating renewable energy sources. PCMs are growing interest due to their thermal energy storage capacity and stability. However, the disadvantages of PCMs, such as low thermal conductivity, excessive volume change, and fluid leakage, limit the effective use of these materials.

The main purpose of this study is to investigate innovative encapsulation techniques to overcome the disadvantages of PCMs, which are widely used in thermal energy storage systems. Thus, a two-layer encapsulation method was developed in the study. First, polyethylene glycol-polymethyl metacrylate core shell polymers were synthesized and in situ parafilm (commercial RT-28, RUBITHERM®) as a PCM was encapsulated in the copolymer network. After evaluation the encapsulation efficiency and heat storage ability, second layer coating was applied with three

techniques (i) silica coating with a Stöber process (ii) carboxymethyl cellulose (CMC) and (iii) commercial silicate solution (Flexdub). The purpose of adding a second layer was to ensure that the encapsulated PCM remained mechanically and thermally stable at extruder line for the polypropylene processing temperature (180°C). Meanwhile, it is expected that using polyethylene glycol (PEG)-based core material will also provide an additive effect on thermal storage. Thus, additive effect for the latent heat of fusion (enthalpy of melting) of parafilm and PEG units can be observed. This property is significant for thermal energy storage applications, as it represents multifunctional properties as the amount of energy absorbed or released during the phase change.

The aim of this thesis is to increase the thermal and mechanical performances of PCMs with the developed two-layer encapsulation technique. Thus, increasing the efficiency and use in wide range of these type of PCMs will provide more sustainable and efficient solutions in energy storage with broad range application.

2 PHASE CHANGE MATERIAL (PCM)

A phase change material (PCM) is a substance that releases or absorbs a substantial amount of energy during its phase transition, thereby providing effective heating or cooling. Typically, this transition occurs between the first two fundamental states of matter: solid and liquid. Figure 2.1 illustrates how PCMs work with temperature variations. As the temperature rises, the solid PCM absorbs the latent heat from the environment and transitions to a liquid state. Conversely, when the temperature decreases, the liquid PCM releases the absorbed heat back into the environment, returning to a solid state. The most well-known and abundant PCM is ice/water. However, every chemical compound undergoes a phase change at specific temperatures and pressures. Early research on PCM for thermal energy storage was conducted by researchers at the University of Delaware in the 1970s, where PCM was integrated with solar collectors to store heat. [8] The high energy density of PCMs is attributed to the latent heat of fusion. During a phase change, a substantial amount of energy is absorbed or released without a significant change in measured temperature. This energy change results from the differences in intermolecular energies between the phases. [9]

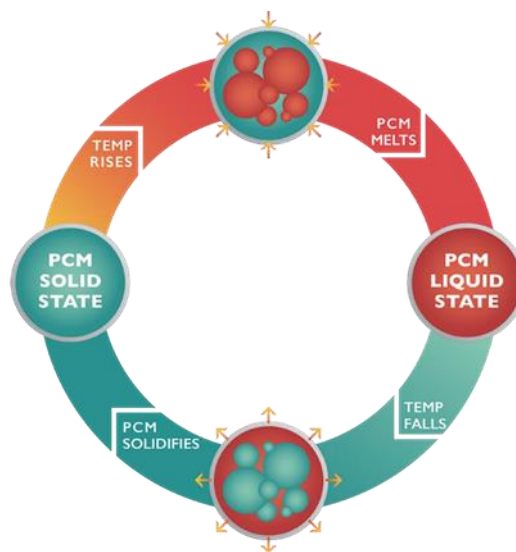


Figure 2.1 Schematic representation of the working mechanism of PCMs

Tetramer Technologies, identifying the shortcomings of current PCMs in terms of performance, durability, and cost, aims to address these issues in their Small Business Innovation Research (SBIR) project by developing new PCMs with enhanced volumetric energy capacity and improved durability through encapsulation. [11] As a result of this research, the final materials are selected and optimized for building applications, aiming to conclude the project with a robust and reliable encapsulation process. The expected outcome of the project is the development of encapsulated PCMs that reduce building cooling costs and improve energy efficiency. The development of new PCMs aims to overcome the known challenges associated with inorganic salt hydrates, such as supercooling, phase separation, and encapsulation difficulties. Achieving a stable material will mark a significant breakthrough for PCMs in building applications, potentially enhancing energy savings and improving thermal demand management. As shown in Figure 2.2. PCMs save building cooling costs and boost energy efficiency by storing energy during the day and releasing it at night.

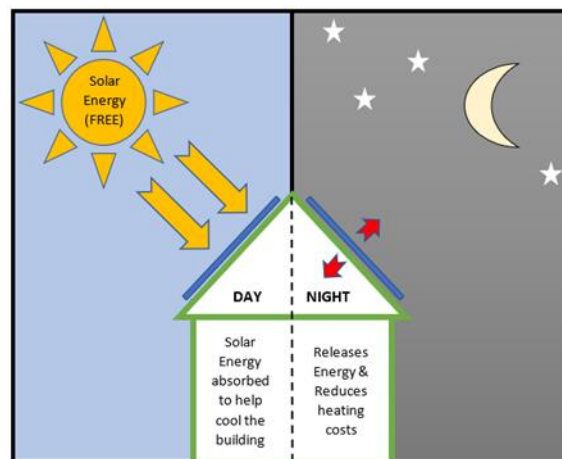


Figure 2.2 PCM's have the potential to reduce building energy usage by 20–30% by using solar energy for cooling and/or heating

2.1 Properties of PCMs

For PCMs to be used as latent heat storage materials, they must exhibit specific desirable thermodynamic, kinetic, and chemical properties. Additionally, economic

considerations and the availability of these materials must be considered. The PCM selected for the design of thermal storage systems should possess the following desirable thermophysical, kinetic, and chemical properties. [9], [12], [13]

2.1.1 Thermal Properties

When selecting a PCM for a specific application, it is crucial to align the PCM's transition temperature with the operating temperature of the heating or cooling system. To minimize the size of the heat storage unit, the latent heat should be as high as possible, especially considering volumetric constraints. High thermal conductivity is also desirable to enhance the charging and discharging efficiency of the energy storage device. Thus, we can conclude as the PCM thermal properties as follow:

- Appropriate phase-transition temperature.
- High latent heat capacity.
- Efficient heat transfer.

2.1.2 Physical Properties

Following physical properties are some of the important parameters:

- Favorable phase equilibrium.
- Minimal volume change.
- High density.
- Low vapor pressure.

High density is preferred to allow for a more compact storage container and maintaining phase stability during freezing and melting aids in effective heat storage. To reduce containment issues, the PCM should exhibit low vapor pressure at operating temperatures and minimal volume changes during phase transitions.

2.1.3 Kinetic Properties

Following kinetic properties are important:

- Absence of supercooling.
- Adequate crystallization rate.

One of the main challenges in PCM development, particularly for salt hydrates, has been supercooling. Supercooling of any degree can hinder effective heat extraction

from storage, and it can be entirely prevented by maintaining supercooling between 5 and 10 °C.

2.1.4 Chemical Properties

PCM degradation can occur due to chemical decomposition, loss of hydration, or incompatibility with construction materials. For safety reasons, PCMs should be non-explosive, non-flammable, and non-toxic. Thus, desired chemical properties of PCMs:

- Long-term chemical stability.
- Compatibility with construction materials.
- Non-toxicity.
- Non-flammability

2.1.5 Economic Factors

The low cost and widespread availability of phase change materials are also crucial factors. Low-cost PCMs are preferred to help reduce costs in large-scale applications. Easy accessibility prevents potential disruptions in the supply chain and ensures a continuous supply of these materials.

2.2 Classification of PCMs

There are numerous phase change materials (eutectic, inorganic, and organic) available across a wide range of temperatures. The classification of a PCM is determined by the specific phase change that occurs within the operational temperature range.[14] Figure 2.3, redrawn from [14], shows the classification of PCMs. Various chemical materials, both organic and inorganic, can be categorized as PCMs based on their melting points and latent heats of fusion.

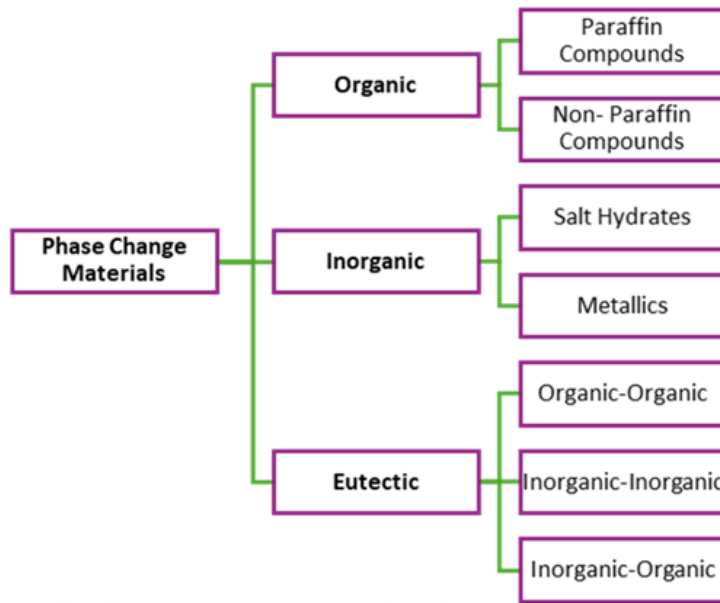


Figure 2.3 Classification of PCMs

Each group of PCMs—organic, inorganic, and eutectic—possesses distinct advantages and disadvantages, which are presented in Table 2.1.

Table 2.1 Comparison of organic, inorganic, and eutectics PCMs

Classification	Advantages	Disadvantages
Organics	1. Low or none undercooling 2. Chemical and thermal stability 3. High heat of fusion and no corrosives 4. Availability in a large temperature range 5. Good compatibility with other materials	1. Low thermal conductivity 2. Lower phase change enthalpy 3. Relatively large volume change 4. Inflammability
Inorganics	1. High thermal conductivity 2. Greater phase change enthalpy 3. Low volume change and cost	1. Undercooling and corrosion 2. Phase separation 3. Lack of thermal stability
Eutectics	1. High volumetric thermal storage density 2. Sharp melting temperature	1. Low thermal conductivity 2. Corrosion in high temperature

Figure 2.4 [14] offers a graphical representation of PCMs categorized by their melting and fusion temperatures. This figure indicates that paraffin wax, fatty acids,

salt hydrates, and eutectic mixtures possess low melting temperatures. In contrast, high melting temperatures are required for fluorides, carbonates, and chlorides. The specific properties and melting temperatures of these materials dictate their applications. For example, according to Zhou et al., considering their melting temperatures, paraffin, fatty acids, salt hydrates and eutectic mixtures are suitable PCMs for latent heat storage in building applications. [14]

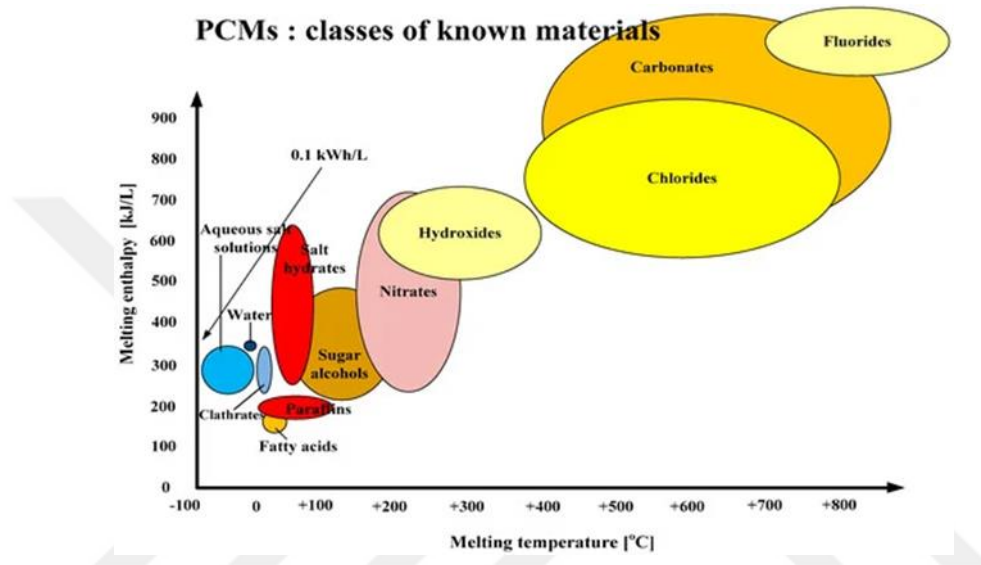


Figure 2.4 Categories of current PCMs

2.2.1 Organic PCMs

Organic compounds can be further categorized into paraffin and non-paraffin materials. Congruent melting, where materials melt and solidify repeatedly without phase separation and thus maintain their latent heat of fusion, and self-nucleation, where materials crystallize with minimal or no supercooling, are phenomena observed in organic materials. Additionally, these materials are generally non-corrosive.

2.2.1.1 Paraffins

Paraffin wax is extensively utilized in latent heat thermal energy storage (LHTES) systems owing to its high latent heat and favorable thermal properties. These include minimal supercooling, a broad range of phase change temperatures, low vapor pressure when melted, good thermal and chemical stability, and self-nucleating characteristics. Chemically, paraffin wax is a colorless or white,

somewhat translucent, hard substance composed of a mixture of solid straight-chain n-alkanes $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$. Its melting points range from approximately 48 °C to 66 °C (120 °F to 150 °F). Paraffin wax is primarily derived from petroleum through the dewaxing of light lubricating oil stocks. It finds applications in candles, wax paper, polishes, cosmetics, and electrical insulators. Additionally, it is used for extracting perfumes from flowers, forming bases for medical ointments, and providing waterproof coatings for wood. In the production of wood and paper matches, paraffin wax aids in ignition by offering an easily vaporized hydrocarbon fuel.

Commercial production of paraffin wax started in 1867, shortly after the first petroleum was established. The wax precipitates from petroleum upon chilling, and technological advancements have enhanced the efficiency and cost-effectiveness of its separation and filtration. Purification involves chemical treatments, decolorization using adsorbents, and the fractionation of waxes through distillation or recrystallization. The wax content varies significantly among crude oils. Post-World War II, synthetic paraffin wax was commercially introduced as a byproduct of the Fischer–Tropsch process, which converts coal gas into hydrocarbons. This synthetic wax, known for its snow-white appearance and higher hardness compared to petroleum paraffin, offers unique characteristics and high purity. It serves as a substitute for certain vegetable waxes and as a modifier for petroleum waxes and plastics such as polyethylene. [16]

Figure 2.5 illustrates the physical appearance and chemical structure of paraffin wax. Part (a) shows the typical solid white appearance of general paraffins. Part (b) depicts the common chemical structure of paraffin waxes. Finally, part (c) presents the chemical structure of a commercial paraffin wax sold under the CAS number 8002-74-2. [17-19]

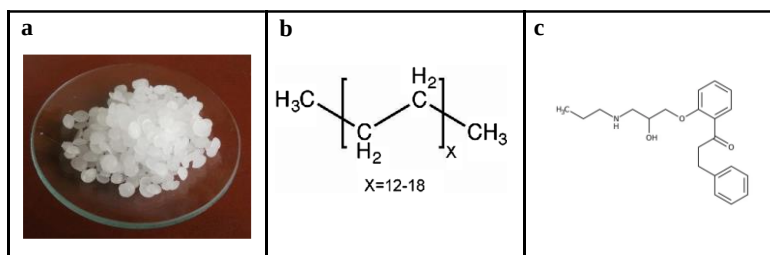


Figure 2.5 Physical appearance and chemical structure of paraffin wax a) typical solid white appearance of general paraffins b) chemical structure of paraffin waxes c) chemical structure of a commercial paraffin wax sold under the CAS number 8002-74-2

Paraffins used in LHTES systems typically exhibit very long freeze-melt cycles because they do not undergo phase segregation, maintain low vapor pressure when melt, and are chemically inert. Differential scanning calorimetry (DSC) has shown that the thermal performance of technical grade paraffin waxes remains unaffected by repeated heat cycling. [20] Table 2.2 presents the thermal properties of various technical grade paraffins, which are essentially mixtures of paraffins rather than fully refined oils. [12]

Table 2.2 Physical properties of some paraffin's

Paraffin	Distribution of C-Atoms	Freezing Point/Range (°C)	Heat of Fusion (kJ/kg)
5913*	C ₁₃ -C ₂₄	22-24	189
Octadecane	C ₁₈	28	244
6106*	C ₁₆ -C ₂₈	42-44	189
5838*	C ₂₀ -C ₃₃	48-50	189
6035*	C ₂₂ -C ₄₅	58-60	189
6403*	C ₂₃ -C ₄₅	62-64	189
6499*	C ₂₁ -C ₅₀	66-68	189

*Manufacturers of Technical Grade Paraffins 5913, 6106, 5838, 6035, 6403 and 6499: Ter Hell Paraffin, Hamburg, FRG

In addition to favorable properties such as congruent melting and good nucleation characteristics, paraffins exhibit several undesirable traits: (i) low thermal conductivity, around 0.2 W/(m·K), (ii) significant volume change during phase transition, (iii) incompatibility with plastic containers, and (iv) moderate flammability. [21], [22] Various solutions have been developed to mitigate the disadvantages of paraffin. Additives can be used to improve its thermal

conductivity, flexible containers can be employed to prevent significant volume changes during phase transitions, and encapsulation techniques can be explored. Controlled heating and cooling can prevent overheating and overcooling.

In this study, we utilized a paraffin-based PCM from Rubitherm with the code RT-28. RT-28 is a noncapsulated type PCM that employs the phase change processes between solid and liquid (melting and congealing) to store and release large quantities of thermal energy at nearly constant temperatures. General technical properties for the RT-28 are shown in the Table 2.3.

Table 2.3 The technical data for RT-28

Melting area	17-19 °C (main peak:18)
Congeaing area	19-17 °C (main peak:17)
Heat storage capacity $\pm 7.5\%$	260 kJ/kg
Density solid at 15 °C	0.88 kg/l
Density liquid at 25 °C	0.77 kg/l
Heat conductivity (both phases)	at 135 °C
Flash point	2 kJ/kg·K

2.2.1.2 Non- Paraffins

The most common type of phase transition material, characterized by a wide range of properties, is the non-paraffin organic substance. Unlike paraffin, which has highly similar properties, each non-paraffin material possesses unique characteristics. This makes them the largest group of potential phase change storage materials. This group includes numerous organic substances such as fatty acids, esters, alcohols, and glycols. The high heat of fusion values of fatty acids are like those of paraffin. Moreover, they freeze without undergoing supercooling and demonstrate consistent melting and freezing behavior. [24],[25] Therefore, they qualify as good PCMs. Their biggest disadvantage is their cost, which is 2-3 times more than technical grade paraffins. Especially carboxylic acid derivatives are corrosive substances. Table 2.4 shows a list of some fatty acids used in low-temperature latent heat thermal energy storage applications. As can be seen in the Table 2.4, the latent heat of polyethylene glycol 600 is 146 kJ/kg at 20-25 °C. In this thesis study, polyethylene glycol was used in the copolymer synthesis for

further usage microcapsules for parafilm. Thus, additive effect of polyethylene glycol and parafilm for latent heat thermal storage can be obtained.

Table 2.4 Melting point and latent heat of fusion for various fatty acids

Material	Formula	Melting Point (°C)	Latent Heat (kJ/kg)
Acetic acid	CH ₃ COOH	16.7	184
Polyethylene glycol 600	H(OC ₂ H ₂) _n OH	20-25	146
Capric acid	CH ₃ (CH ₂) ₈ COOH	36	152
Eladic acid	C ₈ H ₇ C ₉ H ₁₆ COOH	47	218
Lauric acid	CH ₃ (CH ₂) ₁₀ COOH	49	178
Pentadecanoic acid	CH ₃ (CH ₂) ₁₃ COOH	52.5	178
Tristearin	(C ₁₇ H ₃₅ COO)C ₃ H ₅	56	191
Myristic acid	CH ₃ (CH ₂) ₁₂ COOH	58	199
Palmitic acid	CH ₃ (CH ₂) ₁₄ COOH	55	163
Stearic acid	CH ₃ (CH ₂) ₁₆ COOH	69.4	199
Acetamide	CH ₃ CONH ₂	81	241
Methyl fumarate	(CHCO ₂ NH ₃) ₂	102	242

2.2.2 Inorganic PCMs

Inorganic PCM's are classified into salt hydrates and metallics. In general, they are non-flammable, inexpensive, and have a relatively high heat of fusion along with strong thermal conductivity. Nevertheless, most of them experience phase breakdown, supercooling, and corrosion to most metals. Hydrated salts are appealing for thermal energy storage because of their high storage density, approximately 240 kJ/kg, their relatively high thermal conductivity of around 0.5 W/(m·K), and their cost-effectiveness compared to paraffin waxes. [20]

Table 2.5 lists a few salt hydrates that melt between 0 and 120 °C along with their thermophysical characteristics. One of the most well-known materials is Glauber's salt (Na₂SO₄·10H₂O), which has a melting point at 32.4 °C and a high latent heat of 254 kJ/kg. It stands out as one of the most economical solutions for thermal energy storage. However, its use is limited due to issues with supercooling and phase segregation. Phase segregation refers to the inability of the material to achieve uniform mixing between its solid and liquid phases. In this case, the different phases cannot form a homogeneous mixture, which affects the phase change process of the salt hydrates used as PCM and reduces their energy storage efficiency. [21]

Additionally, maintaining the high storage density of hydrated salts during cycling is challenging. As hydrated salts melt, they form lower hydrates, making the process irreversible and leading to a reduction in storage capacity. Although metals such as copper, aluminum have high thermal conductivity, they are not currently popular among PCMs due to their higher densities and high melting temperatures.

Table 2.5 Thermophysical properties a of some salt hydrates

Material	Melting Point (°C)	Heat of Fusion (kJ/kg)	Specific Heat (kJ/kg.K)	Thermal Conductivity (W/m.K)
H ₂ O	0	333	2.09 (s) 4.18 (l)	2.2 (s) 0.6 (20 °C)
KF·4H ₂ O	18.5	231	1.84 (s) 2.39 (l)	-
CaCl ₂ ·6H ₂ O	29.7	171	1.45 (s)	-
Na ₂ SO ₄ ·10H ₂ O	32.4	254	1.93 (s)	0.544
Na ₂ HPO ₄ ·12H ₂ O	35.0	281	1.70 (s) 1.95 (l)	0.514 (32 °C) 0.476 (49 °C)
Zn (NO ₃) ₂ ·6H ₂ O	36.4	147	1.34 (s) 2.26 (l)	-
Na ₂ S ₂ O ₃ ·5H ₂ O	48.0	201	1.46 (s) 2.39 (l)	-
Ba (OH) ₂ ·8H ₂ O	78.0	267	1.17 (s)	-
MgCl ₂ ·6H ₂ O	116.0	165	1.72 (s) 2.82 (l)	-

2.2.3 Eutectic PCMs

A eutectic is a mixture of two or more components that has the lowest melting point. During crystallization, each component melts and freezes in a consistent manner, resulting in a combination of the individual component crystals. These mixes have an advantage in their high melting temperatures because they are designed to provide melting points. [14] These materials have great densities of volumetric storage as well. The existing deficiency in thermo-physical data for eutectic mixtures is a barrier. Greater comprehension of these characteristics will enable determination of the actual potential of eutectic mixtures. Salt-based PCMs are widely utilized in thermal energy storage applications, where continuous improvement is essential to meet diverse requirements. In the study conducted by Isamotu et al., four types of eutectic salt mixtures were synthesized and evaluated

for their melting points and thermal energy storage capabilities as shown in Table 2.6. [26]

Among these, the quaternary eutectic salt mixture ($\text{LiNO}_3 + \text{NH}_4\text{NO}_3 + \text{NaNO}_3 + \text{NaCl}$), with a melting point of 84.4°C and latent heat of 119 kJ/kg , exhibited the highest thermal energy storage capability due to its superior latent heat content compared to the others. Among the ternary eutectic salt mixtures, the mixture of $\text{LiNO}_3 + \text{NH}_4\text{NO}_3 + \text{KNO}_3$ demonstrated the best thermal energy storage capability with a melting point of 80.5°C and a latent heat of 114 kJ/kg . The study concludes that increasing the number of salts in the eutectic salt mixture improves its thermal energy storage capability. [26]

Table 2.6 Eutectic salt PCM and their thermal properties

Material	Composition	Melting Point ($^\circ\text{C}$)	Latent Heat (kJ/kg)
$\text{LiNO}_3 + \text{NH}_4\text{NO}_3 + \text{NaNO}_3$	2.5+6.5+1	79.5	112
$\text{LiNO}_3 + \text{NH}_4\text{NO}_3 + \text{HNO}_3$	1.77+3.9+1	80.5	114
$\text{LiNO}_3 + \text{NH}_4\text{NO}_3 + \text{NH}_4\text{Cl}$	5.4+13.6+1	81.4	109
$\text{LiNO}_3 + \text{NH}_4\text{NO}_3 + \text{NaNO}_3 + \text{NaCl}$	1.77+2.94+1+1	84.4	119

3

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Differential scanning calorimetry (DSC) examine how solid and semi-solid materials behave at different temperatures and help to calculate the heat capacity (C_p) of the material. Figure 3.1 shows a typical DSC analysis curve. As can be seen, this technique gives the following data: glass transition temperature (T_g), melting and crystallization enthalpies, melting point (T_m), crystallization point (T_c) and decomposition temperature (T_d). It is also possible to measure the specific heat capacity of a material.

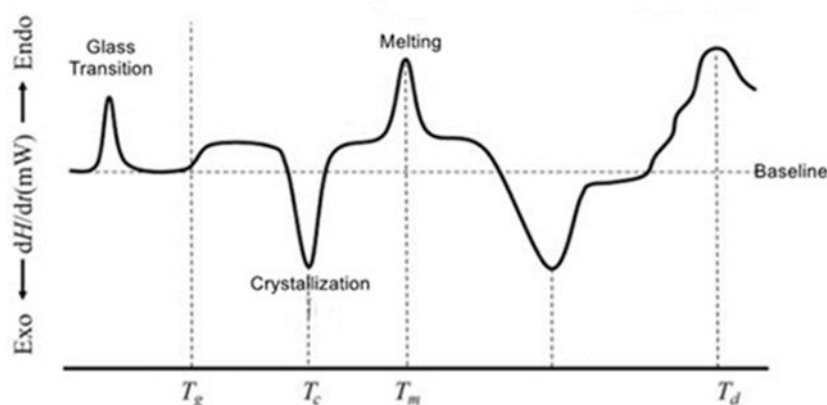


Figure 3.1 Typical DSC analysis curve

A variety of materials, including polymers, metals, pharmaceuticals, thin films, and proteins, can be characterized using data gathered from DSC analysis. Utilizing this technique can be useful in assessing the durability of various materials at elevated temperatures as well as figuring out the best temperatures for processing and storing heat-sensitive items. Determining contaminants that alter a material's thermal characteristics is another beneficial application of DSC. Figure 3.2 shows the inside of the DSC device schematically. The equipment used in DSC analysis consists of two melting crucibles: one is empty and serves as a reference, while the other contains the material to be examined (sample). The material for reference and the sample is heated or cooled steadily throughout the DSC analysis. Phase transitions

and enthalpies as a function of temperature or time are observed by heat flow monitoring.

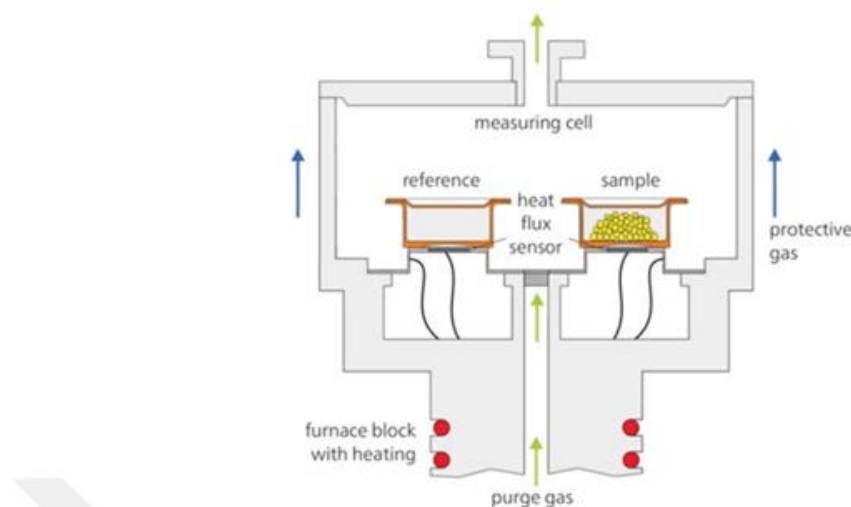


Figure 3.2 Schematic representation of the inside of the DSC device

A plot of heat flow vs temperature profile is called a thermogram. Reactions either release or absorb heat during a thermal process. The sample heating device is energized, and a positive signal is received when ΔH is positive (endothermic reaction); on the other hand, the reference heating device is energized, and a negative signal is acquired when ΔH is negative. The DSC peak regions are correlated with the sample amount and reaction heat. [29]

3.1 Thermal Characterization of PCM by DSC Techniques

DSC testing provides qualitative and quantitative information obtained during controlled heating or cooling of small samples of a substance. These tests include data such as phase transition temperature, enthalpy, and specific heat. There are typically two measurement modes used in DSC:

In the isothermal mode, the test cell is maintained at a constant temperature during the experiment. This method reduces temperature gradients within the sample, thereby improving measurement accuracy. However, solid-solid phase transitions cannot be observed in this mode.

Dynamic mode is the most used method. In this mode, the equipment subjects the sample to heating or cooling at constant rates. In both modes, the temperature development of the sample is compared with that of a reference sample, with

differential temperature sensors placed beneath each tray. Changes in heat flow over time and temperature are recorded. [30]

Due to the thermal resistance of the sample, the temperature difference between the reference and the sample is proportional to the heat flow. Therefore, the area under the heat flow curve is related to enthalpy and is commonly referred to as the shaded area shown in Figure 3.3. Thus, the following formula can be employed to calculate the enthalpy:

$$\Delta H = K \int_0^t \Delta T dt \quad (3.1)$$

K = Constant

ΔT = Temperature difference between reference and sample

t = testing time

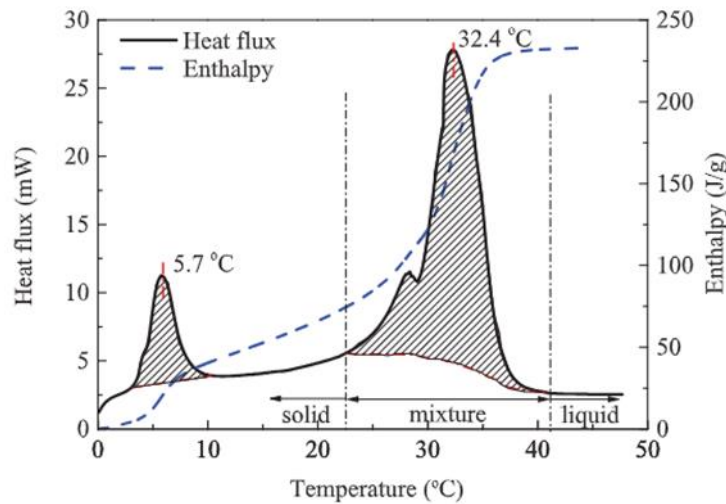


Figure 3.3 DSC test curves illustrating the temperature-dependent relationship between enthalpy and heat flux

DSC is a commonly employed standard technique for the thermal analysis of PCMs. [31] Velmurugan et al. determined the latent heat of fusion and melting point of paraffin wax using the DSC analysis method. For DSC analysis a 5.4 mg sample of the paraffin wax was placed in an aluminum sample holder and heated at a rate of 5 K/min with nitrogen used as the working fluid. Figure 3.4 shows the result of this DSC analysis. [32]

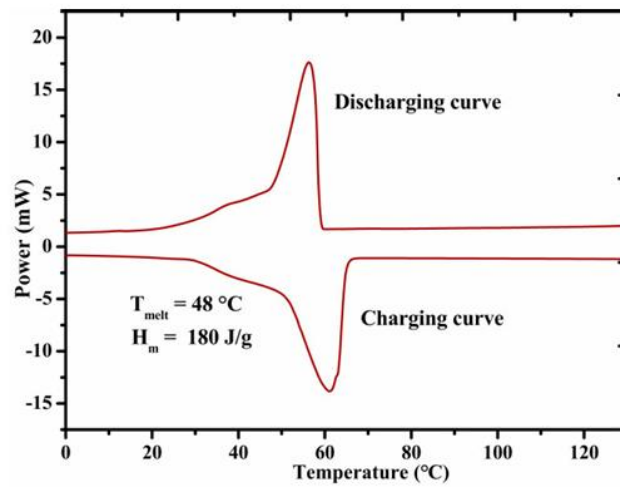


Figure 3.4 Characterization of paraffin wax with DSC

It was observed that melting point of the paraffin wax was $48\text{ }^{\circ}\text{C}$, the latent heat of fusion was 180 J/g , and the thermal conductivity was $0.2\text{ W/m}\cdot\text{K}$.

Chinnasamy and Appukuttan [33] prepared a binary eutectic mixture of lauric acid (40%) and myristyl alcohol (60%) and examined its thermal properties.

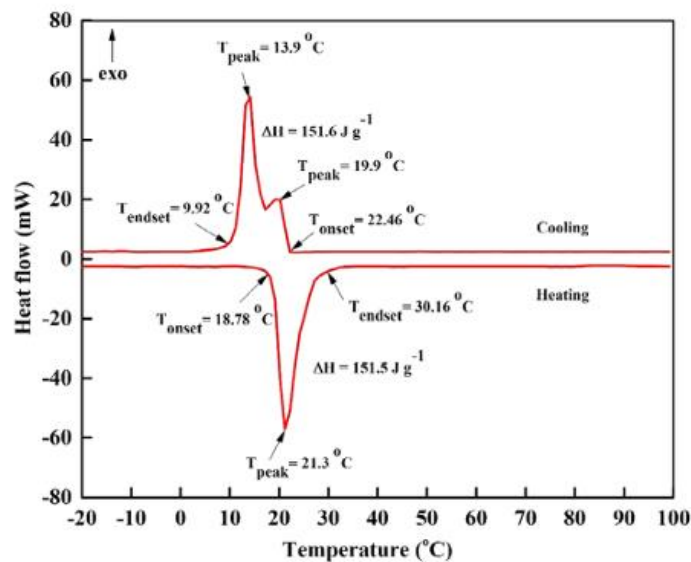


Figure 3.5 DSC analysis of lauric acid and myristyl alcohol binary eutectic mixtures

Figure 3.5 indicated that the PCM has a melting temperature of $21.3\text{ }^{\circ}\text{C}$ and a latent heat of 151.5 kJ/kg . The freezing temperature and latent heat were found to be $19.9\text{ }^{\circ}\text{C}$ and 151.6 kJ/kg , respectively. Additionally, the thermal stability and changes in

thermophysical properties of the prepared eutectic mixture over repeated thermal cycles were determined using again DSC analysis. From the DSC analysis results provided in Figure 3.6, it was observed that the prepared eutectic PCM maintained its thermal stability and thermal properties without change for up to 1000 thermal cycles.

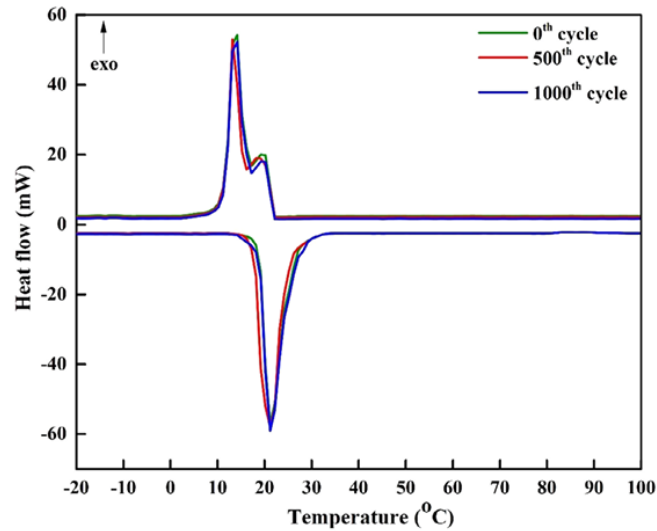


Figure 3.6 For eutectic PCM at 0,500, and 1000 thermal cycles DSC curves

The consistent and reliable measurement of the thermo-physical properties of PCM is crucial for the system layout of thermal energy storage and consequently for the selection of materials.

Müller and colleagues presented a potential evaluation of the maximum operating temperature in their study due to the absence of any method proposed by existing standards in the literature specifically for analyzing the properties of PCMs. They introduced a measurement method applicable to PCMs with melting temperatures ranging from -50 to 190 °C. For the DSC measurement, some preliminary preparations were done in the study. [34] The DSC was turned on approximately one hour before the measurement to allow the furnace to reach thermal equilibrium. Nitrogen gas was used, and calibration was performed using indium. The purge gas flow was set to 20 mL min⁻¹, and the protective gas flow was always maintained 10 mL min⁻¹ higher to prevent sample vapors from entering the internal parts of the DSC. Crucibles should be compatible with the measured PCM aluminum crucibles are used most frequently. For liquid samples, care should be taken to ensure homogenization, and the sample should be mixed if necessary. The bottom of the

crucible should be completely covered to ensure proper heat transfer. Typically, a sample volume of 5 μ are used for liquids, while 5-10 mg are used for solids. Additionally, thermal changes or contamination of the sample should be prevented during the preparation process. The temperature programming can be conducted over several cycles at two different heating or cooling rates. The fast-heating rate can be set to 10 K per minute, while the slow heating rate can be set to 2 K per minute. The first cycle is performed to erase the thermal history of the sample, followed by six additional thermal cycles. For accurate statistical measurement, each PCM was measured three times, and the integrity of the crucible is verified by weighing it. To confirm the accuracy of the method by comparing it with data available in the literature. For example, the data for paraffin 18-97 (octadecane) were compared with the values obtained from round robin tests specified in the literature. In the measurement protocol presented here, the coefficient of variation (CV) for enthalpy and initial temperature during an experiment ranged from 0.02 % to 0.12 % and from 0.06 % to 0.38 %, respectively. This indicates the high precision of the protocol. Additionally, different laboratories using various devices conducted repeated round robin tests, further demonstrating the accuracy of the presented protocol. According to results, the proposed DSC analysis protocol provides highly accurate and consistent results for PCMs. This protocol introduces a standard for DSC analysis, which plays a crucial role in PCM characterization and will serve as a reference for future research.

To sum up DSC analysis is frequently used in examining the thermal properties of PCMs due to its quick and easy procedure.

PCMs can absorb or release energy by changing phase (solid to liquid or liquid to solid) within certain temperature ranges. These features enable PCMs to be used in energy storage and thermal management applications. The direct use of PCM in its liquid form can result in leakage during melting, environmental reactivity, and increased phase change volume. [35] Therefore, microencapsulation technology is highly important for PCMs. With the microencapsulation technique, these disadvantages of PCMs can be mitigated. Additionally, it significantly addresses application issues, as the encapsulation process facilitates the incorporation of PCM material into a wide range of applications such as fibers, fabrics, coatings, physiotherapy devices, insulation panels, and walls. Encapsulation with a physically and chemically suitable shell ensures that PCM microcapsules maintain their structural integrity during end-use and production processes, while also providing enhanced thermal properties and mechanical strength. [36] Currently, there have been many developments on organic PCMs [37] such as paraffin [38], polyethylene glycol [39] and palmitic acid [40] due to their high latent heat capacities, non-polluting and recyclability. However, organic PCMs also have disadvantages such as low heat conduction capacity, easy leakage and flammability as discussed in Chapter 2.

4.1 Literature Survey

Various thermal conductivity enhancing substances can be added to PCMs to increase their limited thermal conductivity. [41] Generally, metals and their oxides, carbon-based substances [42] and other substances such as silica [43], [44] and boron nitride [45] are used as fillers to increase conductivity. When Wang et al. employed paraffin/aluminum foam PCMs to prevent Li-ion batteries from overheating, they discovered that the rate of heat absorption increased by almost 25%. [46] Xiao et al. reported that copper and nickel foams with various porosities and pore sizes were impregnated with pure paraffin using vacuum assistance (Figure 4.1). A steady-state test system, which considered the thermal contact

resistance between the specimen and adjacent surfaces, was established to measure the effective thermal conductivities of the composite PCMs. The results indicated that the thermal conductivities measured using the steady-state method were consistent with theoretical predictions and that the thermal conductivities of the composite PCMs were notably improved. Specifically, the thermal conductivities of the paraffin/copper foam composite PCMs fabricated with copper foams having porosities of 96.95%, 92.31%, 88.89%, and a pore size of 25 Pores Per Inch (PPI) were approximately 13, 31, and 44 times greater than that of pure paraffin, respectively. [47]

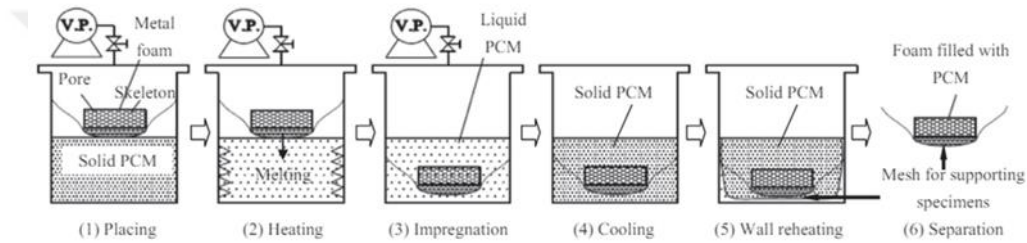


Figure 4.1 Process of vacuum impregnation used in the preparation of composite PCMs

Also, numerous studies have demonstrated that incorporating a thermal network within PCMs can substantially enhance their thermal conductivity. While these techniques can effectively increase the thermal conductivity of various organic PCMs, the latent heat tends to decrease with an increase in filler content. Additionally, molten organic PCMs are susceptible to leakage, which is a significant factor contributing to heat loss. Therefore, the most effective method to reduce PCM leakage at high temperatures is microencapsulation.

A new encapsulated phase change material (EPCM) consisting of a silica shell derived from sodium silicate and a paraffin wax core was prepared using an in-situ dehydration and condensation reaction. [48] DSC, TGA, and leakage tests demonstrated that the EPCMs exhibit low supercooling, excellent thermal stability, and leak-proof performance. The performance of the capsule was evaluated over 50 thermal cycles, DSC results (see Figure 4.2) showed that the enthalpies of melting were 94.32 J/g in the first cycle and 93.95 J/g in the 50th cycle, and the enthalpies of crystallization were 93.18 J/g in the first cycle and 92.82 J/g in the 50th cycle,

indicating only a 0.39 % decrease between the two enthalpies. Moreover, after 50 heating-cooling cycles, the melting and crystallization peaks remained at the same positions, indicating thermal stability. Silica shell-paraffin wax core demonstrated high thermal reliability and confirmed the potential of EPCMs for reliable and long-term applications due to stable melting and crystallization enthalpies.

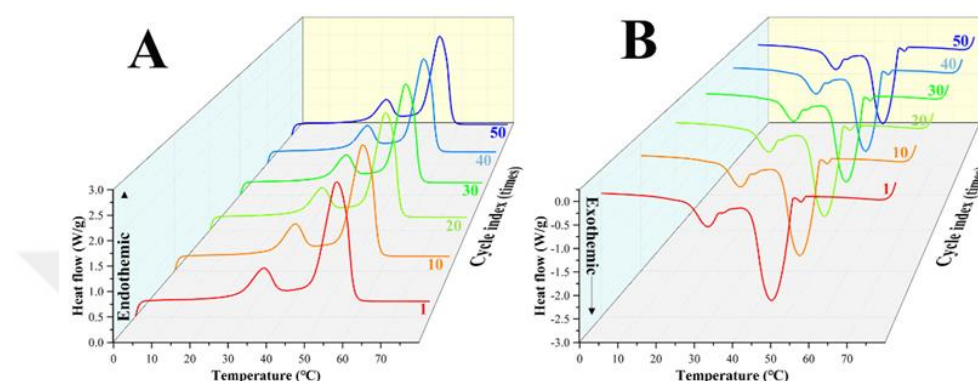


Figure 4.2 Dsc analysis of PS-5 during 50 cycles

Chaiyasat and colleagues prepared poly(divinylbenzene) (PDVB) microencapsulated octadecane (OD) (PDVB/OD) using phase inversion emulsification (PIE) for use as a heat storage material. Figure 4.3 schematically illustrates the synthesis stages. [49] Polyvinyl alcohol and sodium dodecyl sulfate were used as the surfactant and cosurfactant, respectively, in the PIE process, resulting in capsules with approximately 1.5 mm size, a narrow particle size distribution, and good colloidal stability throughout the polymerization. The thermal properties and stability of PDVB/OD microcapsules were determined using DSC and thermogravimetric analysis. From DSC analysis, it was observed that the onset melting temperature (T_m) of encapsulated OD (22.6 °C) was slightly lower than bulk OD (28.7 °C), and there was a significant difference in crystallization temperature (T_c) (12.4°C and 26.3°C for encapsulated and bulk OD, respectively). The melting latent heat (H_m , 192 J/g-OD) and crystallization latent heat (H_c , 195 J/g-OD) of encapsulated OD were found to be quite close to those of bulk OD (215 J/g and 220 J/g, respectively). This study demonstrates the potential application of PDVB/OD microcapsules in heat storage applications.

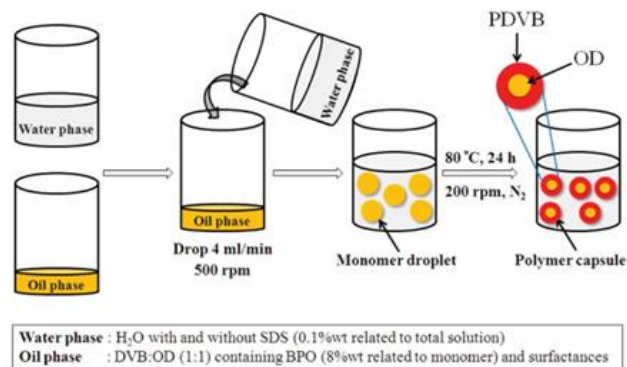


Figure 4.3 Process for preparing PDVB/OD microcapsules

Sanchez et al. developed cheap and technically applicable method, for the encapsulation of PCMs. Different types of PCMs (paraffin wax PRS[®], tetradecane, Rubitherm[®] RT27, Rubitherm[®] 20, nonadecane) were encapsulated in polystyrene shells by this method based on suspension polymerization. [50] The procedure and reaction conditions used for obtaining the microcapsules containing paraffin are given in Table 4.1. However, this method is a more suitable method for non-polar PCMs, but it is not successful in encapsulating polar PCMs. Thermal properties, morphology and particle size distribution of the obtained capsules were examined. It was observed that almost 50% by weight of the prepared microcapsules consisted of PCM. The results obtained from this study showed that encapsulated paraffin wax had a better performance in terms of energy storage.

Table 4.1 The procedure and reaction conditions used for obtaining microcapsules containing paraffin

	Ingredients	Measure
Discontinuous phase (g)	Polyvinylpyrrolidone (PVP)	3.77
	Water (mili-Q)	377.40
Continuous phase (g)	Benzoyl Peroxide (PBO)	1.26
	Styrene (St)	78.40
	PRS [®] paraffin wax	27.04
Reaction temperature (°C)		110
Stirring rate (rpm)		900
Reaction time (h)		6

Maharaj and colleagues focused on microencapsulating phase change material n-tetradecane (C-14) using poly (methyl methacrylate-co-methacrylic acid) as the shell material via oil-in-water emulsion polymerization technique. [35] They varied

the crosslinking agent from 3 % to 20 %, the core-to-shell ratio from 1:1 to 2:1, and the initiator amount from 1 % to 3 % to enhance the latent heat storage properties of the microcapsules. The average particle size of the microcapsules ranged from 0.1 to 1.5 μm . Results showed that using 20 % w/w crosslinker yielded microcapsules with a higher melting enthalpy of 127.3 ± 0.06 J/g and a microencapsulation efficiency of 66.72 %. The thermal stability of the PCM was improved by 30 ± 2 °C through encapsulation.

The shell material of encapsulated PCMs does not always consist of substances with phase change properties. This results in the enthalpy change during the phase transition processes of encapsulated PCMs being lower compared to that of pure PCMs. To address this, Wang and colleagues encapsulated stearic acid PCM with PEG in their study. This PEG-based shell is a solid-solid PCM with a cross-linked structure, which prevents the encapsulated PCM from leaking even at 80 °C. [51] The enthalpy values of the microencapsulated PCM obtained were recorded as 113.4 J/g for solidification and 115.3 J/g for melting, respectively. This indicates that it is an excellent candidate for thermal energy storage. Additionally, as seen in the DSC results in Figure 4.4, the obtained microcapsule exhibited dual temperature ranges during the phase transition, providing a wide and effective temperature range and demonstrating better thermal stability than pure stearic acid. Furthermore, the study found that the thermal property changed very little even after 100 thermal cycles. [52]

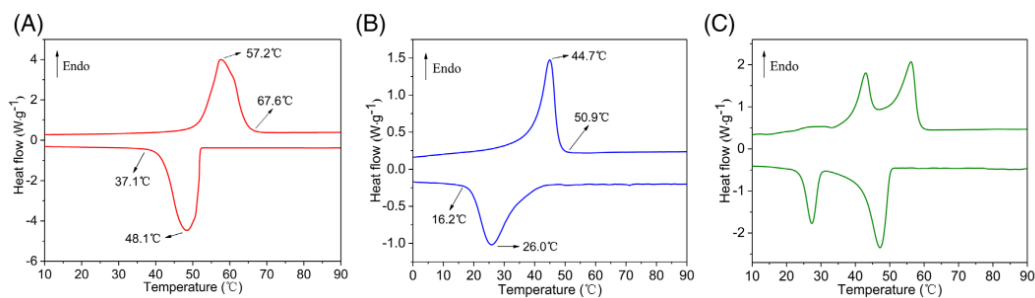


Figure 4.4 DSC analysis of A) stearic acid B) capsule material C) encapsulated stearic acid

A review of the literature reveals that encapsulation studies of PCMs are also conducted with double-shell structures. For example, the surface of the paraffin chosen as the core material was first coated with TEOS hydrolyzed silica and then with modified spherical silica as the second layer (Figure 4.5). The FTIR analysis results showed that the paraffin combined well with the inorganic shell material. The thermal analysis results indicated that the thermal conductivity increased by 133.33%, and the material maintained good impermeability at 65°C. [53]

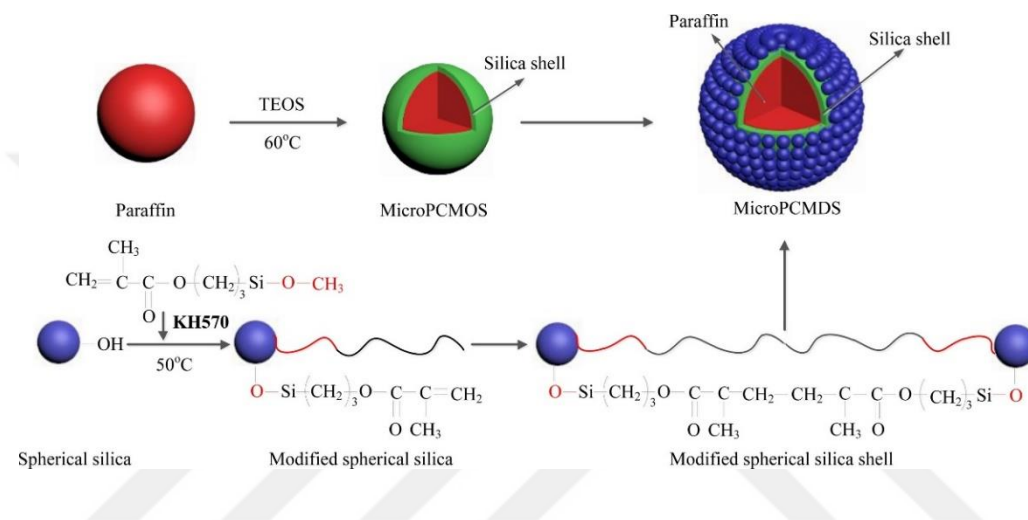


Figure 4.5 Schematic diagram of the formation of double silica coating PCM capsules

In another study depicted in Figure 4.6, a new phase change microcapsule type, copper-polyurea encapsulated, was synthesized for use in building materials to reduce energy consumption. Thermal analysis results indicated that the microcapsule's phase change temperature range was between 22.3 °C and 23.3 °C. As the amount of PCM interior material increased from 3 g to 9 g, the microcapsule's latent heat value also increased from 82.2 J/g to 139 J/g. Additionally, both types of encapsulated capsules remained stable over 250 thermal cycles. The use of these composite microcapsules in building materials enhances their thermal properties. Among additive amounts ranging from 5 % to 15 %, the composite containing 15 % microcapsules exhibits the highest performance, increasing the duration that the room temperature remains within the comfort range by 77.15 minutes. [54]

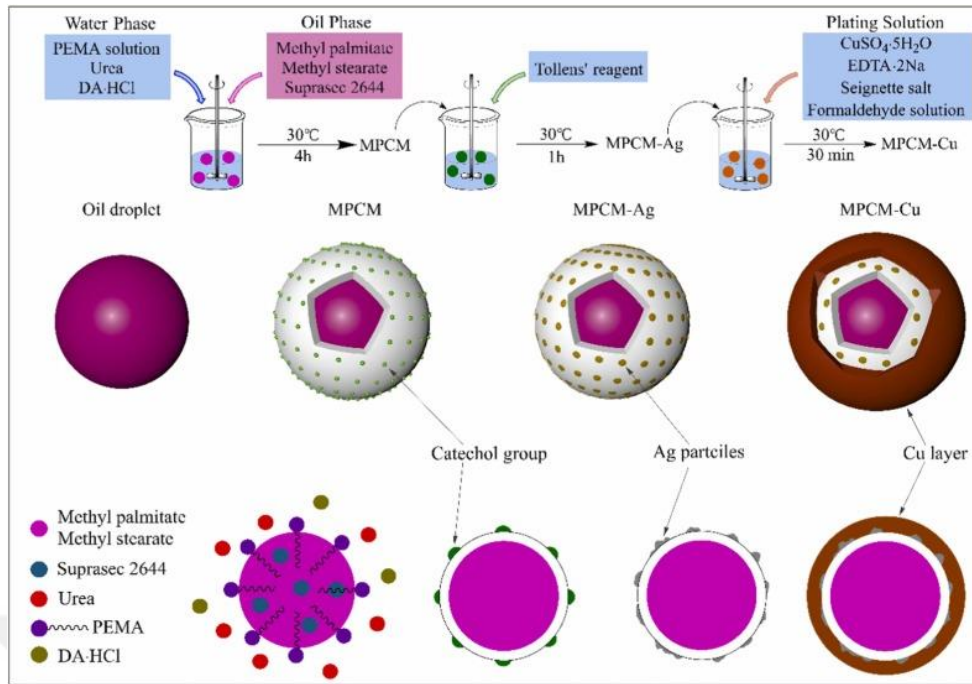


Figure 4.6 Schematic representation of the preparation of copper-polyurea composite microcapsule

As evidenced by various studies, different encapsulation materials and processes have proven highly successful in addressing the drawbacks associated with PCMs, such as leakage issues and improving thermal conductivity. These studies clearly demonstrate that encapsulated PCMs offer sustainability in thermal energy storage and possess significantly higher potential.

5

EXPERIMENTAL

5.1 Materials & Methods

5.1.1 Used Chemicals

Phase change material (RT-28) was provided from RUBITHERM®, methyl methacrylate (MMA), Polyethylene glycol diacrylate (PEGDA M_n :250 g/mol, 575 g/mol, 700 g/mol) were provided from Sigma Aldrich, Azobisisobutyronitrile (AIBN) was provided from Sigma Aldrich, Tetraethyl Orthosilicate (TEOS) was supplied by Şişecam Company Istanbul, Türkiye. Commercial Flexdub silicate solution was provided from Flexdub Company, Ankara Türkiye. Carboxymethyl Cellulose (CMC) 0,1 N HCl was provided from Sigma Aldrich, methanol (Merck, 99.8%), ethanol was used as received. Polypropylene (PP) powder with a melting temperature of 130-171 °C was supplied by MTN Plastic Company, Istanbul Türkiye.

5.1.2 Used Equipment and Device

FT-IR (Fourier Transform Infrared Spectroscopy) spectroscopy (Perkin-Elmer, FT-IR), Differential Scanning Calorimetry (NETZSCH DSC 3500) was employed to determine the thermal properties of the prepared capsules. The analysis was conducted in two cycles with temperature increases of 5 °C per minute, starting from -10 °C to 100 °C, or up to 140 °C or 150 °C. Low- Pressure Plasma Systems (Electronic Diener Plasma- Surface- Technology, Femto) was used to surface oxidation of microcapsule. Thermogravimetric analysis (Perkin-Elmer, Diamond TGA/DTA- Seiko Instruments SII, Exstar 6300 TG/DTA) was used to determine the thermal stabilities of prepared capsules. The samples were heated in the temperature range from 35 °C to 650-700 °C at a heating rate of 5 °C/min. Microinjection Device (Microlab Twin Screw- Rondol) was used for the injection of polypropylene composite materials. The first of the five zones of the device was set to 80 °C, the others were set to 180 °C, Transmission Electron Microscope TEM (Hitachi HighTech HT7700) was used for the microscopic structures and surface morphology of capsules. XPS (Thermo K-Alpha X-ray Photoelectron

Spectroscopy) was used for detecting the characteristic electrons on the surface of capsules.

5.2 Recrystallization of AIBN

Recrystallization of AIBN was conducted as follow: 5 g AIBN and 100 ml methanol are mixed in an erlenmeyer flask by heating at 45-48 °C for 6 hours. Then, the liquid is filtered with filter paper and solution was cooled to room temperature and left overnight at -18 °C. and crystals were formed. These crystals were then filtered with filter paper, washed several times with cold methanol and dried in vacuum.

5.3 Preparation of MMA-PEG Based Core Shells Filled With PCM

MMA-PEG based copolymer capsules filled with PCM were obtained in a completely closed system using methyl metacrylate and PEGDAs monomers with three different molecular weights (M_n : 250 g/mol, 575 g/mol, 700 g/mol).

5.3.1 Synthesis of (PMMA-PEGDA₅₇₅-PCM)

In a typical example, 0.075g AIBN, 0.5g PEGDA (M_n :575 g/mol) and 2g MMA were placed in a beaker and mixed under nitrogen gas at room temperature for 30 minutes. Then, 1 g RT-28 and 10 g distilled water were added to the reaction medium and mixed under nitrogen gas in an 85 °C oil bath for 5 hours. At the end of the reaction, a white solid product was formed at the bottom of the beaker. The mixture was then brought to room temperature and transferred into 1-liter distilled water. Polymer precipitate was filtered with a glass gooch crucible and after washing several times with water and dried at under vacuum. The yield of the resulting product was calculated as 60%.

5.3.2 Synthesis of (PMMA-PEGDA₂₅₀-PCM) and (PMMA-PEGDA₇₀₀-PCM)

Core shell study using PEGDA M_n = 250 g/mol and PEGDA M_n = 700 g/mol was carried out in a similar procedure. The obtained materials are called as PMMA-PEGDA₂₅₀-PCM and PMMA-PEGDA₇₀₀-PCM.

5.4 Preparation of MMA-PEG Based Core Shells Without PCM (PMMA-PEGDA₅₇₅)

The same system, methods and materials were used to prepare PMMA-PEGDA₅₇₅ based core shells without PCM. However, at the end of the reaction, the products were washed with ethanol (2x20 ml) instead of distilled water. After drying under vacuum, white solid products were obtained in approximately 60% yield.

5.5 Double Layer Coating of the Surface of MMA-PEG Based Core Shells Filled With PCM

The secondary encapsulation studies (PMMA-PEGDA₅₇₅-PCM) were continued on the core-shell sample. Initially, to achieve a homogeneous coating on the surface of the core-shell, it was ground into a powder using a mortar. For the secondary coating of the core-shell, two different methods were employed. In the first method, the polymeric surface was coated with CMC, silica and a commercial silicate solution called Flexdub without any prior treatment. In the second method, the surface was modified using a plasma treatment device, and the capsules were coated with CMC, silica, and a commercial silicate solution called Flexdub.

5.5.1 Surface Coating Without Plasma Treatment

5.5.1.1 Coating the Surface of the Core Shell With CMC (CMC-(PMMA-PEGDA₅₇₅-PCM))

1 g of PMMA-PEGDA core shell powder encapsulated PCM was added to 100 ml of 1 % CMC solution and stirred at room temperature for 5 hours. Then, residual CMC was separated by centrifugation, remaining powder was washed with distilled water several times, and dried under vacuum.

5.5.1.2 Coating the Surface of the Core Shell With Silica (Silica-(PMMA-PEGDA₅₇₅-PCM))

The surface of the PMMA-PEGDA core shell powder encapsulated PCM was covered with silica core according to the procedure reported by Li et al. [55] TEOS, 0.1 N HCl solution was prepared at a ratio of 3:1(v/v). The solution was stirred at room temperature until it turned from cloudy to clear. 30 ml of this prepared solution was mixed with 0.5 g of powdered core shell at room temperature

overnight. Then, the liquid part was discarded by centrifugation and the solid was placed in a petri dish and kept in the oven at 100 °C for 2 hours.

5.5.1.3 Coating the Surface of The Core Shell With Commercial Silica Solution Flexdub (Flex-(PMMA-PEGDA₅₇₅-PCM))

0.13 g of PMMA-PEGDA core shell powder encapsulated PCM was added to a mixture of 9 ml Flexdub and 1 ml of distilled water and stirred overnight at room temperature. Then, residual Flexdub solution was separated by centrifugation and washed with distilled water several times. After that product was dried with lyophilizer.

5.5.2 Surface Coating After Plasma Treatment

During the plasma treatment, the chamber pressure was reduced to 0.2 mbar, and the surface of the capsules was modified using oxygen plasma generated at 30 W for 60 seconds.

5.5.2.1 Coating the Surface of the Core Shell With CMC (PT-CMC-(PMMA-PEGDA₅₇₅-PCM))

0.25 g of modified PCM capsules powder was added to 25 ml 2 % CMC solution and stirred at room temperature for overnight. Then, CMC was separated by centrifugation, washed with distilled water several times, and dried with lyophilizer.

5.5.2.2 Coating the Surface of the Core Shell With Silica (PT-Silica-(PMMA-PEGDA₅₇₅-PCM))

According to the literature [55] TEOS, 0.1 N HCl solution was prepared at a ratio of 3:1 (v/v). The solution was stirred at room temperature until it turned from cloudy to clear. 20 ml of this prepared solution was mixed with 0.25 g of modified PCM capsules powder at room temperature overnight. Then, the liquid part was discarded by centrifugation, washed with distilled water and the solid was placed in a petri dish and kept in the oven at 100 °C for 1.5 hours.

5.5.2.3 Coating the Surface of the Core Shell with Commercial Silica Solution Flexdub (PT-Flex-(PMMA-PEGDA₅₇₅-PCM))

0.25 g of modified PCM capsules powder was added to a mixture of 18 ml Flexdub and 2 ml of distilled water and stirred overnight at room temperature. Then, residual

Flexdub solution was separated by centrifugation and washed with distilled water several times. After that product was dried with lyophilizer.

5.6 Preparation of Polypropylene Composites Possesing CMC-(PMMA-PEGDA₅₇₅-PCM) and Silica-(PMMA-PEGDA₅₇₅-PCM)

1 g double layer coated (coated with CMC or silica) PMMA-PEGDA₅₇₅-PCM capsules CMC and silica-coated capsules were mixed by hand with 5 grams of powdered PP (obtained from the MTN Plastic company, Istanbul, Türkiye) to achieve a 20 % by weight mixture, and then injected using a microinjection device. In this twin-screw microinjection device, the initial temperature of the first zone was set to 80 °C, while the other zones were maintained at 180 °C. The screw rotation speed was set to 15 rpm, and the injection process was carried out.

RESULTS AND DISCUSSIONS

Leakage issues encountered by PCMs during phase transitions limit their operational efficiency. However, various polymer materials have been identified as effective solutions to mitigate these leakage problems in phase change energy storage systems. A wide range of polymers with diverse structures and properties have been researched for energy storage applications. Significant research have been conducted to enhance the stability of PCM-based materials during use. One of the methods employed to address these issues is encapsulation technology. In this study, while PMMA and PEGDA copolymers were synthesized in situ, the paraffin-based PCM material RT-28 was added as a dispersion, and simultaneous encapsulation was achieved in the polymerization environment. Meanwhile, PEG is reported in literature as a PCM and exhibits heat storage properties, as noted by Liu et al. and Yang et al. [56], [57] Our aim was to achieve a synergistic effect by encapsulating PCM using both paraffin and PEG units, as illustrated in Fig. 6.1. In the second part of the study, we aimed to improve the stability of the PCM-coated capsules using a double-layer coating method. This approach included applying (i) silica coating via the TEOS route, (ii) coating with CMC, and (iii) utilizing Flexdub, a commercial silicate solution, as the coating material. In addition to encapsulation studies, the behavior of double layer capsules in an extruder line was investigated by incorporating certain proportions of coated PCMs into a polypropylene matrix, and the phase change properties were examined. Characterization studies of both the single-layer and double-layer capsules were conducted, and their thermal properties were examined. The chemical structures of polymer-based microcapsules were analyzed using FTIR, thermal behaviors were assessed with TGA and DSC, surface morphology and microscopic structures were investigated using TEM and surface elemental analysis was performed by using XPS.

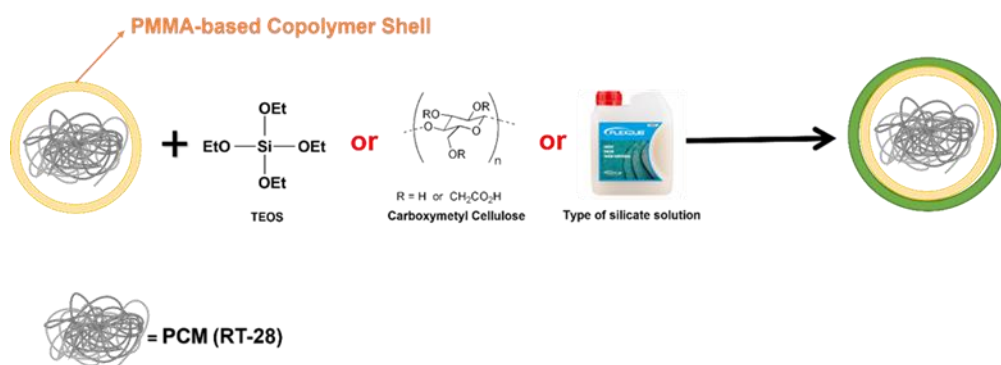


Figure 6.1 Schematic representation of the production of two-layer PMMA-PEG based PCM filled capsules

6.1 Encapsulation of PCM in PMMA-PEG core shell

6.1.1 Synthesis and Characterization of PMMA-PEG based core shells filled with PCM

For the first layer encapsulation studies of the paraffin-based phase change material RT-28, PMMA-PEG-based copolymer shells were obtained using suspension polymerization techniques using AIBN as a free radical initiator, as depicted in Figure 6.2, which outlines the chemical reaction mechanism.

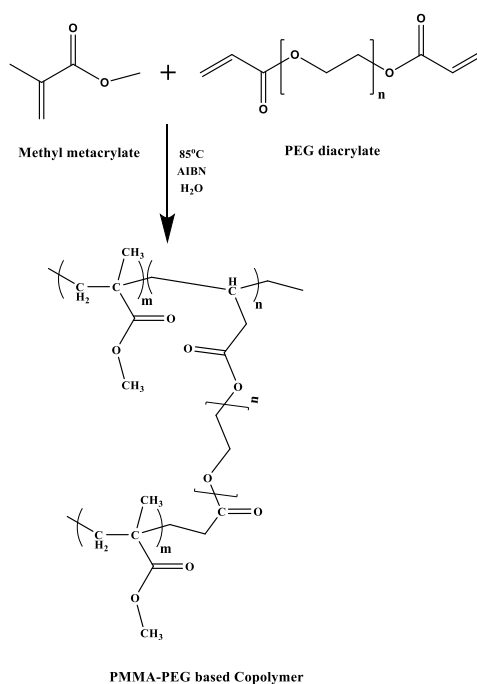


Figure 6.2 Reaction mechanism of PMMA-PEGDA based copolymer

During the reaction, PEG diacrylate monomers (PEGDA M_n = 250, 575, 700 g/mol) with different molecular weights were used in for the copolymerization synthesis. The experiments were conducted in a completely closed reaction system under a nitrogen atmosphere. However, over time, the stability of this system could not be maintained, and it was observed that the beaker's lid was opened during the reaction due to evolution of gaseous products, allowing air to enter the system. Additionally, temperatures 60 °C and 70 °C were tested; however, due to the thermal decomposition kinetics of AIBN, effective polymerization conversion was not achieved at these temperatures. Therefore, the polymerization reactions were conducted at 85 °C.

Since the cross-linked polymer precipitated during polymerization, the purification process involved filtration. Due to the cross-linked nature of the capsule, polymer matrix was insoluble in any solvent. FTIR analysis was conducted for characterization. Here, FTIR analysis for PMMA-PEGDA₅₇₅-PCM is given as a typical example (Figure 6.3).

DSC analysis further confirmed the presence of PCM within the capsule. However, it can be asked that PCM might not be present in the polymer core but could adsorb onto the surface of the copolymer shell. To confirm this situation, a modeling study was carried out where PCM was ground with empty copolymer (PMMA-PEGDA₅₇₅) and subsequently analyzed using FTIR. The characteristic stretching peaks of PCM were observed in the FTIR spectrum that indicate PCM on the surface. In spite of that, RT-28 present in the polymer capsules (as proven in DSC analysis) did not show the specific FTIR peaks at 2900 cm^{-1} , C-H stretching at 1470 cm^{-1} , and 716 cm^{-1} (see Figure 6.3). When comparing the FTIR spectra of the empty and the capsule filled with PCM, no peaks corresponding to PCM were detected. The reason for this PCM is trapped in the polymer core and laser do not penetrate inside the core efficiently and thus characteristic stretching bands do not appear in the FTIR spectrum.

Encapsulated RT-28 in PMMA-PEGDA based copolymer matrix exhibited peaks at 1724 cm^{-1} [58], corresponding to the carbonyl group stretching specific to PEGDA and MMA, at 2950 cm^{-1} [59] corresponding to the C-H bond of MMA and located around at 1095 cm^{-1} corresponding to the -C-O-C stretching of PEGDA [60]. Additionally, the disappearance of the peak at 1633 cm^{-1} , which corresponds

to the C=C double bond, indicates that MMA and PEGDA have reacted to form a copolymer, and no residual monomers remained in the copolymer matrix. To conclude FTIR data confirm that the encapsulation process has been successful and there is no chemical interaction between PCM and the PMMA-based copolymer shell, non-adsorbing PCM onto the polymer matrix and indicating only physical encapsulation in the copolymer core.

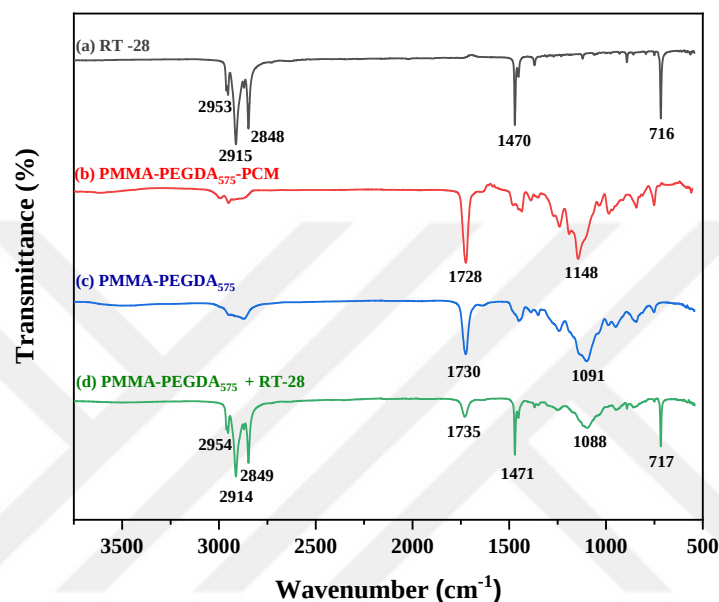


Figure 6.3 FTIR spectrum of **a)** RT-28, **b)** PMMA-PEGDA₅₇₅-PCM, **c)** PMMA-PEGDA₅₇₅ and **d)** RT-28 dripped over PMMA-PEGDA₅₇₅

The successful synthesis of encapsulated RT-28 in PMMA-PEGDA based copolymer shell material is based on physically rather than chemically. When the resulting capsule was washed with ethanol and acetone, RT-28 was separated from the capsule and as a result, no transition was observed in the DSC analysis. Thus, we washed the polymer capsules with using water while using ordinary filtration.

6.1.1.1 Thermal Behavior of PMMA-PEG based core shells filled with PCM (PMMA-PEGDA₅₇₅-PCM)

DSC analysis was performed to confirm the encapsulation of the PCM and to assess potential leakage. Figure 6.4 shows the DSC analysis of pure RT-28 conducted within the temperature range of -10 °C to 140 °C. Clearly, the melting peak of RT-28 during the phase change is observed at point 31.6 °C, and the crystallization peak is observed at point 22.05 °C. RT-28 is a type of paraffin used as a PCM. It has a

high energy storage capacity of approximately 250 kJ/kg. The melting temperature range is between -9 °C and 100 °C, making it suitable for various applications. RT-28 remains stable over long periods during thermal cycling and is chemically inert, exhibiting no supercooling effect.

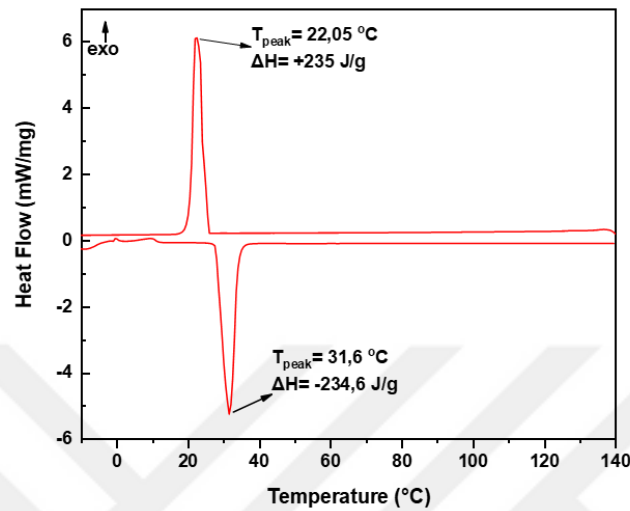


Figure 6.4 The DSC curve of RT-28

The DSC analysis for RT-28 filled capsules was conducted within the temperature range of -10 °C to 100 °C, with temperature increments of 5 °C, over two cycles. Figure 6.5 illustrates the DSC results of microcapsules filled with RT-28. Noteworthy, the presence of the melting peak of RT-28 around 29 °C in the second cycle, like the first cycle suggest that RT-28 remains within the capsules without leaking. Additionally, the enthalpy values for the peak areas were calculated from the DSC results. For the first heating and cooling cycles, the enthalpy values were -82.6 and +93.8 J/g, respectively, while for the second heating and cooling cycles, they were -83.9 and +93.5 J/g, respectively. When compared to the enthalpy value of 260 J/g for uncapsulated RT-28, it is evident that the encapsulation process was successful, however a dramatic decrease in enthalpy value (from 260 J/g to 93.8 J/g) was observed due to the encapsulation efficiency (quantity of PCM material in the core) and polymer matrix might prevent the efficient heat transfer to the core PCM.

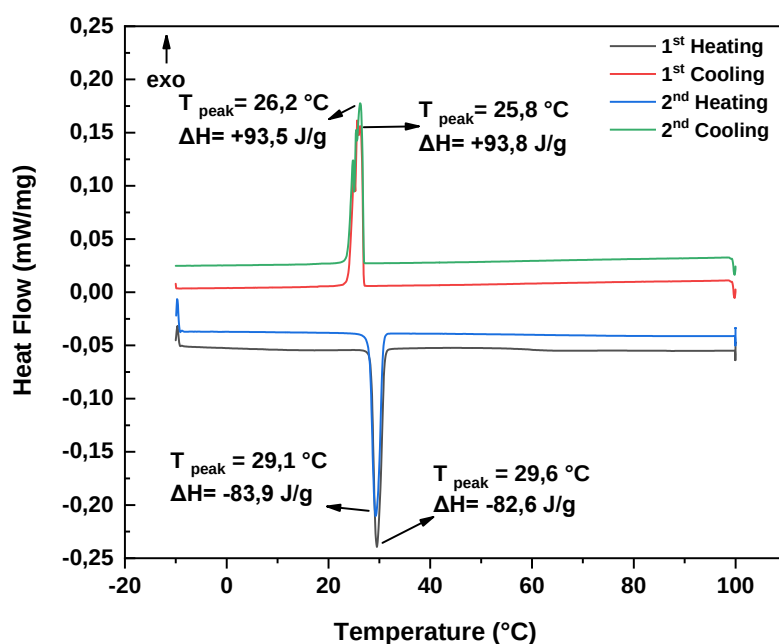


Figure 6.5 DSC analysis of PMMA-PEGDA₅₇₅-PCM

During the DSC analysis, when the temperature was reached 200°C, the integrity of the shell was compromised and result in the release of the PCM from the matrix. The melting and crystallization peaks of RT-28 was not clearly distinguishable. This observation indicates that the microcapsules lost their stability temperatures exceeding 100 °C and failed its thermal storage properties.

To assess the thermal stability and leakage resistance of PMMA-PEGDA₅₇₅-PCM at temperatures below 100 °C, a cyclic heating-cooling protocol was employed. Samples were subjected to repeated heating to 80 °C for 5 minutes in an oven, followed by cooling to room temperature, over a total of 50 cycles. Subsequently, the samples were analyzed using DSC within the temperature range of -10 °C to 100 °C, and the results are presented in Figure 6.6.

A distinct melting point peak of RT-28 was observed at 29.5 °C. This observation highlights the integrity of RT-28 within the capsules, demonstrating its sustained containment without leakage during the phase transition. Additionally, two endothermic peaks were observed during the cooling process in the DSC at 21.6 °C and 25.3 °C. The polymer matrix may have undergone phase separation during the repeated thermal cycling. This can lead to the formation of different crystalline

domains within the microcapsules, each with distinct melting or crystallization temperatures. The paraffin might also migrate and create regions with varying paraffin content. These regions can crystallize at different temperatures, resulting in multiple peaks. The two peaks represent the crystallization temperatures of these different phases solid-solid phase transition and solid-liquid transition (melting), respectively.[61] From this DSC analysis performed at the end of 50 thermal cycles, the change in heat capacity was also examined and the exothermic enthalpy value was found to be +72.8 J/g. After 50 cycles, a decrease in the enthalpy values of 93.8 J/g was observed.

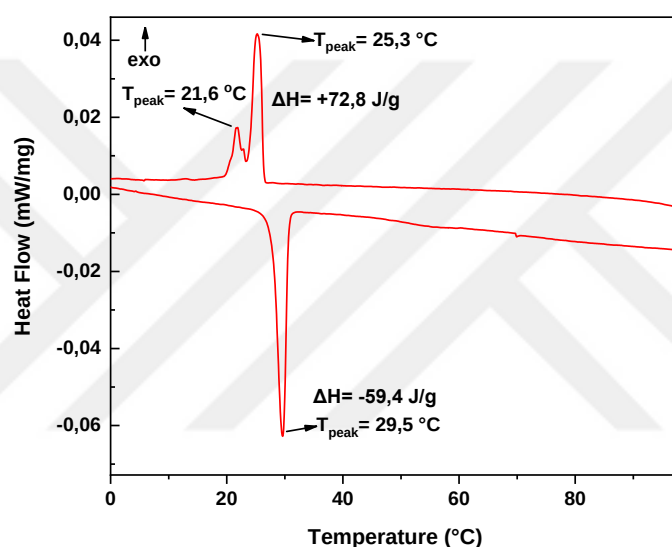


Figure 6.6 DSC analysis of MMA-PEGDA₅₇₅-PCM at 50 cycles at 80 °C

TGA analysis was conducted to evaluate the thermal stability of the capsules and determine the amount of PCM in the polymer matrix. As shown in Figure 6.7, when comparing PMMA-PEGDA₅₇₅ and PMMA-PEGDA₅₇₅-PCM, it is observed that PMMA-PEGDA₅₇₅-PCM begins to degrade at 150 °C and reaches a mass loss of 31.47 % at 200 °C. This indicates that the PMMA-PEGDA₅₇₅-PCM capsule, which contains RT-28, encapsulates approximately 30 % of the PCM.

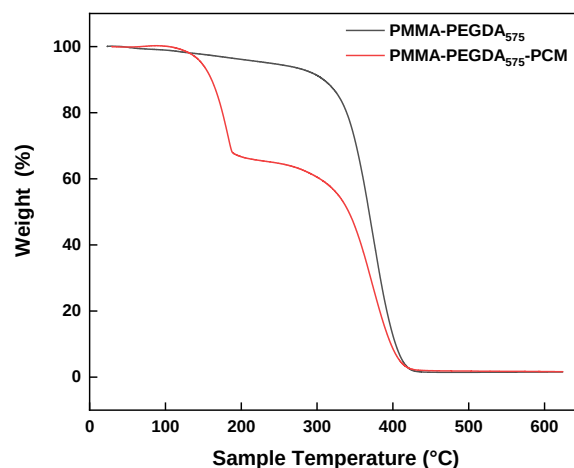


Figure 6.7 TGA analysis of PMMA-PEGDA₅₇₅ and PMMA-PEGDA₅₇₅-PCM capsules

6.2 Double Layer Coating of PMMA-PEGDA₅₇₅-PCM Capsules

To achieve homogeneous secondary coating of the capsules, first single-shell capsules were pulverized into a powder form. The pulverization process was conducted by grinding in a mortar, and any adverse effects after grinding were evaluated using DSC analysis. Because grinding might break up the shell and PCM can leak out from the capsules.

DSC analysis was performed on the pulverized PMMA-PEGDA₅₇₅-PCM with temperature increments of 5 °C per minute within the range of -10 °C to 100 °C over two cycles. The results are shown in Figure 6.8. According to the DSC results, it can be concluded that the grinding process in the mortar did not damage the capsule and there was no leakage of PCM, as evidenced by the preservation of the melting peak in the second cycle.

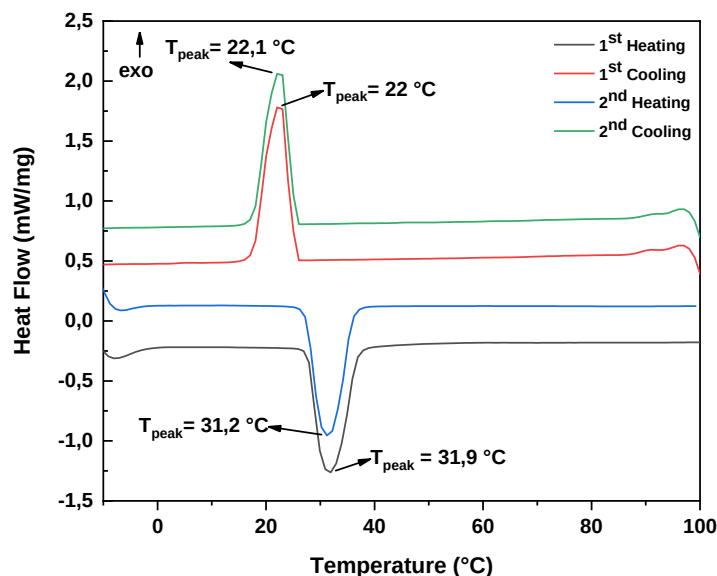


Figure 6.8 DSC analysis of the pulverized PMMA-PEGDA₅₇₅-PCM

To achieve second layer on the single shell capsule, different methods (with and without plasma treatment) were employed using various coating materials. The coating materials included (i) silica, (ii) carboxymethyl cellulose (CMC), and (iii) commercial Flexdub (silica coating) solution. Here we also applied plasma treatment onto the single shell capsules to investigate the efficiency of the second layer coating against to non plasma treated samples.

The plasma treatment process can introduce polar groups such as hydroxyl, carboxyl groups onto the surfaces of the capsules, enhance the adhesion of the coating material to the surface.[62] Additionally, compared to other surface modification approaches like chemical oxidation, the plasma treatment process does not require any additional solvents or chemicals, simplifying the modification process and shortening the preparation time. After the plasma treatment, these surfaces were coated with silica, CMC, and Flexdub solution.

6.2.1 Synthesis and Characterization of Double Layer Coating of PMMA-PEGDA₅₇₅-PCM Capsules Without Plasma Treatment

Although plasma treatment is a simple and cost-effective method, it requires the use of specialized equipment. Therefore, in the first part of the study, we aimed to evaluate the success of this encapsulation technique performed without plasma treatment. The surfaces of powdered capsules were coated with (i) silica (using the Stöber process), (ii) CMC and (iii) commercial silica solution Flexdub. The

resulting double-shelled capsules underwent various characterization studies to assess their properties and performance. Furthermore, the distribution of these capsules within a polypropylene matrix was examined to determine the efficacy of the coating method under thermochemical deformation at the process condition of polypropylene composite matrix. This comprehensive analysis aimed to evaluate whether the applied technique successfully met the intended objectives, specifically considering whether the plasma treatment was necessary for achieving the desired outcomes.

FTIR analysis was conducted to determine the presence second layer on the microcapsules (Figure 6.9). After coating with CMC, the characteristic peaks of CMC can be clearly observed, including CH₂ vibrations at 2900 cm⁻¹ and 1400 cm⁻¹, a broad peak corresponding to the OH group at 3440 cm⁻¹ and carbonyl groups at 1600 cm⁻¹ (Figure 6.9b) .[63] Silica coating resulted in polymer degradation. The ester groups from the PMMA-PEG based copolymer shell at 1730 cm⁻¹ were hydrolyzed (Figure 6c). Applying Stöber process in acidic condition resulted in ester hydrolysis and thus the polymer matrix degradation was occurred. However, specific peaks corresponding to silica, observed at approximately 960 cm⁻¹ and 790 cm⁻¹ [64], are visible with slight shifts in both the double-shell capsules and the single-shell capsule. These changes indicate that the silica formation process took place. When the DSC analysis of the silica coating via Stöber process were examined, the degradation of the polymer matrix resulted in lysis of RT-28 from the capsule and as a result, no thermal transition of PCM was observed. In the coating performed with the commercial Flexdub solution, characteristic peaks corresponding to Si-OH at 900 cm⁻¹ and Si-O-Si silicon groups at approximately 1000 cm⁻¹ are observed. [65] Additionally, the ester group in the PMMA-PEG-based copolymer shell did not undergo hydrolysis (Figure 6.9d). This indicates that the second silica coating based on the Flexdub solution was successfully achieved.

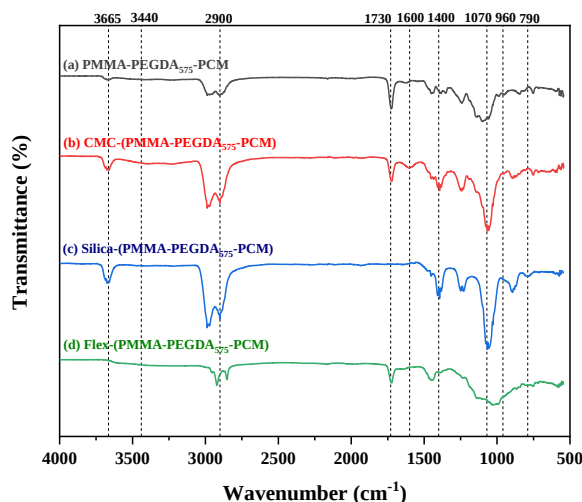


Figure 6.9 FTIR analysis of (a) PMMA-PEGDA₅₇₅-PCM capsule, (b) CMC-(PMMA-PEGDA₅₇₅-PCM) capsule, (c) Silica-(PMMA-PEGDA₅₇₅-PCM) capsule, (d) Flex-(PMMA-PEGDA₅₇₅-PCM) (second layer was prepared without plasma treatment)

TEM and XPS analyses were also performed to investigate the surface of the second layer.

The microscopic structures and surface morphology of PMMA-PEGDA₅₇₅-PCM, CMC-(PMMA-PEGDA₅₇₅-PCM) and Silica-(PMMA-PEGDA₅₇₅-PCM) were studied by TEM. Figure 6.10 shows the TEM images of the capsules. It can be observed that the PMMA-based single-shell capsules encapsulated RT-28 during their formation (Figure 6.10 a,b,c,d). When comparing the single-shell capsules with the double-shell capsules coated with CMC and silica, the darker black rings indicate the presence of the second layer. Additionally, it is evident that the surface roughness increases after the second coating.

These images show that RT-28 loaded polymer microcapsules appear to be well-formed, with a generally spherical shape. The size of the microcapsules are in the micron scale. The presence of the CMC coating can be inferred from a slight increase in the thickness of the shell around the microcapsules, compared to images a and b (as indicated by arrow in the image). The coating appears to be uniformly distributed around the microcapsules, suggesting that the CMC successfully adhered to the surface of the microcapsules, providing an additional protective layer.

Figure 6.10 images e and f show the polymer microcapsules after being coated with a silica-based second layer. The silica coating is likely contributing to an increase in the rigidity and stability of the microcapsules, which could be advantageous for certain applications. Unfortunately, silica coating is not well observed due to the hydrolysis of the polymer matrix during the Stöber process and distinct layer compared to the CMC coating was not observed.

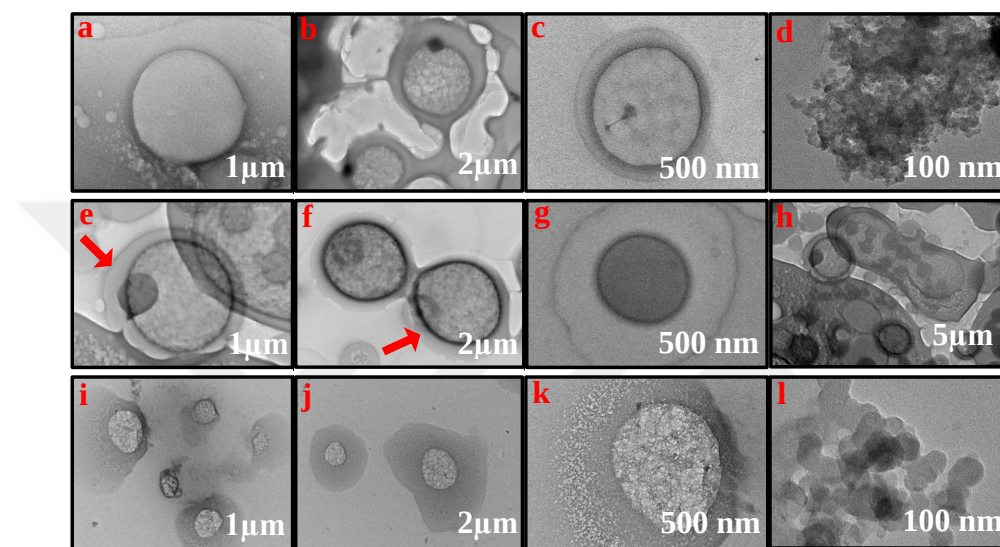


Figure 6.10 TEM images a,b,c,d: PMMA-PEGDA₅₇₅-PCM, e,f,g,h: CMC-(PMMA-PEGDA₅₇₅-PCM), i,j,k,l: Silica-(PMMA-PEGDA₅₇₅-PCM)

XPS is a spectroscopic technique with high surface sensitivity that utilizes the photoelectric effect to identify elements on the surface of a material and analyze their properties. XPS data are provided in Table 6.1. The binding energies of the C1s, O1s and Si2p₃ on the capsules surface are approximately 300, 535 and 100 eV, respectively.

The C1s peaks (Figure 6.11a-d) indicate the presence of C=C/C–C (284.8 eV), C–O (286.1 eV), and O–C=O (289.5 eV) bonds. [66] The O1s peaks of the single-shell capsule exhibit C–OH (531.7 eV) and C=O (533.5 eV) bonds, while the peaks observed around 530-536 eV after Flexdub coating indicate the presence of SiO₂ (Figure 6.11 b-e). Characteristically, after the polymer microcapsules are coated with silica solution, an increase in the concentration of silica and oxygen atoms on the surface is expected. The XPS peak of silicon shows the elemental silicon in the Si2p₃ region which indicates the presence of silicon on the surface of the substrate.

Silica was similarly observed in the single shell capsule containing RT-28. The reason for this silicon element may present in commercial RT-28. For this reason, the effect of the silica atom coming from flexdub on the total concentration was not very quantitative. However, it was observed that only Si2p3/2 is more concentrated after Flexdub coating. Additionally, a significant increase was observed in the amount of elemental oxygen. If the polymer core is not fully covered by the silica layer, you might still detect a carbon (C1s) signal, typically around 284.8 eV. This indicates that some parts of the polymer surface are exposed.

The intensity of the carbon peak can also provide information about the thickness or performance of the silica coating. Relatively lower carbon signal is observed after Flexdub coating. This suggests a thick silica layer coating on the polymer capsules.

Table 6.1 XPS data for PMMA-PEGDA₅₇₅-PCM and Flex- (PMMA-PEGDA₅₇₅-PCM)

PMMA-PEGDA ₅₇₅ -PCM		Flex-(PMMA-PEGDA ₅₇₅ -PCM)	
Name	Atomic %	Name	Atomic %
C1s Scan A	36.1	C1s Scan A	37.1
C1s Scan B	21.58	C1s Scan B	14.26
C1s Scan C	6.89	C1s Scan C	8.79
O1s Scan A	19.67	O1s Scan A	18.09
O1s Scan B	7.5	O1s Scan B	7.41
Si2p3 Scan A	8.26	O1s Scan C	1.72
		O1s Scan D	4.65
		Si2p3 Scan A	6.65
		Si2p3 Scan B	1.33

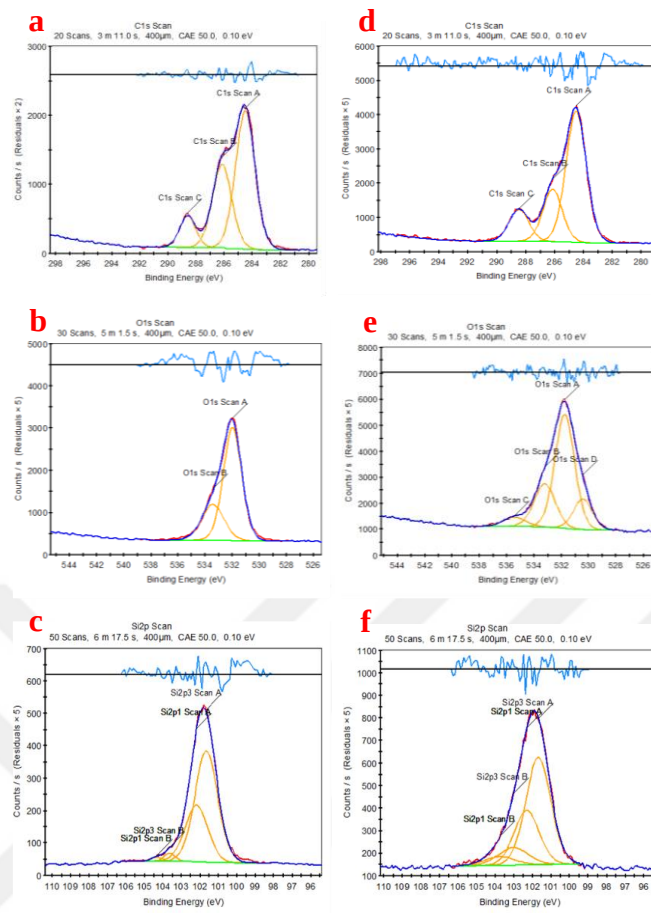


Figure 6.11 Photoelectron spectra of PMMA-PEGDA₅₇₅-PCM: C1s (a), O1s (b) and Si2p3(c); photoelectron spectra of Flex- (PMMA-PEGDA₅₇₅-PCM) C1s (d), O1s (e) and Si2p3(f)

6.2.1.1 Thermal Behavior of Double Layer Coating of PMMA-PEGDA₅₇₅-PCM Capsules Without Plasma Treatment

The thermal behavior of the obtained capsules, which were coated with both CMC, silica (Stöber process) and commercial silica solution Flexdub as a second layer, was analyzed using DSC and TGA. Previous studies showed that single-shelled capsules withstand temperatures up to 100 °C. It was expected that this temperature threshold would increase after the second coating. Therefore, DSC analysis was conducted over a temperature range of -10 °C to 140 °C with a heating rate of 5 °C per minute over two cycles. Figure 6.12a shows the DSC results of 2nd cycles for the capsules coated with CMC, Figure 6.12b shows the results of 2nd cycles for those coated with silica and Figure 6.12c shows the results of 2nd cycles for the capsules coated with Flexdub. The results indicate that the melting peak of PCM is

not clearly observed in the capsules coated with CMC and silica, whereas for the capsule coated with Flexdub, the melting peak at 29.7 °C and crystallization peaks still observed at 11-20 °C. However, the crystallization enthalpy was drop to 6.5-7 J/g. The multiple crystallization peaks observed in the DSC graph indicate complex thermal behavior likely due to degradation, phase separation, formation of new crystalline phases, or changes, such as crystal size, distribution, and perfection, in the microstructure of the paraffin-loaded microcapsules.

Most probably mechanical stress such as stirring speed applied during the coating process, it could displace the RT-28 from the microcapsule while coating with CMC. The CMC solution might not be viscous enough to keep the RT-28 in microcapsule during the process of second layer coating. As mentioned above, as a result of the hydrolysis of the polymer during the silica coating with the Stöber process, RT-28 came out of the microcapsule and polymer capsule did not show any phase change.

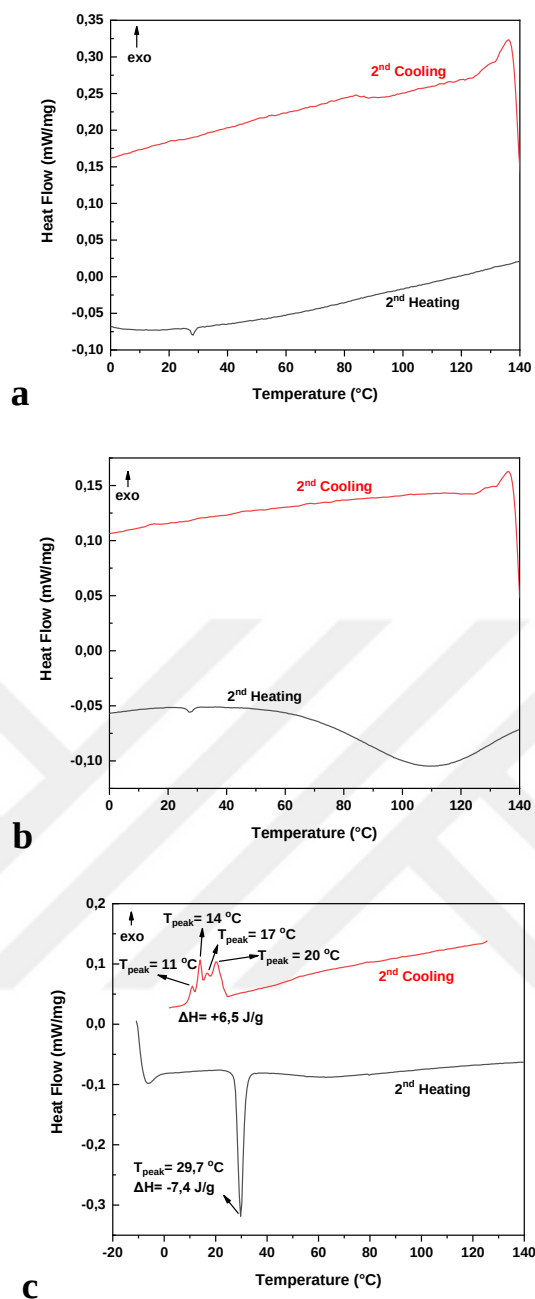


Figure 6.12 DSC analysis for 2nd cycles of **a)** CMC-(PMMA-PEGDA₅₇₅-PCM) **b)** Silica-(PMMA-PEGDA₅₇₅-PCM) **c)** Flex-(PMMA-PEGDA₅₇₅-PCM)

The thermal stabilities of empty PMMA-PEGDA₅₇₅, PMMA-PEGDA₅₇₅-PCM, CMC-(PMMA-PEGDA₅₇₅-PCM), Silica-(PMMA-PEGDA₅₇₅-PCM) and Flex-(PMMA-PEGDA₅₇₅-PCM) capsules were evaluated using TGA, and the findings are presented in Fig. 6.13. Empty capsule PMMA-PEGDA₅₇₅ exhibited complete decomposition without any residual char at 700 °C, with their initial decomposition temperature recorded at 300°C. In contrast, the capsules filled with RT-28 displayed an initial decomposition temperature around 150 °C. For the two-layered capsules,

those coated with CMC completely decomposed at 700 °C without any residual carbon. However, the capsules coated with silica left approximately 78% carbon residue, indicating that second layer coating with silica via Stöber process increased the thermal stability of the single layer capsules. Silica nanoparticles formed during the process may not have been fully washed and removed from the environment. For this reason, a significant increase was observed especially in the amount of char residue. But it should be pointed out that coating with this method resulted in loss of the RT-28 in the core shell of polymer matrix as discussed above.

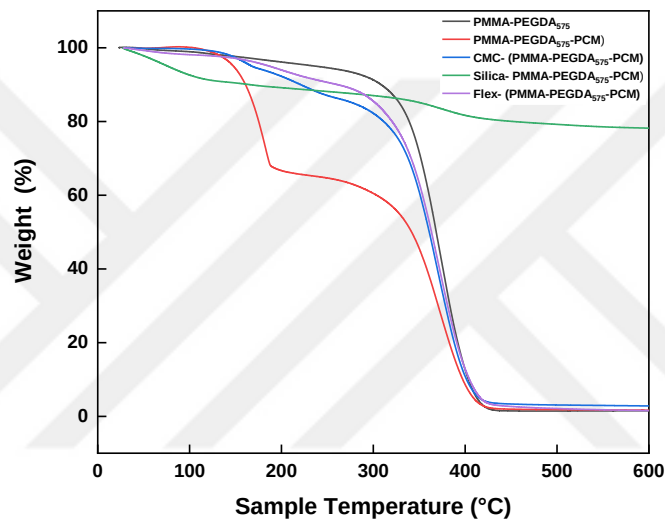


Figure 6.13 TGA analysis of PMMA-PEGDA₅₇₅, PMMA-PEGDA₅₇₅-PCM, CMC-(PMMA-PEGDA₅₇₅-PCM), Silica-(PMMA-PEGDA₅₇₅-PCM) and Flex-(PMMA-PEGDA₅₇₅-PCM) capsules

6.2.1.2 Introducing PCM Loaded Capsules Into The Polypropylene Matrix

To examine the behavior of the obtained double-layer coated PCM loaded polymer capsules within a polypropylene (PP) polymer matrix, composites containing 20 % by weight of double layer coated capsules were prepared using a microinjection molding device. Figure 6.14 shows the twin-screw microinjection device used in the preparation of the composites. During the microinjection process, powdered PP was utilized instead of granules to ensure the homogeneous dispersion of the powdered capsules throughout the matrix. The initial zone temperature of the device was set to 80 °C, while the other zones were maintained at 180 °C. This setup facilitated the production of PP composites embedded with powdered PCM

capsules. The careful selection of processing parameters and materials aimed to optimize the distribution and integration of PCM capsules within the polymer matrix, thus allowing the investigation of the functionality of the resulting composites in thermal energy storage applications.

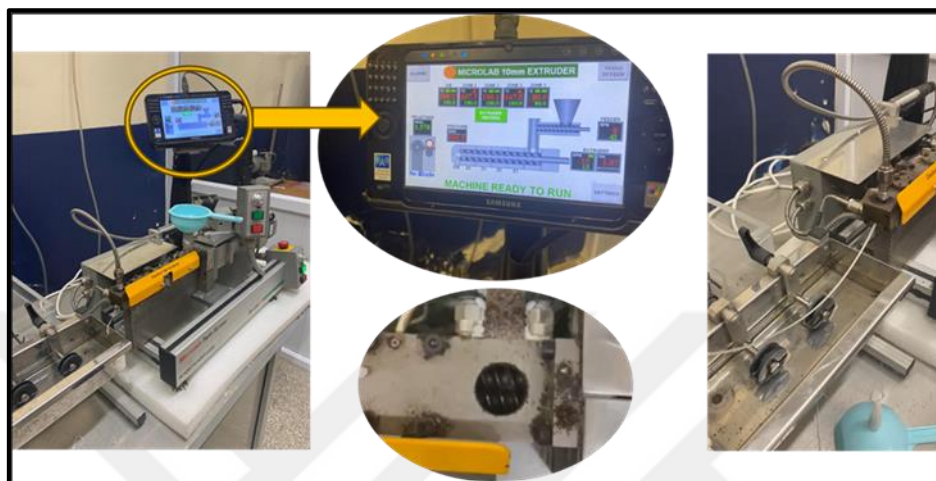
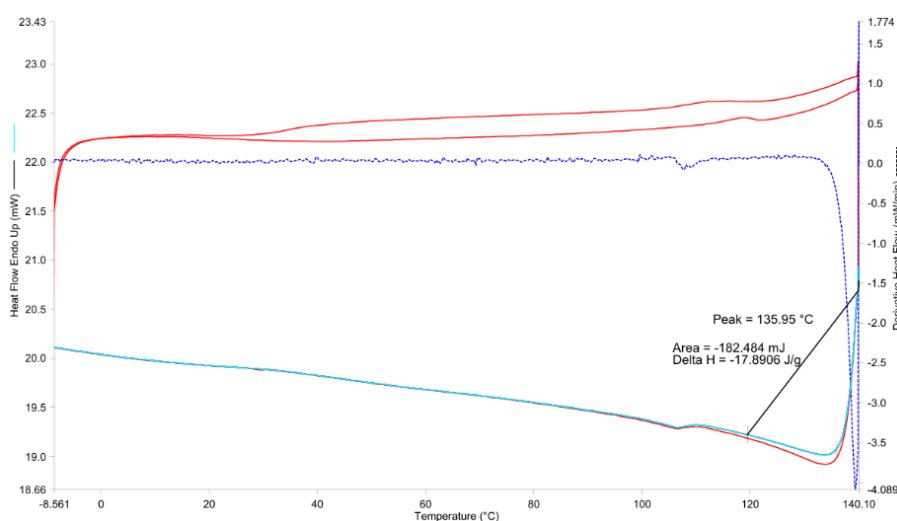


Figure 6.14 Twin-screw microinjection device

To evaluate the potential of the prepared composite materials for thermal energy applications, DSC analysis was conducted on randomly cut segments from approximately 2-meter-long PP rods. The DSC analysis was performed over a temperature range of -10 to 140 °C, with a heating rate of 5 °C per minute, across two cycles. Figure 6.15 illustrates these DSC results; (a) CMC-(PMMA-PEGDA₅₇₅-PCM) within PP and (b) Silica-(PMMA-PEGDA₅₇₅-PCM) within PP. As evident from the DSC results, there is no melting peak associated with the PCM; only the melting peak of PP at 135 °C is observed. This suggests that the encapsulation process may have failed, leading to PCM leakage. Mechanical deformation of the capsules during the extruder process should not be figured out as well. Consequently, this study demonstrates that PP composites prepared with 20 % double-layered PCM capsules with CMC coating and silica coating via Stöber process are not suitable for thermal energy storage applications.

a)



b)

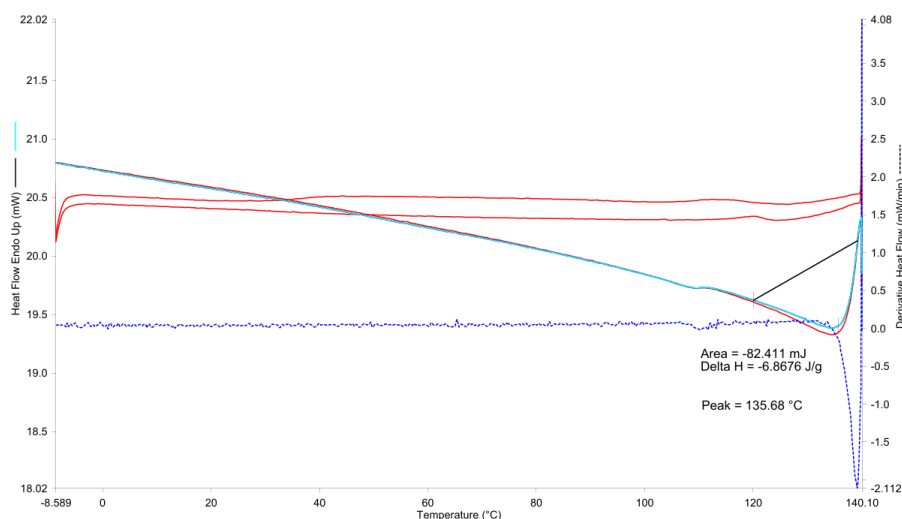


Figure 6.15 DSC analysis of **a)** by weight 20 % loaded CMC-(PMMA-PEGDA₅₇₅-PCM) capsule in PP matrix **b)** by weight 20 % loaded Silica-(PMMA-PEGDA₅₇₅-PCM) capsule in PP matrix

6.2.2 Synthesis and Characterization of Double Layer Coating of PMMA-PEGDA₅₇₅-PCM Capsules After Plasma Treatment

Polymer surfaces can be modified using plasma treatment. Before applying plasma treatment, we observed that the second layer applied to the polymer capsules was not successful enough in thermal energy storage at >100 °C. Therefore, we used plasma treatment to enhance the adhesion of a second shell layer applied to the surfaces of the polymer capsules. Plasma treatment offers various possibilities to

improve polymer surfaces by adjusting parameters such as gas flow, power, pressure, and treatment time. [67] The plasma treatment device used in our study is shown in Figure 6.16. Single-layer capsules placed in the device were subjected to oxygen plasma generated at 30 W for 60 seconds after evacuating the chamber down to 0.2 mbar residual pressure. Subsequently, the surfaces of the modified capsules were coated with silica, CMC, and Flexdub, a commercial silicate solution, appropriately.



Figure 6.16 Plasma treatment device

The surface modification process with oxygen plasma is schematically illustrated in Figure 6.17. After plasma treatment, hydroxyl (OH) or carboxyl (COOH) groups are formed on the surface of the PMMA-PEG based single layer capsules.

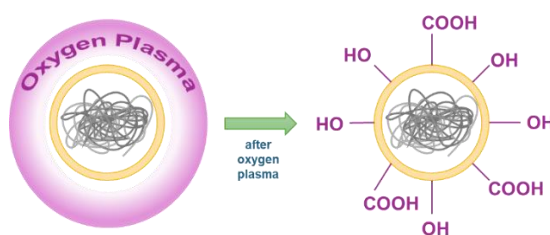


Figure 6.17 Surface modification with oxygen plasma

The -OH or -COOH groups formed on the surface of the capsules after plasma treatment will enhance the adhesion of the second coating to this modified surface. Whether this modification was successful or not, products were characterized by FTIR analysis. Figure 6.18 clearly demonstrate that the peaks associated with the polymeric shell at 3660, 2990, and 2890 cm^{-1} were altered following the coating

processes performed after plasma treatment. This indicates that the capsule surfaces were well coated with each coating materials. Corresponding stretching is very similar to the nonplasma treated microcapsules coating as described above. (See Figure 6.3) Additionally Figure 6.18c reveals that the acid used in the procedure hydrolyzed the ester groups of copolymer structure at 1730 cm^{-1} during the silica coating after plasma treated polymer capsules as well.

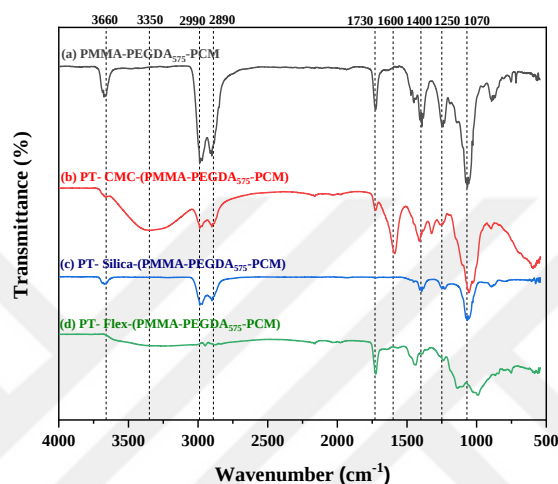


Figure 6.18 FTIR analysis of PMMA-PEGDA₅₇₅-PCM and double-coated PCM capsules prepared after plasma treatment

XPS analysis was performed on the PT-Flex-(PMMA-PEGDA₅₇₅-PCM) sample following plasma treatment and subsequent coating processes. Table 6.2 presents the XPS data. The presence of a silica layer can be confirmed by the detection of a silicon (Si) signal in the XPS spectra. However, as we mentioned above, the polymer containing RT-28 showed elemental silicon in the single capsule. Silicon typically appears as a peak at binding energies around 102–104 eV, corresponding to Si2p. Flexdub coating resulted in more concentrated in the Si2p_{3/2}. Corresponding elemental oxygen (O1s) peak observed around 532–533 eV, which is characteristic of Si–O bonds. Increasing the oxygen content after Flexdub coating also verify silica coating corresponds to SiO₂ or another silicon oxide compound.

Table 6.2 XPS data for PT-Flex-(PMMA-PEGDA₅₇₅-PCM)

PT-Flex-(PMMA-PEGDA ₅₇₅ -PCM)	
Name	Atomic %
C1s Scan A	47.83
C1s Scan B	12.33
C1s Scan C	5.5
O1s Scan A	15.84
O1s Scan B	4.93
O1s Scan C	3.92
O1s Scan D	0.88
Si2p3 Scan A	7.55
Si2p3 Scan B	1.22

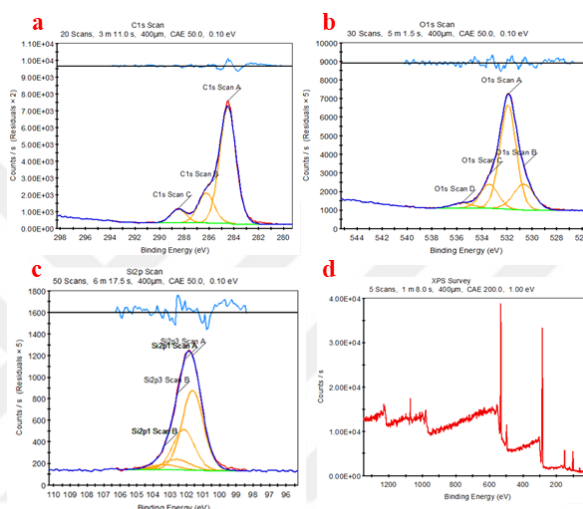
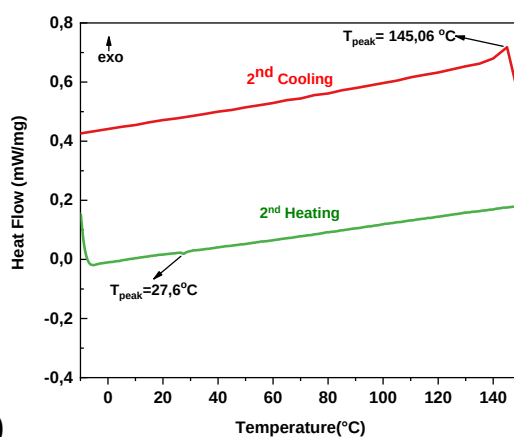


Figure 6.19 Photoelectron spectra of PT-Flex- (PMMA-PEGDA₅₇₅-PCM) C1s (a), O1s (b) and Si2p3(c) and full XPS spectrum of PT-Flex- (PMMA-PEGDA₅₇₅-PCM) (d)

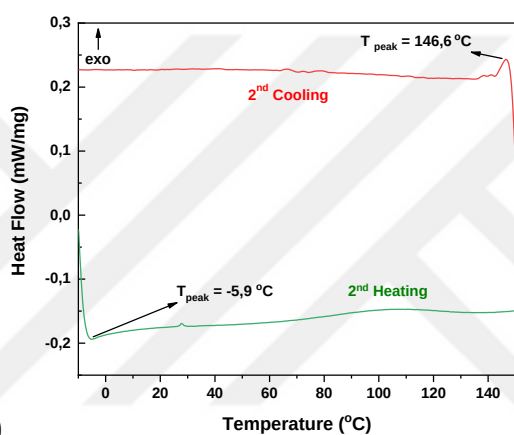
6.2.2.1 Thermal Behavior of Double Layer Coating of PMMA-PEGDA₅₇₅-PCM Capsules After Plasma Treatment

To evaluate the success of plasma treatment in achieving a double-shell capsule, the thermal properties were examined. The success of the coating applied after plasma treatment was also demonstrated by DSC, further confirming the results of the FTIR analysis. DSC analysis was performed on capsules coated with three different coating materials to investigate their potential in thermal energy storage applications. As with other samples, DSC analyses were conducted between -10 °C and 140 °C with a heating rate of 5 °C per minute over two cycles. Figure 6.20 shows the 2nd cycles of DSC analysis.

a)



b)



c)

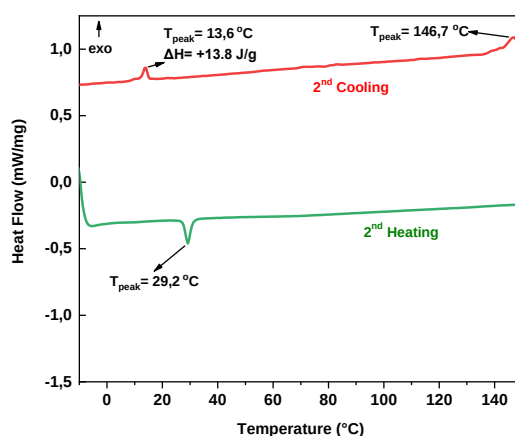


Figure 6.20 DSC analysis of a) PT-CMC-(PMMA-PEGDA₅₇₅-PCM) b) PT-Silica-(PMMA-PEGDA₅₇₅-PCM) c) PT-Flex-(PMMA-PEGDA₅₇₅-PCM)

DSC spectra showed that the melting peak at 29.2 °C in the second cycle of the capsule coated with Flexdub indicates that the double-shell encapsulation process was successfully achieved with plasma treatment. Furthermore, the enthalpy value

was calculated to be 13.8 J/g. This indicates that the initial heat capacity of 260 J/g decreased to 13.8 J/g after the double-shell encapsulation process via commercial silicate solution conducted in our study. However, heat capacity of non-plasma-treated capsules was approximately 6.5-7 J/g. We can conclude that plasma treatment enhanced the efficiency of the coating.

Flexdub is a commercially available silicate solution with a density of 1.4 g/cm³ and a flash point of 700°C.[68] It is effectively used for sealing pool leaks on both wet and dry surfaces. The commercial Flexdub solution forms strong bonds with these groups, successfully encapsulating the PCM with a second layer of the shell. From these it can be concluded that the PCM remained within the capsule in some amount and that its durability from 100 °C to 140 °C significantly improved compared to the single-shell form. It should be noted here that the CMC-coated microcapsule and the silica-coated microcapsule with the Stöber process lost their PCM feature and DSC did not show any transition.

7 CONCLUSION

In this thesis, we focused on enhancing the efficiency of thermal energy storage systems by encapsulating phase change materials (PCMs). Our aim was to address the disadvantages of RT-28, a paraffin-based PCM, particularly its leakage and insufficient thermal conductivity. To this end, we encapsulated RT-28 with a double layer capsule and investigated the performance of the encapsulated PCM.

In the first stage, we encapsulated RT-28 with a PMMA-PEG based copolymer shell. The TGA analysis revealed that 34.5% of the RT-28 was successfully encapsulated. The thermal properties of this single-shell capsule were examined, and DSC analysis up to 100 °C demonstrated successful encapsulation. However, it was observed that the thermal energy storage capacity of RT-28, which is 260 J/g, decreased to approximately 94 J/g when encapsulated in a PMMA-based polymeric single-shell capsule. Additionally, it was observed that this single-shell capsule remained stable after 50 thermal cycles at 80 °C. It was also observed that the PCM properties of the polymer capsules completely disappeared at 200 °C.

In the second stage, different methods were tested for the second layer coating of the capsule. Second layer coatings were applied using (i) silica, (ii) carboxymethyl cellulose, and (iii) commercial Flexdub silicate solution. Coating efficiency was also tested by using plasma treatment onto the microcapsule surface.

FTIR analyses indicate that the encapsulation process occurred physically, without any chemical interaction between the PCM and the capsule material. It was also proven that PCM is located inside the polymer core not adsorbed on the surface.

In the second encapsulation studies, the best results were obtained with capsules coated using Flexdub solution. When comparing these results internally, it was found that the heat storage capacity of the capsules subjected to plasma treatment before coating was 13.8 J/g, whereas for non-plasma-treated capsules, this value was approximately 6.5-7 J/g. This indicates that the plasma treatment enhances the coating of the capsule surface. XPS analysis showed the presence of silica on the surface. When the surface of the RT-28 loaded polymer capsule was applied to

double layer coating, Flexdub gave the best result. The silica coating with the Stöber process caused the polymer to hydrolyze and RT-28 to move away from the matrix. Similarly, in the CMC coating as proven by TEM analysis, RT-28 polymer came out of the capsule and DSC did not show any transition.

The behavior of the obtained double layer capsules within a polypropylene polymer matrix was also investigated, and their potential in composite material production was evaluated. For this purpose, PP composites containing 20% by weight double-layer capsules, CMC coated, and silica coated with Stöber process, were produced using a microinjection device. During this process, the capsules underwent mechanical deformation in the injection line and failed to maintain thermal stability at temperatures of 180-200 °C. Consequently, the resulting PP composites containing encapsulated PCM did not exhibit heat storage properties.

This thesis showed that the double-layer encapsulation technique can be used to address the significant challenges of leakage and thermal conductivity in PCMs. The findings indicate that PCMs can be utilized more effectively in thermal energy storage systems, contributing significantly to the literature in this field. However, the study revealed that encapsulation efficiency was relatively low. To enhance this, various emulsifying surfactants, as observed in similar examples in the literature, could be added to the reaction medium. Additionally, to enable the PP composite to exhibit heat storage properties, the secondary coating material could be modified; for instance, TiO₂ could be used. Our study provides an important reference for future research on energy storage and sustainability.

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PUBLICATIONS FROM THE THESIS

Conference Papers

1. E. Kırtay, T. Eren, A. B. Hazar Yoruç, Ç. Elibol, B. Evren, O. Sazcı, U. Özer, M. Ekşi Altan, M. Eryıldız, “Development of Polymer-Based Microcapsule Reinforced Composite Material”, *8th International Icontech Congress on Innovative Surveys in Positive Sciences*, Oral Presentation (online), Baku, Azerbaijan, 2024, s. 619-620.

Projects

1. Project Manager Assoc. Prof. Çağatay ELİBOL, Researchers Prof. Dr. Tarık EREN and Prof. Dr. Afife Binnaz HAZAR YORUÇ, Scholarship Holders Elmas KIRTAY and Umutcan ÖZER- TUBITAK- Project no :122N239- Design and Production of High-Efficiency Porous Paraffin/ Metal Structures for Heat Exchange and Thermal Energy Storage Applications, 01.04.2023-01.04.2025.