

FABRICATION AND EVALUATION OF ENCAPSULATED PHASE CHANGE MATERIALS FOR LATENT HEAT STORAGE

**A Thesis Submitted
in Partial Fulfilment of the Requirements for the
Degree of**

DOCTOR OF PHILOSOPHY

by

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CANDIDATE'S DECLARATION

I, **Gunjan Varshney** (Reg. No.: 2K21/PhDAC/501) hereby certify that the work which is being presented in the thesis entitled “*Fabrication and Evaluation of Encapsulated Phase Change Materials for Latent Heat Storage*” in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy, submitted in the **Department of Chemical Science and Engineering**, Delhi Technological University (Formerly Delhi College of Engineering), Delhi is an authentic record of my own work carried out during the period from January 2022 to June 2026 under the supervision of **Dr. Raminder Kaur**, Department of Chemical Science and Engineering, Delhi Technological University, Delhi and **Prof. Mohammad Zulfequar**, Department of Physics, Jamia Millia Islamia, Delhi

The matter presented in the thesis has not been submitted by me for the award of any degree of this or any other Institute.

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ABBREVIATIONS

TES	Thermal energy storage
SHS	Sensible heat storage
LHS	Latent heat storage
PCMs	Phase change materials
TCHS	Thermochemical heat storage
ESE	n-Eicosane
PEG	Polyethylene glycol
CA	Capric acid
LA	Lauric acid
MA	Myristic acid
PA	Palmitic acid
EPCMs	Encapsulated PCMs
UF	Urea formaldehyde
MF	Melamine formaldehyde
NPCM	Nanoencapsulated PCM
MPCM	Microencapsulated PCM
MacroPCM	Macroencapsulated PCM
PMMA	Polymethylmethacrylate
RC	Red cabbage
AIBN	2,2-Azobisisobutyronitrile
BPO	Benzoyl peroxide
PF	Phenol formaldehyde
PS	Polystyrene
NPs	Nanoparticles

RTPCM	Reversible thermochromic PCMs
TGA	Thermogravimetry analysis
SSPCMs	Shape-stabilized PCMs
EG	Expanded graphite
EP	Expanded perlite
DT	Diatomite
EV	Expanded vermiculite
TCP	Temperature-controlled packaging
PETRA	Pentaerythritol triacrylate
DVB	Divinylbenzene
CNTs	Carbon nanotubes
MWCNTs	Multi-walled carbon nanotubes
ATH	Anthocyanin
SM	Styrene monomer
BA	Butyl acrylate
PBA	Polybutylacrylate
PBMA	Polybutylmethacrylate
PLMA	Polylaurylmethacrylate
PSMA	Polystearylmethacrylate
SLS	Sodium lauryl sulphate
DDM	Dodecyl mercaptan
SMA	Stearyl methacrylate
EGDMA	Ethylene glycol dimethacrylate
ESE/Poly(St-co-BA)	n-Eicosane/polystyrene-co-polybutylacrylate
Poly(St-co-BA)	Polystyrene-co-polybutylacrylate

ESE/Poly(SMA-co-BA)	n-Eicosane/polystearylmethacrylate-co-polybutylacrylate
Poly(SMA-co-BA)	Polystearylmethacrylate-co-polybutylacrylate
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
PXRD	Powder X-ray diffraction
PSD	Particle size distribution
DLS	Dynamic light scattering
FE-SEM	Field-emission electron microscopy
TEM	Transmission electron microscopy
IFT	Infrared thermography
POM	Polarized optical microscopy
EDX	Energy dispersive X-ray spectroscopy
SDGs	Sustainable development goals
E_R	Encapsulation ratio
E_{ES}	Encapsulation efficiency
C_{es}	Thermal storage capacity
L_R	Loading ratio
E	Heat storage efficiency
ZnO	Zinc oxide
FeO	Iron Oxide
SiO ₂	Silicon oxide
CaCO ₃	Calcium carbonate
TiO ₂	Titanium oxide
SrTiO ₃	Strontium titanate
CuO	Copper oxide

$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	Zinc acetate dihydrate
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	Iron (II) chloride tetrahydrate
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Iron (III) chloride hexahydrate
HCl	Hydrochloric acid
NaOH	Sodium hydroxide
ZnATH-(O) NPs	Anthocyanin mediated zinc oxide NPs
FeATH-(O) NPs	Anthocyanin mediated iron oxide NPs

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ABSTRACT

The growing global energy demand and overreliance on fossil fuels like coal and petroleum have resulted in serious environmental issues such as climate change, greenhouse gas emissions, and ecological imbalance. The pursuit of sustainable energy management technologies that can boost energy efficiency while lessening the demand on non-renewable resources has accelerated due to these concerns. Among numerous approaches, thermal energy storage (TES) systems have emerged as a viable alternative for storing excess thermal energy and releasing it whenever it is required. Phase change materials (PCMs) have drawn a lot of attention in this regard because of their capacity to store and release a significant quantity of latent heat during phase transition at constant temperatures.

Among the several PCMs, Eicosane (ESE) is well known for its high latent heat storage capacity, non-corrosive nature, chemical stability, and appropriate melting temperature for applications involving low-temperature TES. The core PCM in this work is ESE, which has a melting point of about 38.9 °C and a melting enthalpy of 239.9 J.g⁻¹. Despite its benefits, paraffin-based PCMs have numerous intrinsic drawbacks that limit their practical application, including limited thermal conductivity, poor structural stability, and leakage during the phase change process. As a result, the current thesis is focused on producing advanced material techniques to overcome these obstacles and broaden the application of paraffin-based PCMs.

To achieve the desired objectives, ESE was first microencapsulated into polymeric shell of polystyrene (PS) by a mini-emulsion polymerization process aided by probe sonication, where polybutylacrylate (PBA) copolymer shell was also used to increase structural integrity. The resultant microencapsulated phase change materials (MPCMs) showed an encapsulation ratio of 91.9%, encapsulation efficiency of 91.6%, with a melting enthalpy of 220.5 J.g⁻¹. The thermal stability and behaviour of the microcapsules were systematically analyzed using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) while diffusion tests were carried out to assess leakage resistance. The findings demonstrated that, in comparison to pure ESE, the microencapsulated systems had noticeably improved thermal stability.

Additionally, paraffin was encapsulated at the nanoscale to produce nanoencapsulated phase change materials (NPCMs), which further enhanced heat transfer properties and interfacial

interactions. The PCM's thermal responsiveness is improved by the increased surface area that the smaller particle size offered, which promotes interaction between the PCM and its surroundings. The synthesized NPCMs possessed an encapsulation ratio of 93.6%, encapsulation efficiency of 87.2%, and melting enthalpy of 224.6 J.g^{-1} . The efficient encapsulation of ESE within the polymeric shell of polystearyl methacrylate was verified using Fourier Transform Infrared Spectroscopy (FTIR), while the particle size distribution of the produced nanocapsules was ascertained.

Further research includes the development of microcapsules with varying crosslinking agent ratios within the polymer shell in order to optimize the thermal stability of the MPCM and investigate their effects on structural strength. The thermal performance and stability of these MPCMs were assessed using DSC and TGA techniques, and significant thermal parameters were calculated from the thermograms in order to assess their performance as TES systems. Among the investigated formulations, EPD5 exhibited a melting enthalpy of 170.5 J.g^{-1} , an encapsulation ratio of 62.4%, and an encapsulation efficiency of 68.3%.

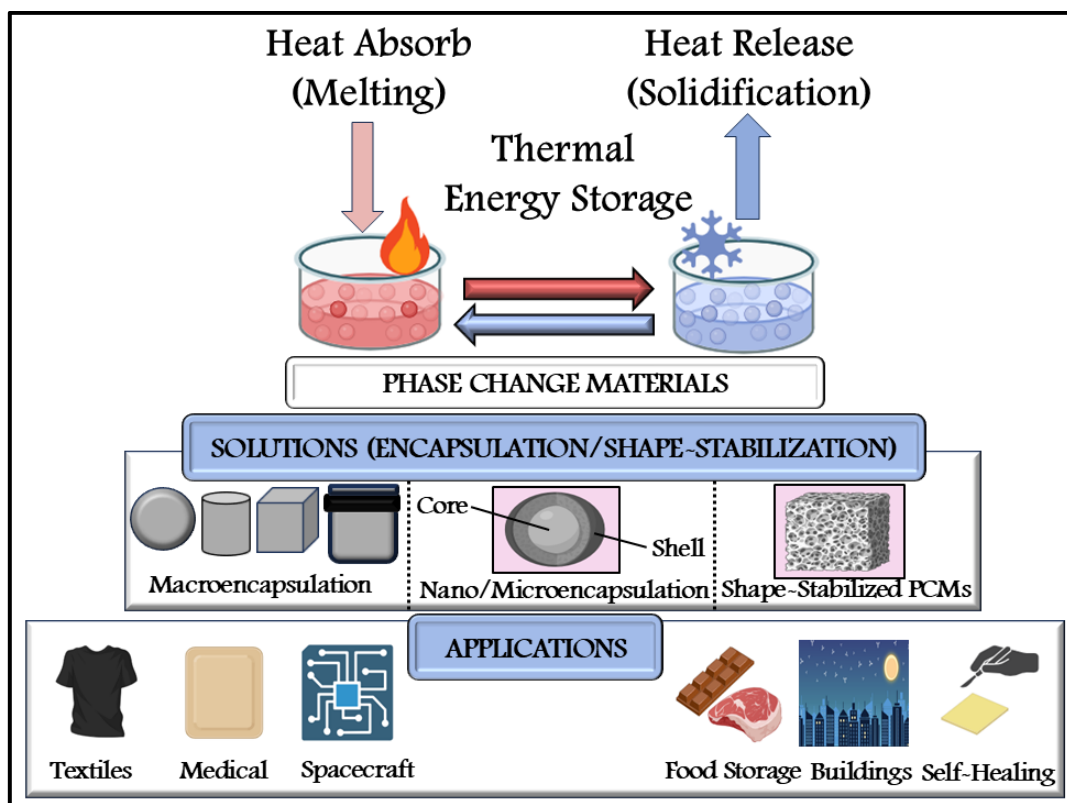
The encapsulated PCM system was supplemented with synthesized thermal conductive nanoparticles (NPs) to improve the overall thermal performance of the tailored microcapsules. Powder X-ray Diffraction (PXRD) analysis revealed the amorphous nature of the surrounding polymer shell and validated the structural properties of these NPs. The inclusion of NPs improved the thermal response of the encapsulated PCM system. The ZnATH-(O) NP-doped MPCM (Z7) showed a melting enthalpy of 186.8 J.g^{-1} , while the FeATH-(O) NP-doped MPCM (F5) exhibited a melting enthalpy of 226.2 J.g^{-1} , with encapsulation ratios of 77.9% and 94.3%, respectively.

In addition to encapsulation techniques, shape-stabilized phase change materials (SSPCMs) were produced using porous supporting material to mitigate seepage during the phase transition of the PCMs. The optimized ESE/MWCNT SSPCM (SS-EM@9) achieved a melting enthalpy of 215.3 J.g^{-1} and crystallization enthalpy of 212.7 J.g^{-1} , with a thermal storage capacity of 99.8%. The morphological features of the composites were evaluated using Field-Emission Scanning Electron Microscopy (FE-SEM), which revealed the efficient inclusion of PCM inside the porous structure. The obtained SSPCMs showed enhanced thermal stability and remarkable structural integrity.

Overall, this study provides a thorough investigation into the design, synthesis, and characterization of MPCMs, NPCMs and SSPCMs for efficient TES. The synthesized novel materials exhibit improved stability and performance, indicating their potential for real-world applications in TES technologies. This research makes a substantial contribution to the fields of materials engineering, polymer science, and energy storage. It also offers a viable solution to lessen reliance on non-renewable energy sources while promoting sustainable energy management.

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW



Publication from this chapter: Gunjan Varshney, Pooja Singh, Sarla Yadav, Raminder Kaur (2024) "A Review on Unleashing the Potential Solution of Thermal Comfort: Exploring the Cutting-edge Progress of Advanced Engineering Application of Phase Change Materials Integrated Textiles", *Sustainable Energy Technologies and Assessments*, 72, 104089, DOI: <https://doi.org/10.1016/j.seta.2024.104089> (I.F.=7.1) (SCI indexed) (Elsevier)

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

The worldwide growing energy demands, usually satisfied by fossil fuels, pose a serious threat to our planet. These non-renewable resources are rapidly depleting due to their extensive dependency and worldwide usage. The unsustainable reliance on fossil fuels needs an immediate shift to sustainable energy systems in order to assure resource security. Furthermore, the urgency of moving toward sustainable energy solutions is underscored by growing apprehensions about climate change, which have been brought to light by recent extreme weather occurrences [1][2]. In this instance, renewable energy sources that encompass wind, hydro and solar energy are growing attention, as they provide a perpetual supply with minimum environmental impact and are projected to gradually prevail over fossil fuels in the future. Nevertheless, renewable energy sources exhibit fluctuations. Moreover, if these energy sources account for a substantial portion of the total power generation, the stability of the energy system would be greatly influenced; enough to satisfy demand [3]. On the other side, it is crucial to enhance energy efficiency and utilization, which necessitates energy flexibility in order to supply energy on demand and prevent superfluous waste [4].

Thermal energy storage (TES) can be a viable approach to control energy supply and demand, that can proficiently increase energy flexibility [5]. As a result, TES has been widely promoted in the recent decades. TES systems can bridge the gap between energy supply and demand and overcome the intermittent and fluctuating nature of the renewable energy sources by storing energy when the energy supply is abundant and releasing it when the energy supply is limited [6][7]. Moreover, TES systems may recover and utilize waste heat from industries or other domains, greatly boosting energy efficiency and utilization [8].

1.1. Classification of TES

Three types of TES systems can be distinguished: sensible heat, latent heat, and thermochemical heat storage systems (absorption and adsorption systems) [9]. **Figure 1.1** shows the schematic representation of each TES [10].

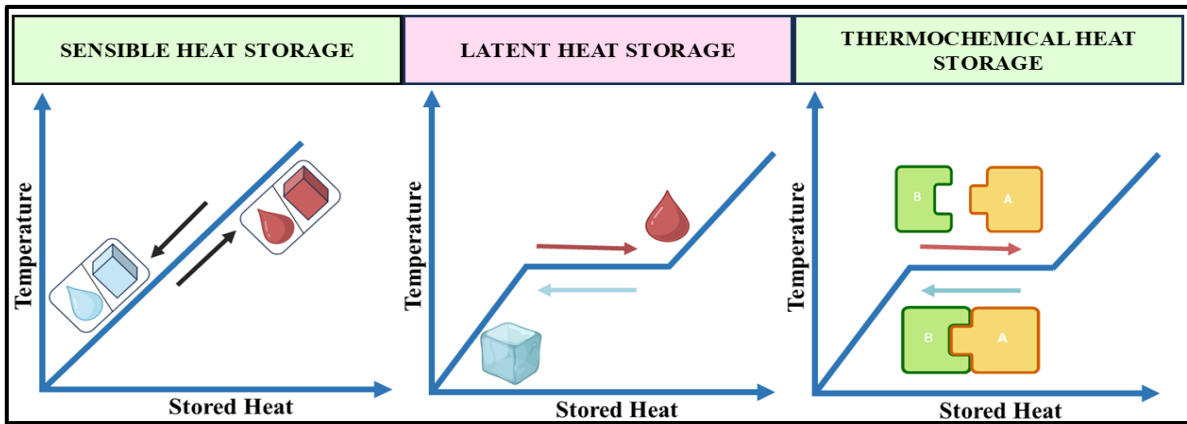


Figure 1.1: Schematic representation of different types of TES

1.1.1. Sensible Heat Storage (SHS)

SHS raises the temperature of solid or liquid materials without changing their phase in order to store thermal energy. The amount of thermal energy stored within the material relies on the material's quantity, heat capacity and the temperature difference between the initial and final state of the material [11]. The materials utilized for storage were rock beds, sand, oil, bricks or soil. Reduced corrosion, a wide operating temperature range, and inexpensive material costs are merely a few benefits of SHS. But the energy density of this system is quite low [12]. Equation (1.1) is employed to express the total amount of heat energy (Q_S) stored or emitted in SHS [13]:

$$Q_S = \int_{T_i}^{T_f} m C_p \Delta T = m C_p (T_f - T_i) \quad (1.1)$$

Where, Q_S is the amount of heat stored in Joules (J), T_i and T_f are the initial and final temperatures of the storage material in Kelvin (K), m is the mass of heat storage medium in kilogram (kg), C_p is the specific heat ($J.kg^{-1}.K^{-1}$)

Table 1.1 displays the SHS capacity of numerous solid-liquid materials. Since water is affordable and has a high specific heat, it seems to be the best SHS liquid available. However, liquid metals, oils, and molten salts have been used over 100 °C. Rock bed-style storage materials are employed for air heating applications [14].

Table 1.1: A list of selected solid–liquid materials for SHS [14]–[16]

Material	Phase	Density (kg.m ³)	Temperature Range (K)	Specific Heat (J.kg ⁻¹ .K ⁻¹)
Brick	Solid	1600	20	840
Rock	Solid	2560	20	879
Engine Oil	Liquid	888	Upto160	1880
Caloria HT43	Liquid	867	12-260	2200
Octane	Liquid	704	≤126	2400
Ethanol	Liquid	790	≤ 78	2400
Butanol	Liquid	809	≤ 118	2400
Water	Liquid	1000	0-100	4190

1.1.2. Latent Heat Storage (LHS)

The LHS system is primarily based on the latent heat of fusion principle during the phase change process. In the phase change process, phase change material (PCM) absorb latent heat during melting and release the stored heat during crystallization. Thus, the most significant factor in LHS systems is the high heat of fusion. There are several ways to accomplish the phase transition of materials i.e. solid-solid, solid-liquid, liquid-gas, and solid-gas [17]. The solid-liquid phase transition is the most viable option due to high latent heat and the slight volume change during phase transition. A PCM should have congruent melting, high thermal conductivity, a melting temperature range appropriate for its intended use, no subcooling, excellent stability, non-toxic and non-corrosive traits [13]. The ability of LHS to offer a high energy storage density per unit mass or volume has drawn a lot of interest of researchers. The LHS system is chosen over sensible storage as it attains almost isothermal conditions during the process of charging and discharging.

Equation (1.2) provides the energy store by latent energy source [13]:

$$Q_L = m \cdot L \quad (1.2)$$

Where, m is the mass in kilogram (kg) and L is the specific latent heat (KJ.kg⁻¹)

Equations (1.3) and (1.4) can also be used to formulate PCM's storage capacity [14]:

$$Q_L = \int_{T_i}^{T_m} m C_{sp} dT + m a_m \Delta h_m + \int_{T_m}^{T_f} m C_{lp} dT \quad (1.3)$$

$$Q_L = m[C_{sp}(T_m - T_i) + a_m \Delta h_m + C_{lp}(T_f - T_m)] \quad (1.4)$$

Where, Q_L is the stored energy in joule (J), T_m , T_i and T_f are the melting, initial and final temperature in degree celsius ($^{\circ}\text{C}$), m is the mass of heat storage medium in kilogram (kg), C_{sp} is the average specific heat between T_i and T_m , C_{lp} are the average specific heat between T_m and T_f , a_m is the fraction melted, Δh_m is the heat of fusion (J.kg^{-1}).

1.1.3. Thermochemical Heat Storage (TCHS)

TCHS exploits materials that release or store heat through sorption or dissociation processes in reversible exothermic and endothermic chemical reactions [18]. These thermochemical materials can be differentiated based on the type of reaction that occurs, which is generally described by equation (1.5). An endothermic reaction occurs when heat is introduced into the reactant AB during the charging process, dissociating it into products A + B. The products can be kept separately for a set period of time.

Products A and B recombine in an exothermic reaction during the discharge process, releasing the necessary heat. **Figure 1.2** shows a schematic representation of the storage cycle. In contrast to SHS and LHS, TCHS has a higher energy storage density because of the strong chemical bonding forces that are involved in the process. Furthermore, since the stored chemical potential energy is neither released into the environment nor transformed into other forms of energy, any thermal losses during the storage period can be disregarded [19].

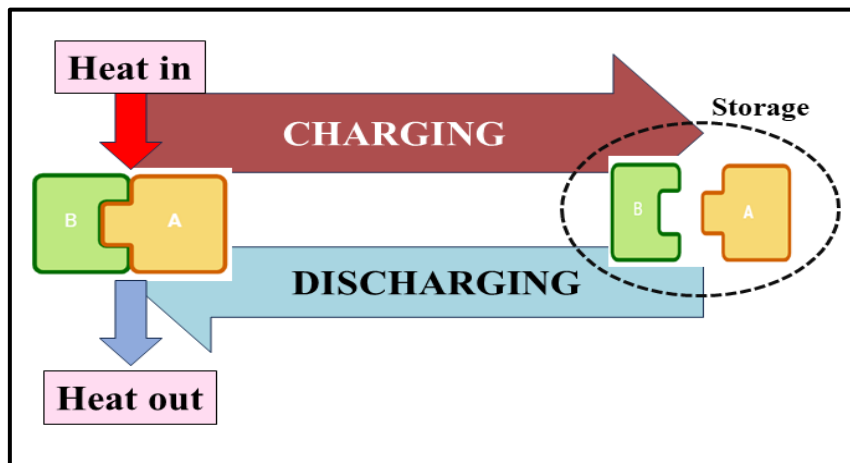
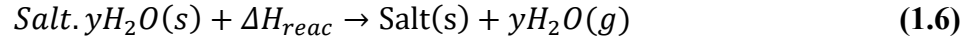


Figure 1.2: Representation of TCHS processes

Hydrated salts serve as an example of a sorption process, with an endothermic dehydration reaction serving as the charging phase. In contrast, an exothermic hydration reaction is employed for the heat discharge. This type of process is described by equation (1.6) [1].



The forward and reverse reactions can occur in distinct steps at different temperatures, resulting in the formation of intermediate hydrate phases.

TCHS is a promising technique for efficiently using off-peak electricity, IWH, and renewable energy due to the aforementioned benefits. Additionally, TCHS can improve the thermal performance of the storage system without sacrificing environmental sustainability or energy economy when combines with long-term seasonal TES approaches [20]. Although TCHS is the newest TES technology in the recent decades, it is still in the laboratory research stage, despite the fact that there are numerous possible TCHS processes.

1.2.Comparative Analysis of TES Technologies

Despite the increasing amount of research on TES technologies, there are still major technical and systemic obstacles to real-world deployment. There is an imbalance between experimental viability and real-world application since these barriers are often left behind in existing literature. In order to facilitate the broader adoption of TES systems, a critical analysis of deployment case studies identifies a number of recurrent problems. As **Table 1.2** illustrates, a comparative study of TES technologies shows that each system has distinct benefits as well as drawbacks. TCHS performs adequately in long-duration and high-temperature instances, LHS provides more density and compactness, and SHS is affordable and simple. To optimize performance and cost-effectiveness, strategic selection based on application requirements is crucial [21].

Table 1.2: Comparison between SHS, LHS and TCHS [21]–[23]

Key Parameters	Heat Storage Technology		
	SHS	LHS	TCHS
Basic	Through the process of heat transfer, energy can be stored or released by heating or cooling a liquid or solid storage substance.	During the phase transition (melting and crystallization), energy is stored.	Energy is stored after a dissociation reaction and then recovered in a chemically reverse action.
Phase Transition	System without phase transition	System with phase transition	System without phase transition
Temperature	Temperature varies	Temperature remains constant	Include 3 main processes: (i) Charging (ii) Storing (iii) Discharging
Energy	Energy exchange between matter and surrounding	Change in internal energy of the matter	Change in internal energy of the matter
Energy Density	100–300 kWh/m ³ (typical range for water-based systems)	150–400 kWh/m ³ (typical for PCMs)	500–1000 kWh/m ³ (depending on material)
Response Time	10–30 min	5–15 min	30–60 min
Storage Duration	Short to medium (hours to days)	Medium to long (up to several days)	Long (several days to months)
Advantages	Simple technology, mature, widely available	Higher energy density, more compact than sensible heat	Very high energy density, long-term storage capabilities
Limitations	Low energy density, lower efficiency for large-scale storage	Limited material options, cost of materials can be high	More complex, high system costs, and material degradation risks

1.3. Phase Change Materials (PCMs)

PCMs are latent heat storage materials. When a substance transforms from solid to solid or solid to liquid or liquid to gas or vice-versa, thermal energy is transferred. This is referred to as a "phase" or change in state. Initially, these solid-liquid PCMs behave similarly to conventional storage materials, with temperatures rising, as they absorb heat. In contrast to traditional (sensible) storage materials, PCM releases and absorbs heat at a constant temperature i.e. under isothermal condition. Their heat storage capacity is 5–14 times greater than that of sensible materials like rock, masonry, or water. Numerous PCMs with a wide range of energy capacities are known to melt while retaining heat. However, these materials must have specific desired

kinetic, chemical, and thermodynamic properties in order to be used as LHS materials. Economic factors and the accessibility of these resources must also be taken into account [14].

1.3.1. Mechanism of PCMs

LHS using PCMs represents an efficient thermal energy management mechanism, wherein energy is reversibly stored and released through temperature-driven phase transitions at nearly constant temperatures. The temperature of a solid-liquid PCM continuously increases as it is subjected to the heating process. A storage material starts to melt completely and uniformly when its temperature approaches the melting point. Since the melting process is endothermic, thermal energy from its surroundings is absorbed and stored as latent heat in a liquid state. Additionally, the temperature of the storage material continuously drops when the cycle is reversed and the temperature drops gradually. The PCM releases the same amount of stored energy in the environment during the cooling phase and returns to its solidified condition (Figure 1.3) [24], [25].

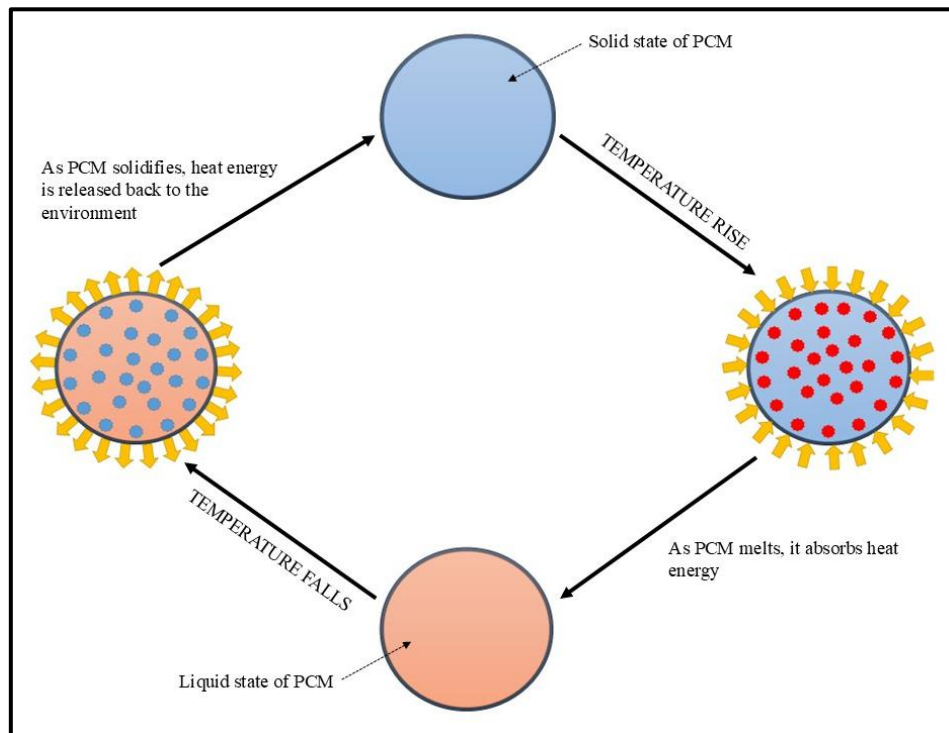


Figure 1.3: Working principle of PCMs

1.3.2. Selection Criteria of PCMs for the TES Applications

Different PCMs are chosen for different applications, based on their properties, such as their physical, chemical, and thermal characteristics as well as their economic aspects, which are shown in **Figure 1.4**.

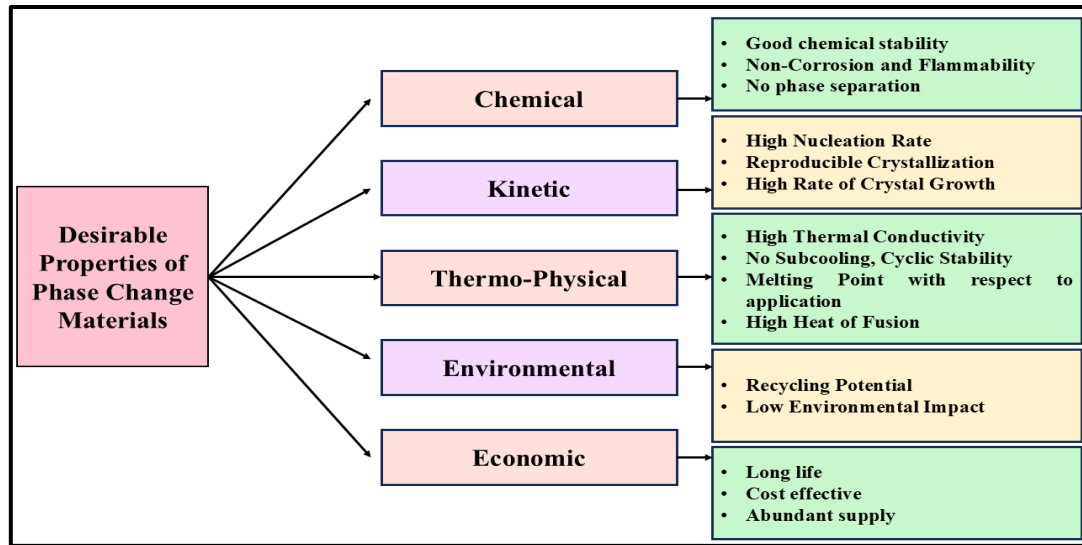


Figure 1.4: Selection criteria of PCMs

1.3.3. Classification of PCMs

PCMs can be categorized as liquid–gas, solid–solid, solid–liquid, and solid–gas. The liquid–gas and solid–gas phase transitions are incompatible with latent heat TES applications because of low latent heat for phase shift and the impact of volume change [26]. Solid-liquid PCMs demonstrated a wide range of applications as they have high energy storage density and wide range of phase transition temperature, which makes them ideal for utilization in TES. Accordingly, solid-liquid PCMs are identified by reclassifying three categories: organic [27], inorganic [4], and eutectic [28], as illustrated in **Figure 1.5**.

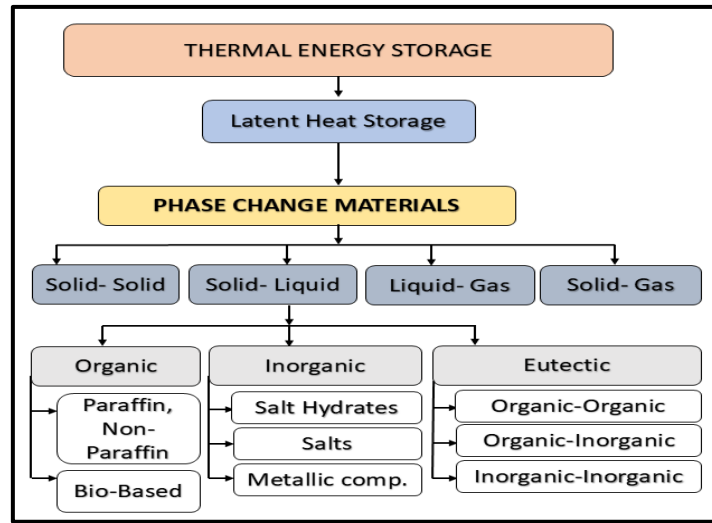


Figure 1.5: Classification of solid-liquid PCMs

1.3.3.1. Organic PCMs

As listed in **Table 1.3**, organic PCMs include both paraffinic and non-paraffinic compounds, such as fatty acids, alcohols, and glycols [29]. These organic PCMs have garnered interest as a consequence of their suitable phase transition temperature, enhanced LHS capacity, and chemical and physical stability. Nevertheless, they have several limitations that prevent them from being used practically, such as low thermal conductivity, substantial volume fluctuations, and liquid release during their phase transitions [30].

a) Paraffin: This chemical is produced as a by-product of the petroleum refinement. It has the formula of C_nH_{2n+2} , where, n denotes the number of carbons (C) in the molecule, and is composed of single bonds connecting carbon and hydrogen atoms. The substance is gaseous, when n is between 1 and 4; liquid when n is between 5 and 17; and solid when n is greater than 17. Paraffin wax is a material with a n value ranging from 20 to 40.

b) Fatty Acids: With the formula $CH_3(CH_2)_{2n}COOH$, it has a long hydrocarbon chain of hydrogen and carbon atoms, ranging from 10 to 30. The carboxyl group (COOH) at the end of the chain provides protection, making PCMs based on fatty acids non-toxic, having a limited corrosive activity, and being chemically and thermally robust. Moreover, they are present in natural goods and are not derivatives of fossil fuels. There are saturated and unsaturated fatty acids. Unsaturated fatty acids have lower melting temperatures due to their molecular structure,

which permits closer molecular interactions. Additionally, PCMs with a variety of melting temperatures can be produced by combining different fatty acids.

Table 1.3: List of organic PCMs [31]–[35]

PARAFFIN-BASED PCMs				
Material	Formula	Molecular Weight (g.mol ⁻¹)	Melting Point (°C)	Latent Heat (kJ.kg ⁻¹)
n-Tetradecane	C ₁₄ H ₃₀	198.4	5.5	226
n-Pentadecane	C ₁₅ H ₃₂	212.4	10	205
n-Hexadecane	C ₁₆ H ₃₄	226.4	16.7	237
n-Heptadecane	C ₁₇ H ₃₆	240.5	22	215
n-Octadecane	C ₁₈ H ₃₈	254.5	28.2	245
n-Nonadecane	C ₁₉ H ₄₀	268.5	31.9	222
n-Eicosane (ESE)	C ₂₀ H ₄₂	282.5	37	247
NON-PARAFFIN-BASED PCMs				
PEG 400	H(OCH ₂ CH ₂) _n OH (n=8.7)	380-420	8	100
Caprylic Acid	CH ₃ (CH ₂) ₆ COOH	144.2	16	148
PEG 600	H(OCH ₂ CH ₂) _n OH (n=13.2)	500-600	17-22	127
1-Dodecanol	CH ₃ (CH ₂) ₁₁ OH	186.33	26	200
D-Lactic Acid	C ₃ H ₆ O ₃	90.1	26	184
Capric Acid (CA)	CH ₃ (CH ₂) ₈ COOH	172.3	32	152.7
Lauric Acid (LA)	CH ₃ (CH ₂) ₁₀ COOH	200.3	42-44	178
Myristic Acid (MA)	CH ₃ (CH ₂) ₁₂ COOH	228.4	49-51	205
PEG4000	H(OCH ₂ CH ₂) _n OH (n=69-84)	3000-4800	53-59	174.2
Palmitic Acid (PA)	CH ₃ (CH ₂) ₁₄ COOH	256.4	64	185.4
Stearic Acid	CH ₃ (CH ₂) ₁₆ COOH	284.5	69	202.5
Xylitol	HOCH ₂ [CH(OH)] ₃ CH ₂ OH	152.1	94	263
Erythritol	HOCH ₂ [CH(OH)] ₂ CH ₂ OH	122.1	120	340

c) Sugar Alcohols: Sugar alcohols can also be used as PCMs. They are the hydrogenated form of carbohydrates and have a hydroxyl group attached to each carbon atom. It is chemically represented as HOCH₂[CH(OH)]_nCH₂OH. They melt at temperature between 90 and 200 °C. They have more latent heat since they are denser.

d) Polyethylene Glycol (PEG): PEG, sometimes referred to as polyethylene oxides or polyoxyethylenes, is a condensation polymer of ethylene glycol. They have the chemical formula $[\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O}) \text{M}_n-\text{H}]$, where the subscript M_n denotes their average molecular weight. PEGs are hydrophilic, toxic, and possess minimal supercooling. Their thermal conductivity is around $0.205 \text{ W.m}^{-1}.\text{K}^{-1}$, and they have a flash point of 182°C and beyond. They have excellent thermal stability, and their cost is determined by their molecular weight [36].

1.3.3.2. Inorganic PCMs

Metals, salts, and salt hydrates are the three categories of inorganic PCM. This type of material has fewer benefits than organic PCM like high heat of fusion, good thermal conductivity, non-flammable. Conversely, phase separation, corrosion, sub-cooling, and lack of thermal stability are all drawbacks, but their higher phase change enthalpy is an asset [37], [38].

a) Salt Hydrates: Salt hydrates are odourless, crystalline and coloured ionic substances that can be encountered in nature, or prepared from aqueous solutions of the suitable salts (Table 1.4). An inorganic salt and water of crystallization bound together by dipole–dipole interactions form the repeating crystal structure of salt hydrates. The formula $\text{X}_n\text{Y}_m.a\text{H}_2\text{O}$ describes the inorganic salts that contain water molecules in a particular ratio as part of the crystal, where X stands for the cation, Y for anion, and a for the amount of water molecules. In a salt hydrate, the phase transition occurs during the heating cycle when the bonds between the salt and the crystallized water break at a specific temperature and the salt dissolves into that liquid water. The temperature at which it occurs is known as the salt hydrate's melting point, despite the fact that no melting occurs. The point at which the salt hydrate recrystallizes by regaining its initial water of crystallization is referred to as the freezing point, much like the freezing point during the cooling cycle. Salt hydrates are considered fire retardants since they release water. They are very hydrophilic and metal-corrosive. The stoichiometric balance of water during crystallization can be disrupted by a small amount of moisture, which results in the salt hydrate losing its capacity to retain heat. They show comparatively minimal volume change during the phase transition, and their thermal conductivity is between 0.5 and $1 \text{ W.m}^{-1}.\text{K}^{-1}$ [39].

Two major problems with salt hydrates are super-cooling and incongruent mixing. The latent heat is not released when the salt hydrate does not crystallize at all or crystallizes at a temperature much below than the expected phase transition temperature. This process is known

as supercooling, and it occurs during a rapid cooling cycle. When the separated anhydrous salt does not dissolve into the water during the heating cycle, incongruent mixing occurs, resulting in a two-phase system. Consequently, crystallization is no longer possible in such a system. Incongruent mixing is mostly caused by differences in density between salt and water, which can be prevented by using thickening agents [40]. The thermal stability of salt hydrates is substantially enhanced by using adequate thickening and nucleating agents.

Table 1.4: List of salt-hydrates utilized as inorganic PCMs [6], [31]–[33]

Material	Formula	Molecular Weight (g.mol ⁻¹)	Melting Point (°C)	Latent Heat (kJ/kg)
Potassium fluoride tetrahydrate	KF.4H ₂ O	130.16	18.5	231
Manganous nitrate hexahydrate	Mn(NO ₃) ₂ .6H ₂ O	287.04	25.8	125.9
Calcium chloride hexahydrate	CaCl ₂ .6H ₂ O	219.08	29.0	190.8
Calcium bromide hexahydrate	CaBr ₂ .6H ₂ O	307.97	34	115.5
Sodium sulphate decahydrate	Na ₂ SO ₄ .10H ₂ O	322	32.4	254
Lithium nitrate hexahydrate	LiNO ₃ .6H ₂ O	68.95	30	296
Sodium carbonate decahydrate	Na ₂ CO ₃ .10H ₂ O	286.14	34.2	246.5

b) Salts: The chemical formula for anhydrous salts is A_xB_y, where "A" stands for an s or d-block metal and "B" for a p-block non-metal or a cation complex. Anhydrous salts are white, amorphous solids. These salts can be obtained from salt hydrates or extracted from natural sources. At high temperatures, salts undergo a phase change that results in a molten liquid with dissociated ions when the ionic link between A and B is disintegrated. Salts having melting points that are either near or lower than the ambient air temperature are known as ionic liquids. When melted, they are highly reactive and corrosive. They are highly hydrophilic and sensitive to moisture. The range of their thermal conductivity is 0.6 to 1 W.m⁻¹.K⁻¹. These salts are used for higher temperature ranges since their enthalpy is lower than that of salt hydrates [36]. An example of high-temperature energy storage is a concentrated solar power plant that stores energy in salt for later use.

c) **Metals:** The massive atomic structure of metals is held together by strong metal bonding and breaking them requires the large amount energy. The energy required for metals to transition phases is far higher than that of non-metals. This form of inorganic PCM includes metals with low melting points and metal eutectics (**Table 1.5**). When volume is an issue in the system, they are excellent candidates to be considered for higher temperatures of phase transition because of their high heat of fusion per unit volume. The characteristics of this type of PCM are low specific heat, high thermal conductivity and low vapor pressure. Metal PCM was primarily employed in electronic systems.

Table 1.5: List of metals served as inorganic PCMs [36], [41]

Material	Molecular Weight (g.mol ⁻¹)	Melting Point (°C)	Latent Heat (kJ.kg ⁻¹)
Cesium	132.9	28.5	16.4
Gallium	69.7	30	80.3
Rubidium	85.5	38.8	25.7
Potassium	39.1	63.2	59.6
Indium	114.8	156.8	28.6
Tin	118.7	232	60.5

1.3.3.3. Eutectic PCMs

Eutectics are a group of chemical mixtures or constituents that have a single chemical configuration that crystallizes at a lower temperature than any other configuration developed via the same constituents. There are three conceivable pairings: inorganic–inorganic, organic–organic, and inorganic–organic [42]. The organic-organic eutectic PCMs are made up of two or more organic components whose melting points are lower than those of their constituents and which melt and solidify cohesively. The organic eutectic PCM can be easily tailored to the ideal temperature range with a high latent heat of fusion per unit volume. The main components of organic eutectic PCM include fatty alcohols, fatty acids, amides, paraffin, ester and so forth. When these constituents are combined in the appropriate proportions, binary, ternary eutectic PCMs can be produced. Organic eutectic PCMs are frequently used in low and medium-temperature applications. There may be two or more inorganic components in the mixture of inorganic-inorganic PCMs. The main components used in the manufacture of inorganic-inorganic eutectic PCM are metals, salt hydrates, and molten salts. Although they typically

have a higher energy density than organic PCMs, the main drawbacks of inorganic-inorganic eutectic PCMs are their supercooling degree and phase instability. The inorganic-inorganic eutectic PCM is worthwhile for a larger range of temperature applications, particularly in high-temperature applications, due to its substantial latent heat and good thermal conductivity. There is a minimum of one organic or inorganic component in the organic-inorganic eutectic PCM. The investigation revealed that organic-inorganic eutectic PCM is uncommon, owing to the incompatibility of organic and inorganic materials [43]. Numerous eutectic blends are well-known in cooling applications and can be employed as PCM (Table 1.6).

Table 1.6: List of eutectic PCMs [33], [44], [45]

Material	Composition	Melting Point (°C)	Latent Heat (k.kg ⁻¹)
Na ₂ SO ₄ +NaCl+KCl+H ₂ O	31+13+16+40	4	234
Na ₂ SO ₄ +NaCl+NH ₄ Cl+H ₂ O	32+14+12+42	11	n.a.
C ₅ H ₅ C ₆ H ₅ +(C ₆ H ₅) ₂ O	26.5+73.5	12	97.9
Na ₂ SO ₄ +NaCl+ H ₂ O	37+17+46	18	n.a.
Ca(NO ₃) ₃ .4H ₂ O+Mg(NO ₃) ₃ .6H ₂ O	47+53	30	136

1.3.4. Merits and Demerits of Organic, Inorganic and Eutectic PCMs

PCMs are broadly classified into organic, inorganic, and eutectic types, each exhibiting distinct advantages and limitations, as illustrated in the Figure 1.6. Organic PCMs, such as fatty acids and paraffins, are characterized by chemical stability, congruent melting, negligible supercooling, and good compatibility with container materials; however, their relatively low thermal conductivity and potential flammability restrict heat transfer efficiency and large-scale applications. Inorganic PCMs, including salt hydrates and metallic PCMs, offer higher LHS density and superior thermal conductivity, making them suitable for compact thermal storage systems, but issues such as phase segregation, supercooling, corrosiveness, and poor long-term cycling stability remain major drawbacks. Eutectic PCMs, formed by combining two or more components, provide sharp melting points and tunable phase change temperatures with relatively high latent heat; nevertheless, their complex preparation routes, limited

thermophysical data, and potential component separation during repeated thermal cycling hinder widespread utilization.

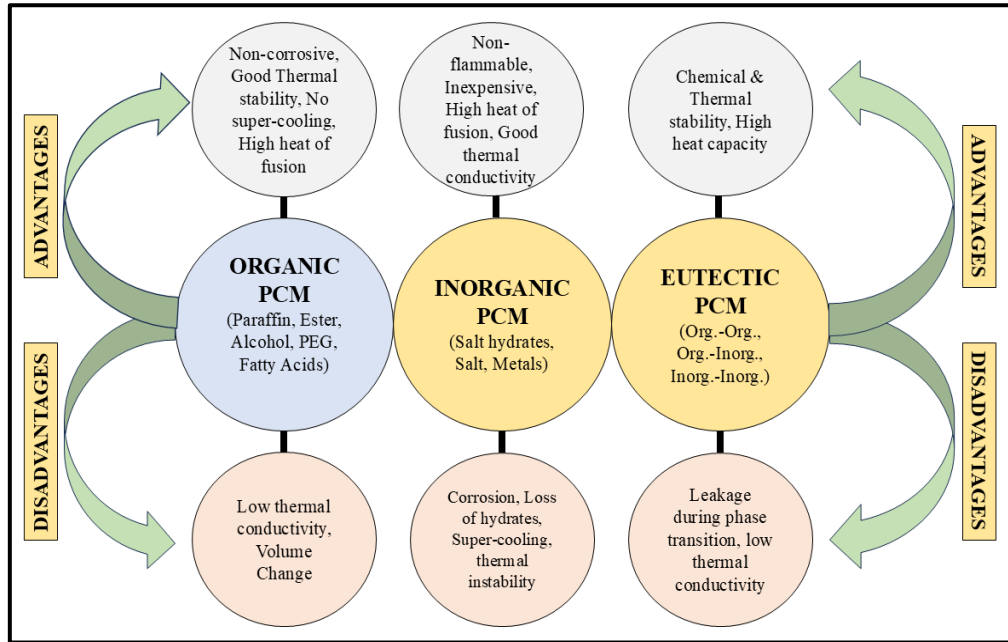


Figure 1.6: Pros and cons of different types of PCMs

1.3.5. Problems Associated with PCMs

Despite offering several advantages over conventional SHS systems, PCMs-based latent heat TES systems suffer from multiple limitations that restrict their large-scale implementation, particularly in applications. These challenges arise from intrinsic material properties as well as practical and economic constraints. The major problems associated with PCM-based TES systems are summarized below [46]:

1.3.5.1. Leakage

One of the most critical drawbacks of solid-liquid PCMs is their tendency to leak during phase transition. Upon melting, the PCM turns into a liquid state, which can escape from the storage medium, leading to contamination of the surrounding environment and deterioration of system performance [47]. Leakage not only compromises thermal reliability but also poses environmental and safety concerns, especially in wearable and textile-based applications. To

mitigate this issue, PCMs are commonly encapsulated within polymeric or inorganic shells, which physically confine the molten phase and enhance structural integrity.

1.3.5.2. Supercooling

Supercooling is another major limitation of PCMs, particularly during the discharge process. In this phenomenon, the liquid PCM cools below its melting temperature without undergoing solidification, thereby remaining in a metastable state. As a result, the latent heat of fusion is not released at the expected temperature, leading to inefficient heat extraction [48]. Supercooling occurs due to sluggish nucleation rates or slow crystal growth, or a combination of both [49]. If the degree of supercooling exceeds a few degrees, the heat release process can be significantly delayed or even completely inhibited. The extent of supercooling is influenced by several factors, including heat transfer area, cooling rate, operating temperature, and the presence or absence of nucleating agents.

1.3.5.3. Incongruent Phase Change

Incongruent phase change represents another significant challenge in PCM storage systems. For effective TES, the phase change temperature of the PCM must align with the operational temperature range of the application. Incongruent melting leads to irreversible phase separation of components during repeated melting and solidification cycles, which reduces the reversibility of the phase transition. This, in turn, diminishes the LHS capacity over time. Therefore, PCMs with congruent melting behavior are preferred to ensure stable and repeatable thermal performance throughout prolonged operational cycles.

1.3.5.4. Long-Term Stability of Thermal Properties

Long-term thermal and chemical stability is a crucial requirement for PCM-based storage systems. The usable lifetime of the PCM container system and the number of thermal cycles it can endure without degradation significantly influence its practical applicability [50]. Both the PCM core and the encapsulating shell must withstand repeated melting and freezing cycles without loss of latent heat capacity, phase change temperature shift, or mechanical failure. Degradation may occur due to poor material stability under cyclic thermal stress, corrosion of the container material, or chemical incompatibility between the PCM core and the shell material, all of which adversely affect system durability.

1.3.5.5. High Cost

The relatively low thermal conductivity of most PCMs necessitates the use of heat transfer enhancement techniques, such as the incorporation of conductive fillers, fins, or metal foams. While these approaches improve thermal performance, they substantially increase the overall system cost. Consequently, PCM-based TES systems must demonstrate clear economic advantages to compete effectively with traditional SHS technologies, particularly for large-scale or commercial applications.

1.3.5.6. Other Limitations

Additional challenges associated with PCMs include abrupt volume changes during the solid–liquid phase transition, which can induce mechanical stress and structural failure in containment systems. Liquid flow or ramping during melting may further complicate heat management and material stability. Moreover, corrosion of metallic containers and supporting structures due to chemical interactions with certain PCMs can limit material selection and increase maintenance requirements.

1.3.6. Methods for PCM Protection and Stable TES

To overcome the inherent limitations of PCMs such as leakage, poor thermal stability, and phase segregation; several protection and storage strategies have been developed. Encapsulation techniques (nano-, micro- or macro-encapsulation) physically confine the PCM within a protective shell, thereby preventing leakage, improving thermal reliability, and enhancing chemical compatibility with the surrounding medium. In addition, shape-stabilized PCMs, achieved by embedding PCMs into porous or polymeric supporting matrices, retain their structural integrity during phase transitions, effectively eliminating liquid seepage and improving long-term cycling stability.

1.3.7. Encapsulation of PCMs

The most efficient way to address the aforementioned PCM problems is to encapsulate the PCM with supporting materials. Encapsulation is the process of enveloping small particles or droplets of PCM with a covering material or encasing them in a homogeneous or heterogeneous matrix to provide miniature capsules with beneficial properties [51]. Encapsulated PCMs (EPCMs) typically consist of a core and a shell. The substance that fills the capsules is called

the internal phase, core, whereas the wall is occasionally referred to as a membrane, shell or coating (**Figure 1.7**).

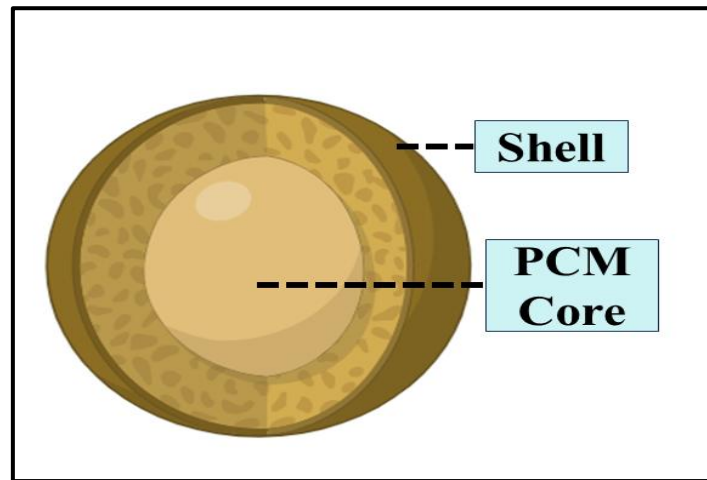


Figure 1.7: Core-shell structure of PCM

1.3.7.1. Selection of Shell Materials for Encapsulation

In encapsulation, more than fifty distinct polymers—both natural and synthetic—can be utilized as wall materials. The materials used for shell coating must meet certain standards. The polymer must be stable, malleable, odourless, and able to produce a thin layer that is cohesive with the core material. It should be soluble in a solvent or aqueous medium, non-reactive with the core material, and chemically compatible. Additionally, it should offer the required coating qualities, including stability, strength, flexibility, impermeability, and optical qualities. Depending on other physical properties of the system and the surface area of the substance to be coated, the film thickness can vary significantly. Additionally, the shell coating material must be inexpensive, medium/low viscosity, and non-hygroscopic [52].

a) Organic Shells: Typically, organic shell materials are composed of both natural and synthetic polymeric materials that exhibit significant structural flexibility, good sealing capabilities, and high resistance to volume change caused by repeated phase transitions of PCMs. Commonly utilized organic shell materials include acrylic resin, urea-formaldehyde (UF) [53], and melamine formaldehyde (MF) [54]. The advantages of MF resin include its low cost, chemical compatibility, and thermal stability [36].

b) Inorganic Shells: There are a number of limitations on the use of microcapsules with organic shells due to their restricted thermal conductivity, poor mechanical properties, and flammability. [36]. In recent years, the production of microcapsules has consistently relied on inorganic shells as an alternative. Compared to biological materials, inorganic materials frequently exhibit thermal conductivity, higher mechanical strength and stiffness. Zinc oxide (ZnO) [55], silica (SiO₂) [56], calcium carbonate (CaCO₃) [57] and titanium dioxide (TiO₂) [58] are the commonly employed as inorganic shell materials.

c) Organic-Inorganic Hybrid Shells: To address the disadvantages of both organic and inorganic materials and combine their benefits, researchers have begun encapsulating PCMs in organic–inorganic hybrid shells. In hybrid organic–inorganic shells, inorganic materials can improve thermal conductivity, mechanical rigidity while organic materials can enhance structural flexibility and thermal stability [36], [59].

1.3.7.2. Encapsulation Methods

Three categories of EPCMs can be distinguished based on particle size (**Figure 1.8**):

- Nanoencapsulated PCM (NPCM) (particle size between 1 to 1000 nm)
- Microencapsulated PCM (MPCM) (particle size between 1 to 1000 µm) and
- Macroencapsulated PCM (MacroPCM) (particle size surpasses 1 mm) [60].

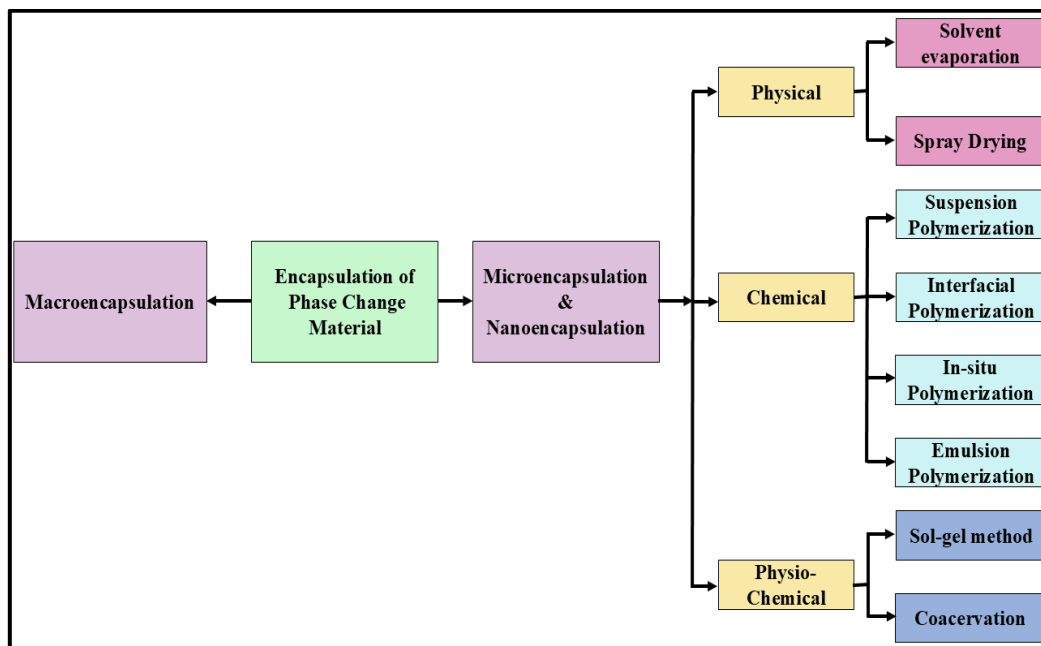


Figure 1.8: Encapsulation methods of PCMs

a) Macroencapsulation

Macroencapsulation is the process of encasing a PCM in a container larger than 1000 μm . The outcome is called a MacroPCM. These containers have spherical, rectangular or tubular geometry and can be stiff, like hollow spheres, panels, or cans or flexible, like tubes, pouches or envelopes as illustrated in **Figure 1.9**. Macroencapsulation can be achieved using either metallic or non-metallic materials. Materials with low thermal conductivity, including ceramics and glass, should be avoided. The thermal conductivity of rigid metallic containers, such as copper, aluminium, and steel, is high. Non-metallic containers can be rigid or non-rigid and are composed of numerous kinds of polyolefins. To acquire desirable properties, metallic and non-metallic materials can be mixed. For example, aluminium foil pouches layered with a plastic sheet [36].

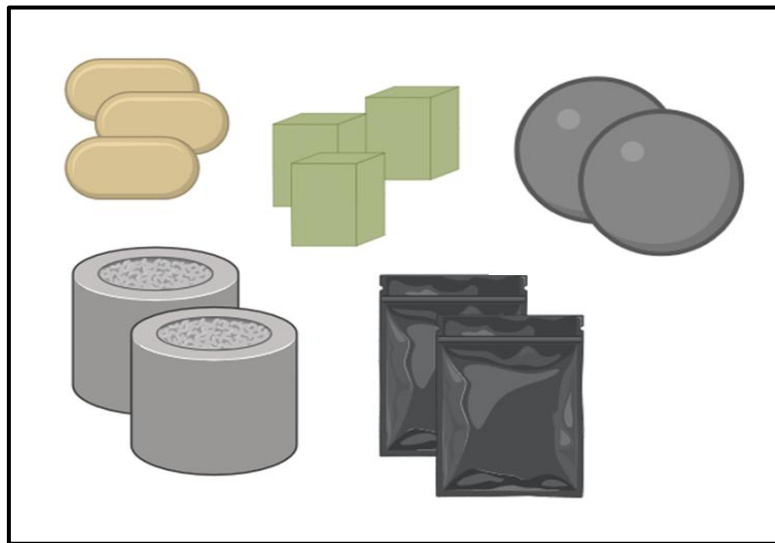


Figure 1.9: Macroencapsulation of PCMs

MacroPCMs are produced by pouring molten PCM into prefabricated shells and sealing the container in an inert atmosphere. This inhibits oxygen and other reactive gases from getting trapped inside the PCM-containing capsule. The PCM should not be overloaded in order to accommodate the expansion of volume that takes place during the phase change. Compared to micro-encapsulated PCMs, macroPCMs are simpler and more affordable to manufacture and recycle, although container rupture is always a risk during production, shipping, or installation

[61]. The geometry of the container greatly affects the phase change properties, and the shape of the container for macroPCMs is much more flexible. The PCM's ability to store heat may be diminished if an inappropriate container geometry is selected. MacroPCMs partially melt PCMs due to their low surface-to-volume ratio, which lowers their heat conductivity. This drawback can be addressed by adding fins to the exterior of the capsule to increase its surface area or by adding thermally conductive materials, such as carbon fiber chips, graphite flakes, metal foam, metal matrix, lessing rings, metal powder and so on, inside the capsule. MacroPCMs are primarily utilized in construction applications including business centers, greenhouses and factories. They can be incorporated into hollow bricks, windows, doors, roofs, walls, ceilings, floors, and fake ceilings, among other things. Additionally, cold compress pouches and ice packs use macroPCMs [62].

b) Microencapsulation

The technique is referred to as microencapsulation when PCM particles or droplets of PCMs are encased or immersed in a uniform matrix, resulting in microcapsules less than 1000 μm in size. A variety of microcapsule morphologies such as particles with irregular cores, diverse cores enclosed within a single capsule, multi-walled microcapsules, simple spheres covered with uniform thickness, and particles embedded in a continuous matrix are represented in **Figure 1.10**. The basic spherical particle is the most common type of microcapsule [41], [63].

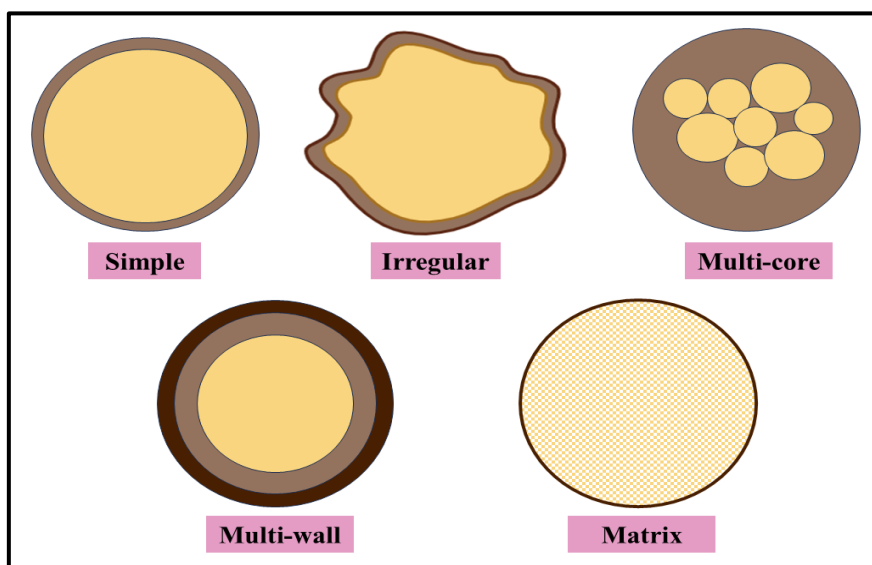


Figure 1.10: Morphology of MPCMs

c) Nanoencapsulation

The shell coating materials must form a thin, stable, and cohesive covering around the core material to protect PCMs. According to certain studies, pumping and raising the final fluid's viscosity can cause MPCMs to disrupt. Consequently, NPCMs with particle sizes ranging from 1 to 1000 nm have been the focus of contemporary study. These PCMs offer distinctive energy management and storage topologies, a large specific surface area, excellent suspension stability and low pumping breakage rate [36].

1.3.7.3. Methodologies of Microencapsulation/Nanoencapsulation of PCMs

EPCMs can be synthesized in three primary ways: chemical, physical, and physio-chemical shown in **Figure 1.8**.

1.3.7.3.1. Physical Methods

The physical methods mechanically condenses the shell over the core component to produce microcapsules with a mean diameter of greater than 100 μm . Solvent evaporation and spray drying processes are commonly employed physical techniques [64].

a) Solvent Evaporation: Bioactive materials exploited in the pharmaceutical sector are frequently microencapsulated using the solvent evaporation and phase separation process. Using this process, oil droplets are produced by dissolving the polymer in a core material (PCM) with the aid of an appropriate solvent, then adding the mixture to a water solution containing surfactant while stirring. As seen in **Figure 1.11**, the solvent's evaporation caused the internal phase separation in the polymer/PCM/solvent droplets. The interaction between the polymer, core, and aqueous phases through interfacial tension results in the phase separation of the polymer-rich portion. Thus, the formation of core/shell MPCMs structure with entirely polymer shell coverage depends on the interfacial tension and polarity of the polymer within the PCM droplets [65]. The synthesized MPCM can occur in three different surface morphologies: (i) acorn-shaped, (ii) core/shell, and (iii) golf ball-like. The polarity, molecular weight, and interfacial tension of the polymer shell, concentration and emulsifier type all have a significant impact on the surface shape of microcapsules [66]. Quan et al. [67] used an eco-friendly solvent evaporation approach to create a variety of PCM/PMMA microcapsules with a range of latent heat (144.13–217.70 $\text{J}\cdot\text{g}^{-1}$) and phase transition temperatures (20–70 $^{\circ}\text{C}$) for TES applications.

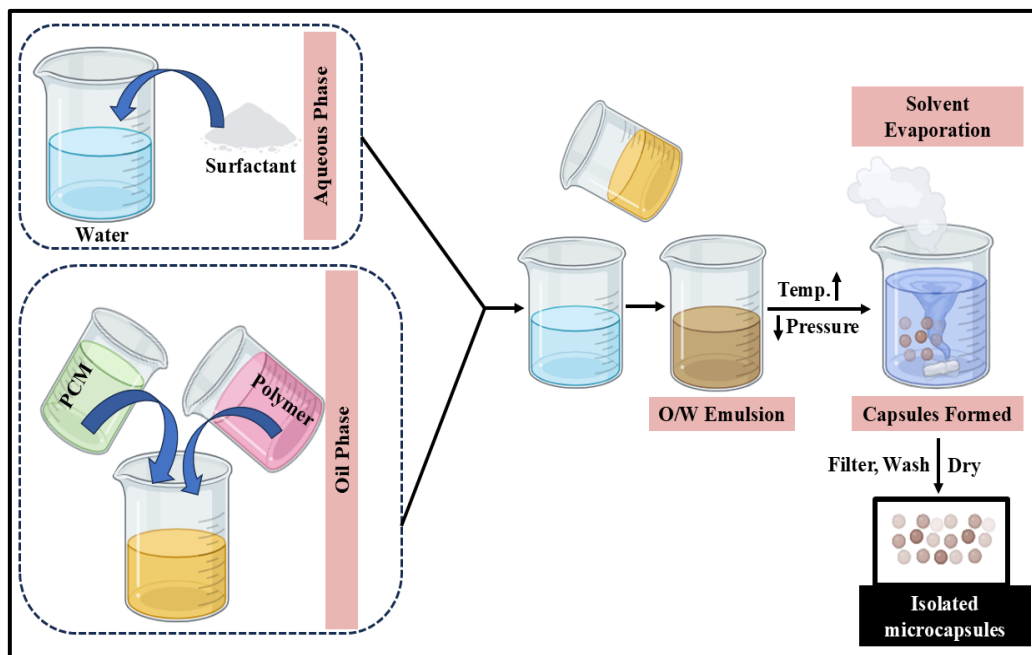


Figure 1.11: Mechanism to produce microcapsules by solvent evaporation technique

Xing et al. [68] encapsulated eutectic mixture of CA and PA by polyvinyl chloride. The optimum composition was microcapsules with a 1:2 ratio, which melted at 17.1 °C (92.1 J.g⁻¹ enthalpy of fusion), crystallizes at 18.8 °C (91.3 J.g⁻¹ enthalpy of crystallization), and yielded an encapsulation ratio of 57.7%. Salaun et al. [69] produced microparticles loaded with sodium phosphate dodecahydrate utilizing various organic solvents and cellulose acetate butyrate crosslinked with methylene diisocyanate as a coating polymer.

b) Spray Drying: This synthesis method begins with the preparation of an emulsion of PCM in a solution that contains the shell material, such as gelatin, using mechanical stirring at a high rpm of 10,000. Drops of a binder, such as gum-arabica, will be introduced while maintaining the proper pH and temperature. After that, this emulsion will be fed at a specific feed rate to an atomizing nozzle. The feed solution is sprayed into a drying chamber at the atomizer as tiny droplets by a high-pressure carrier gas (air or nitrogen). When sprayed droplets in the drying chamber come into contact with the hot drying gas (air or nitrogen), evaporation occurs on the droplet's surface until the moisture content is too low to diffuse through the dried droplet surface. Consequently, the core that produces MPCM is surrounded by a shell. Lastly, the dried MPCM is recovered using an electrostatic precipitator, filter bag, or cyclone [70].

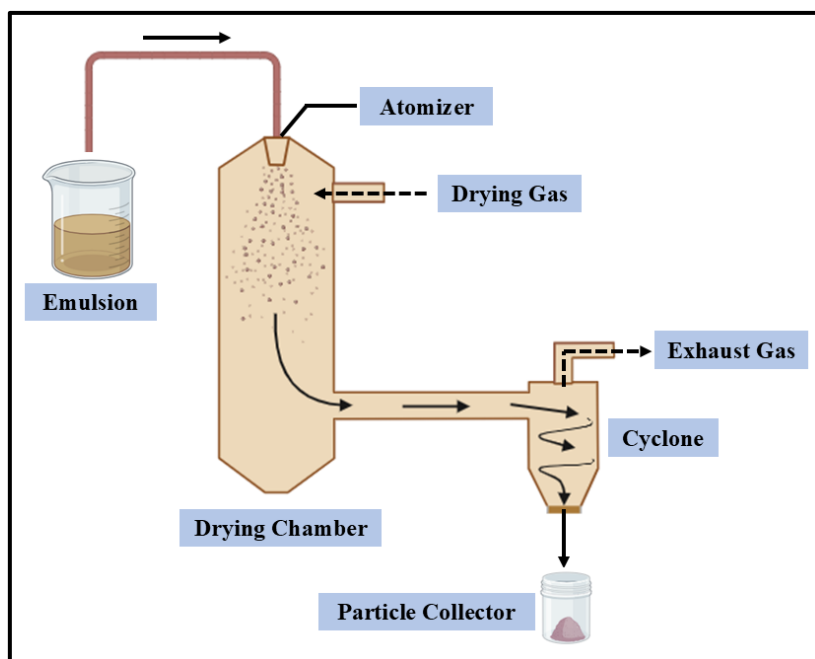


Figure 1.12: Schematic representation of the spray drying process

A sample spray drying apparatus is shown in **Figure 1.12**. A good atomizer design can achieve the desired particle size distribution (PSD), and the process is easily controllable and scalable. Borreguero et al. [71] employed a spray drying process to microencapsulate paraffin PCM both with and without carbon nanofibers utilizing polyethylene-EVA as a polymer shell, resulting in high microencapsulation efficiency while minimizing waste production. Machado et al. [72] produced microcapsules from raw and concentrated red cabbage (RC) extracts, as well as various quantities of maltodextrin and arabic gum. The glass transition temperature between 37 and 90 °C supported the findings, which showed that the interaction between maltodextrin and arabic gum improved the microparticles' thermal stability. Methaapanon et al. [73] investigated the use of sol-gel emulsion in conjunction with spray-drying to microencapsulate methyl palmitate and n-octadecane in SiO₂ shells for passive cooling applications. With an initial PCM to SiO₂ weight ratio of 0.25, the prepared MPCM had the maximum encapsulation efficiency.

1.3.7.3.2. Chemical Methods

These techniques are entirely chemical in nature. Here, free radicals can activate the polymerization by attacking the monomers in response to a trigger, such as a change in pH or heating. This kind of process is known as radical polymerization. Radical polymerization can be divided into two types: suspension polymerization and emulsion polymerization. Other

widely used chemical synthesis methods, including as interfacial polymerization and in-situ polymerization, have also been utilized to encapsulate PCM. Encapsulation can occasionally be achieved by combining several chemical methods [70]. Each of the synthesis methods is explained in further detail below.

a) Suspension Polymerization: When both initiators and monomers are either poorly soluble or insoluble in an aqueous phase solvent, this approach is suggested. The most common liquid used as a solvent is water. Consequently, in this process, monomer, PCM and initiator form the oil phase during emulsification and are suspended as distinct droplets in the continuous aqueous phase (**Figure 1.13**). Continuous mechanical stirring and the addition of surfactants, or emulsifiers, can help in emulsification. This technique is referred to as radical polymerization. When a trigger, like as heat, is applied, initiators release free radicals into the solution, which initiates the polymerization. Common suspension polymerization initiators include 2,2-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO), both are poorly soluble in water. This process is commonly employed with organic shell materials such as polymethylmethacrylate (PMMA). Tanwar et al. [74] synthesized the microcapsules of caprylic acid via suspension polymerization technique, which was surrounded by PMMA shell. Differential scanning calorimetry (DSC) data revealed that the microcapsules contained 66 wt % PCM core encapsulation, and their respective latent heats were 98.7 and 99.0 J. g⁻¹. Their melting and crystallization temperatures were 14.3 and 9.7 °C, respectively.

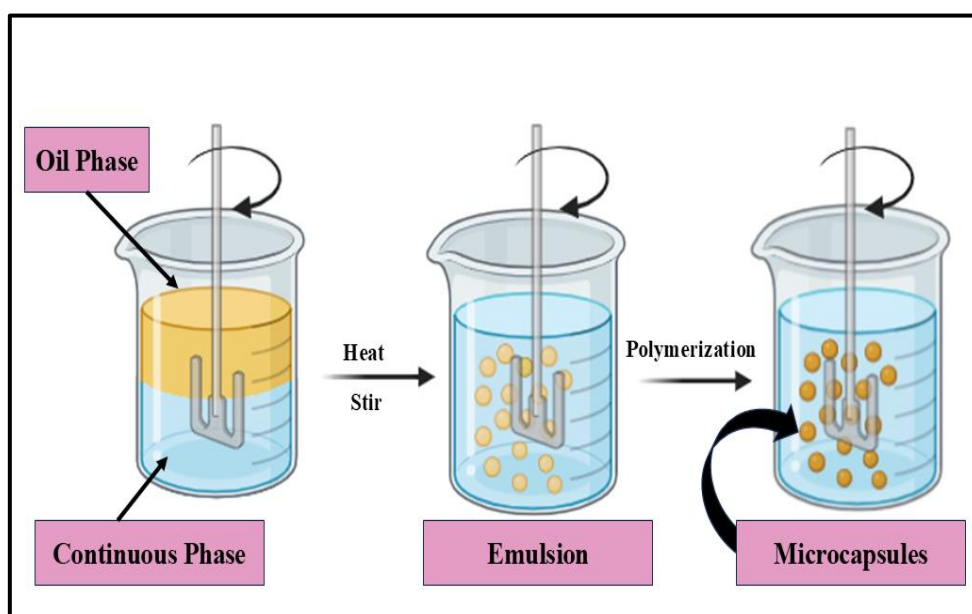


Figure 1.13: Schematic illustration of the suspension polymerization technique

Al-Shannaq et al. [75] successfully microencapsulated the paraffin inside the PMMA polymer shell. A system of mixed surfactants was found to promote monodispersed droplet size distribution and long-term emulsion stability. Ding et al. [76] developed the phase change sub-microcapsules by varying the core PCM including paraffin and docosane with poly(isobornyl methacrylate) shell without high-speed stirring (≥ 1000 rpm) and ultrasonication. The produced sub-microcapsules had submicron particle sizes ranging from 326.5 to 920.6 nm and a uniform spherical microcapsule shape.

b) Interfacial Polymerization: This approach is effective when the final shell polymer has two or more monomers, and when one of the monomers is hydrophilic and the other is hydrophobic. The most common liquid used as a solvent is water. The oil phase is formed by hydrophobic monomers and PCM during emulsification. The aqueous phase contains dissolved hydrophilic monomers. Therefore, as depicted in **Figure 1.14**, the two reactive monomers separated in two immiscible media that only react at the interface between two solutions to form a thin film at the surface. However, the polymer film acts as a barrier to impede the polymerization process as it proceeds. As a result, this type of polymerization may result to form extremely thin shells. This process is usually applied to organic shell materials such as polyurethane and polyurea.

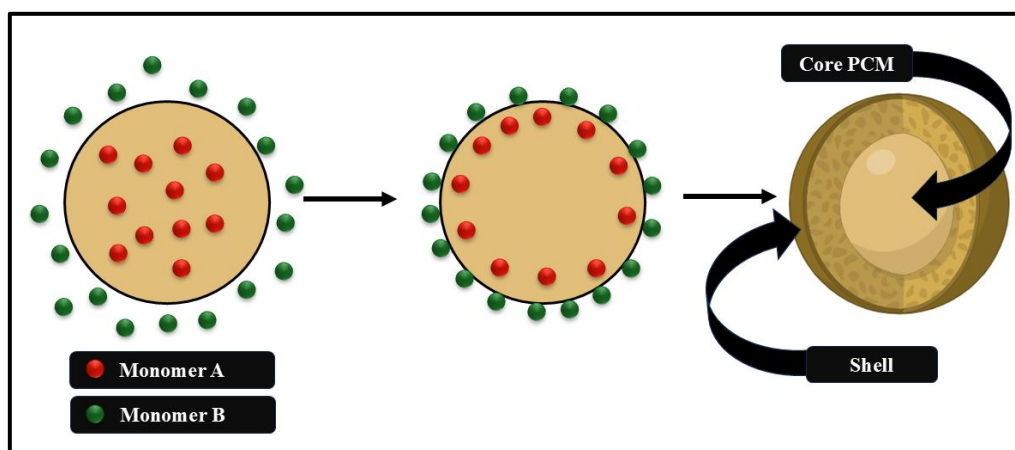


Figure 1.14: Schematic diagram of the interfacial polymerization process for encapsulating PCMs

Shi et al. [77] concentrated on developing paraffin@PMMA nanocapsules using a facile, one-step interfacial polymerization process that didn't require any particular environment protection. Based on the findings, it was verified that the best nanocapsules were made using a

4:3 MMA/PCM mass ratio and 800 rpm stirring speed. Cai et al. [78] used solvent free synthesis route to microencapsulate dodecanol dodecanoate within polyurea shell. The resulting MPCM shown high temperature resistance with an onset evaporation temperature of 234.0 °C and an average latent heat in the range of 103.4–140.3 J.g⁻¹. Ho et al. [79] entrapped the ESE PCM inside the UF polymer shell. It was observed that increased PCM suspension concentrations lead to higher specific and latent heat values.

c) In-situ Polymerization: By polymerizing the prepolymers, the in-situ polymerization method creates a shell on the droplet's surface. This can be achieved in the following steps, as shown in **Figure 1.15**: (1) preparing the O/W emulsion by adding PCMs to surfactant aqueous solution; (2) preparing a prepolymer solution; (3) adding the prepolymer solution to the O/W emulsion following the proper reaction conditions; and (4) microcapsule synthesis.

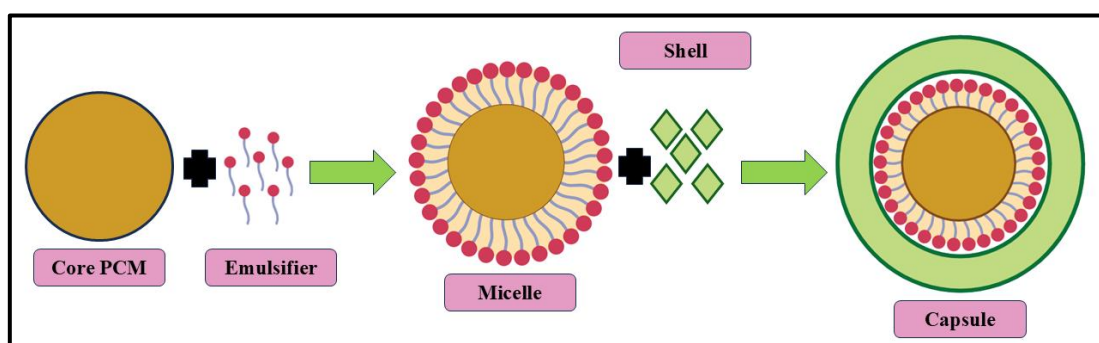


Figure 1.15: Schematic diagram of the in-situ polymerization process for encapsulating PCMs

Liu et al. [80] adopted in-situ polymerization approach to prepare microcapsules composed of ESE core and a phenol formaldehyde (PF) resin shell. According to this study, with a 1% emulsification concentration, an agitation speed of 1000 rpm and a core/shell mass ratio of 3:6.47, the maximum encapsulation and energy storage efficiencies were achieved at 84.2% and 83.4%, respectively. Kumar et al. [81] microencapsulated the 1-dodecanol with MF shell. The microcapsules exhibited thermal stability up to 132.82 °C, which was significantly higher than the pure PCM's operational temperature range. Trivedi et al. [82] designed the MPCM by encasing dimethyl adipate, an organic ester inside the MF shell. The outcomes observed from the experimental investigation was that the MPCM1 and MPCM2 with the shell to core ratio 1.287 and 0.967, reflected the latent heat enthalpy of around 53 J.g⁻¹, 70 J.g⁻¹ and the phase change temperatures as 6.73 °C, 6.35 °C respectively.

d) Emulsion Polymerization: This approach is recommended when the initiator is soluble in an aqueous phase solvent but the monomers are either insoluble or poorly soluble. Water is the most often used solvent. Therefore, during emulsification, only the PCM and monomers form the oil phase, which is dispersed as discrete droplets in the continuous aqueous phase (**Figure 1.16**). The aqueous phase dissolves initiators. Continuous mechanical stirring and the use of surfactants (emulsifiers) can facilitate emulsification. This technique is recognized as radical polymerization. When a trigger, like as heat, is applied, initiators release free radicals into the solution, which instigates the polymerization.

Initiators that are readily soluble in water, such as sodium thiosulphate, ammonium persulphate, and ferrous sulphate, are commonly employed in the emulsion polymerization. Usually, this technique is applied to organic shell materials such as polystyrene (PS) and PMMA.

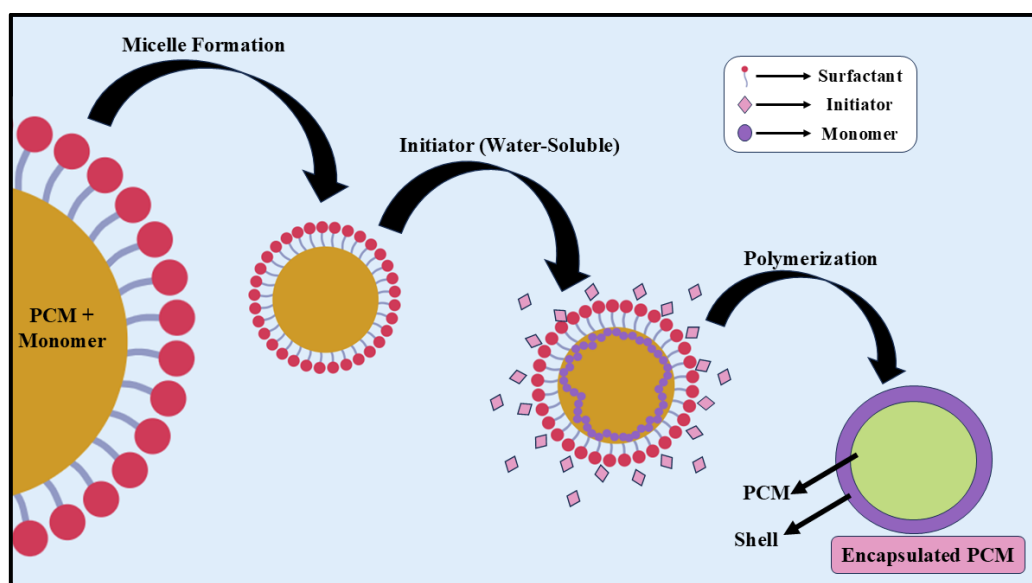


Figure 1.16: Schematic diagram of the emulsion polymerization technique for micro/nanoencapsulating PCMs

Sari et al. [83] designed three types of micro-nanocapsules with PS shell material and fatty acid (CA, LA, and MA) as a core material at three distinct monomer/PCM ratios. The maximum encapsulation ratios of MA, CA and LA into the capsules were found to be 48.7, 45.4 and 43.5 weight percent, according to the DSC data. Konuklu et al. [84] adopted an emulsion copolymerization approach to generate a set of four nanocapsules containing n-alkanes: heptadecane, hexadecane, pentadecane and tetradecane in poly(styrene-co-

ethylacrylate) shell. The impact of the core/shell mass ratio on the nanocapsules' phase change characteristics was the main focus of this study. Ding et al. [85] selected methylacrylic acid as copolymer to produce the paraffin based MPCM. The average MPCM particle size was determined as 42.29 μm , and the paraffin content of the microcapsules was reported as 57.6%. Following the conventional emulsion polymerization, the mini-emulsion polymerization has emerged as a particularly effective route for the synthesis of MPCM and NPCM. In this technique, the monomer/PCM mixture is dispersed into much finer and kinetically stable droplets (typically in the 50–500 nm range) through high-energy input such as ultrasonication or high-shear homogenization, in the presence of a surfactant and a co-stabilizer. Unlike emulsion polymerization that occurs in micelles, mini-emulsion polymerization proceeds predominantly within these preformed nanodroplets, which act as individual nanoreactors. This feature enables efficient encapsulation of PCMs, minimizes Ostwald ripening, and allows precise control over capsule size, shell thickness, and morphology. As a result, the mini-emulsion polymerization is especially suitable for producing PCM capsules with high encapsulation efficiency, reduced leakage during phase transition, and enhanced thermal reliability, making it a preferred method for advanced TES and smart material applications. Karaipekli et al. [86] studied the NPCM of n-nonadecane with poly(styrene-co-methacrylic acid) shell. The latent heat of crystallization and melting for the produced NPCM were determined as 87.4 and 89.1 J.g^{-1} , respectively, while the phase change temperatures ranged between 32.16 and 32.42 $^{\circ}\text{C}$. Şahan et al. [87] investigated the microcapsules of stearic acid with four different types of PMMA based hybrid shell materials. The main goal of their study was to ascertain how the shell material affects the microstructure. Additionally, the results verified that the various functional groups of PMMA hybrids regulate particle surface potential and geometry because of variations in surface tension and polarity. Cervera et al. [88] reported the encapsulation of two organic PCM (i.e. hexadecane and octadecane) in poly(3,4-ethylenedioxythiophene) nanoparticles (NPs) by miniemulsion oxidative polymerization. The results obtained revealed that the conductive NPs formed possess a spherical and homogeneous morphology without the presence of aggregates.

1.3.7.3.3. Physio-Chemical Method

Physio-chemical procedures combine physical and chemical techniques in a hybrid way. Encapsulation is accomplished by combining chemical processes like condensation, hydrolysis, cross-linking, etc. with physical processes like cooling, phase

separation, heating etc. The two most common physio-chemical methods for PCM microencapsulation are sol-gel and complex coacervation.

a) Coacervation: This method is also known as the phase separation method. Agar-agar/gum-Arabic, chitosan/gum-Arabic, chitosan/silk-fibroin, gelatine/gum-Arabic, and other combinations of organic shell materials are commonly used. Two or more polyelectrolytes with opposing charges (polycation and polyanion) interact during coacervation. Usually, Arabic gum (acacia) is the polyanion and gelatine is the polycation. This process involves dissolving the shell polymer material in a solvent to produce a solution. The aforementioned solution is combined with the PCM material to form an emulsion. The dissolved shell is precipitated on the surface of the PCM droplets by vaporizing the solvent and forming a shell around the PCM. There are two types of coacervation processes: a simple one and a complex one. Both processes use the same mechanism for microcapsule synthesis, with the exception of how the phase separation is carried out. In simple coacervation, phase separation is accomplished by a dissolving agent. Conversely, complexation between two polymers with opposite charges is a complex coacervation (**Figure 1.17**).

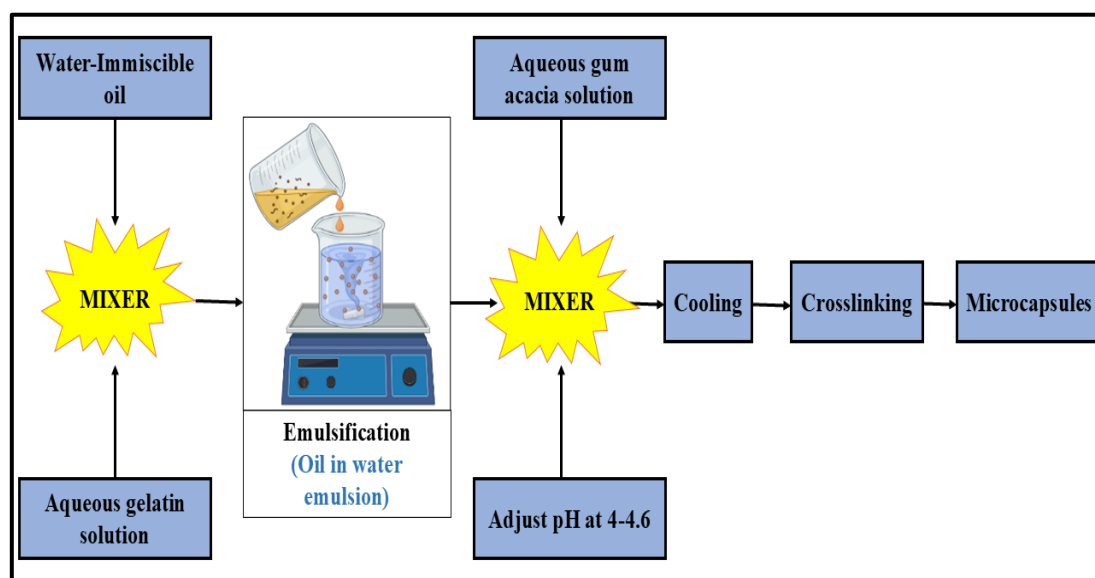


Figure 1.17: Schematic representation of the complex coacervation method for microencapsulating PCMs

Malekipirbazari et al. [89] synthesized PCM microcapsules employing a complex coacervation technique, using gelatin/acacia as the covering material and paraffin wax as the core material.

This study examined the effects of several synthesis parameters on encapsulation efficiency, including crosslinking agent, emulsification time, and core-to-shell ratio. It was found that as the core/shell ratio increased, the need for cross-linking agent reduced, and the emulsification duration increased excessively and the encapsulation efficiency of the produced microcapsules declined. Wu et al. [90] investigated the innovative microencapsulated reversible thermochromic PCMs (RTPCM) which involves 2,2-bis(4-hydroxyphenyl)propane as a color developer, 2-phenylamino-3-methyl-6-di-n-butylamino-fluoran as a color former, and 1-hexadecanol as a co-solvent and PCM. A complex coacervation of modified gelatin and gum arabic produced the RTPCM microcapsules. This was followed by a primary crosslinking reaction between the vinyl groups of modified gelatin and divinyl crosslinker, followed by a subsequent crosslinking with glutaraldehyde, which shows good stability and high encapsulation efficiency.

b) Sol-Gel Method: This method involves first preparing a sol solution, which, when added to PCM emulsion, results in a gel of distinct microcapsules with PCM droplets inside, as shown in **Figure 1.18**. Usually, this technique is applied to inorganic shell materials such as TiO_2 and SiO_2 .

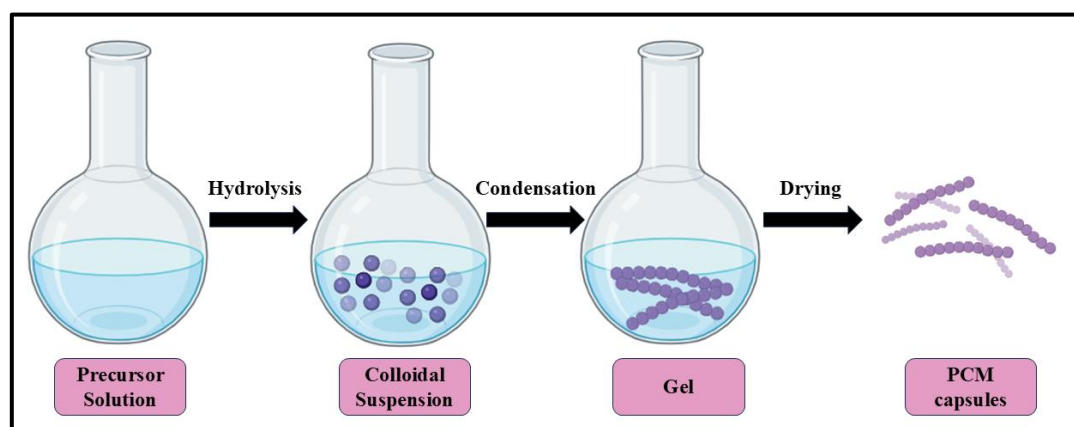


Figure 1.18: Schematic diagram of the sol-gel approach for encapsulating PCMs

The sol solution is made by hydrolyzing precursor compounds such as sodium silicate, methyl triethoxysilane, tetraethylorthosilicate, etc. To encourage the hydrolysis reaction, a low pH (2–3) is maintained in the sol solution. Next, drop by drop, the silicate sol solution is introduced to a PCM O/W emulsion while the emulsion is continuously stirred to avoid the formation of any continuous gel and to solely enable discrete SiO_2 gel walls to form around PCM droplets.

When the SiO₂ solid particles undergo condensation polymerization, a SiO₂ shell will form on the surface of the PCM droplets. The emulsion is kept at a high pH (9–10) in order to promote the condensation reaction. He et al. [56] used sodium silicate precursor to prepare n-octadecane microcapsules by sol-gel technique. The microcapsules exhibited exceptional anti-osmosis properties and strong thermal conductivity due to the thick and compact SiO₂ wall of the produced MPCM. Subramanian et al. [91] fabricated three different compositions of MPCMs containing MA as core and strontium titanate (SrTiO₃) as shell material. DSC investigation verified that the microencapsulated particles of MA@SrTiO₃ with 1:2 ratio had a latent heat of fusion of 91.90 J.g⁻¹ and a higher melting temperature of 53.41 °C compared to its counterparts. Pourmohamadian et al. [92] successfully synthesized microencapsulated PA with SiO₂ shell in alkaline medium using the sol-gel process and sodium silicate precursor. According to thermogravimetric analysis (TGA), these microcapsules decomposed in a single step and showed good thermal resistance. The microcapsule generated at pH 11 had the lowest char yield of 54 wt% at 550 °C due to the maximum PA loading among three samples.

1.3.8. Shape-Stabilized PCMs (SSPCMs)

SSPCMs represent an advanced class of latent heat TES materials developed to overcome the leakage issues commonly associated with conventional solid–liquid PCMs. In SSPCMs, the PCM is physically confined within a solid supporting matrix, allowing it to undergo repeated melting and solidification cycles while maintaining an overall solid form. This characteristic enables the material to retain its structural integrity even when the PCM undergoes a solid–liquid phase transition, thereby preventing leakage and improving long-term operational reliability [93], [94].

The shape stabilization mechanism in SSPCMs is primarily governed by the physical absorption, capillary forces, and surface tension effects between the PCM and the supporting matrix. The molten PCM is adsorbed onto the internal surfaces and confined within the pore network of the matrix, which restricts its mobility during melting (**Figure 1.19**). There are four types of porous skeleton materials often used in SSPCMs: Carbon-based three-dimensional porous materials, such as graphene aerogels, foamed graphite, expanded graphite (EG), and foamed carbon; metal foam porous materials, which include foam nickel-based, aluminum-based, and copper-based; Porous ceramic materials, such as porous clay mineral ceramic materials [expanded perlite (EP), diatomite (DT), expanded vermiculite (EV)], porous oxide and non-oxide ceramic materials (MgO, SiO₂, SiC); organic polymer materials, such as

polyaniline, PMMA, high density polyethylene, and polyethylene terephthalate. These materials provide interconnected porous or network structures capable of retaining the PCM through strong interfacial interactions, thereby ensuring dimensional stability during phase transition [95]. **Table 1.7** summarizes the numerous SSPCM synthesized using different supporting materials.

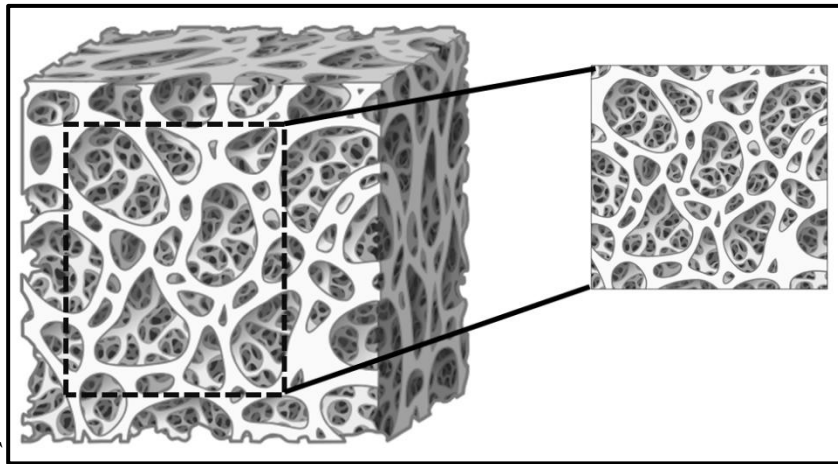


Figure 1.19: Porous structure of the SSPCMs

Compared to MPCMs or NPCMs, SSPCMs offer several advantages, including relatively simple fabrication routes, higher PCM loading capacity, and enhanced thermal conductivity, particularly when thermally conductive supports such as EG or carbon-based materials are used. Improved thermal conductivity promotes faster heat charging and discharging rates, which is essential for efficient TES and release. In addition, SSPCMs generally exhibit good thermal reliability, mechanical stability, and resistance to repeated thermal cycling [32], [96].

SSPCM have attracted significant attention for applications in building energy conservation, solar TES, thermal management of electronic devices, and smart textile systems [97]. In building materials, SSPCMs can be directly incorporated into wallboards, cementitious composites, and insulation panels to improve indoor thermal comfort and reduce energy consumption [98], [99]. In wearable and textile applications, SSPCMs provide effective temperature regulation without the risk of leakage, thereby enhancing user safety and durability [100].

Despite their notable advantages, SSPCMs also present certain limitations. The presence of an inert supporting matrix may reduce the overall LHS capacity per unit mass compared to pure PCMs. Additionally, excessive PCM loading beyond the adsorption capacity of the supporting material may lead to leakage. Therefore, careful optimization of matrix selection, pore structure, and PCM loading ratio is crucial to achieving optimal thermal performance. Overall, SSPCMs offer a practical and reliable approach for leakage-free TES in a wide range of engineering applications [97].

Table 1.7: Numerous SSPCMs synthesized using different supporting materials

S.No.	PCM	ΔH_m (PCM; J.g ⁻¹)	Supporting Material	ΔH_m (SSPCM; J.g ⁻¹)	Ref.
1.	n-Octadecane	228.21	Poly(triallyl isocyanurate-silicone)	137.99	[101]
2.	PEG	183.42	Porous Carbon	91.80	[102]
3.	PEG 6000	221.3	MgO Mg(OH) ₂	129.0 134.90	[103]
4.	N,N-bis(2-hydroxyethyl)dodecanamide	143	Polyamide 12	111	[104]
5.	LA & Stearic Acid (69/31)	162.8	Carboxy methyl cellulose-1	114.6	[105]
6.	Rubitherm® RT35HC; Rubitherm® RT44HC; MA and PA (61:39)	236 270 196	EG	206 220 159	[106]
7.	OH-64 (60 wt% OM-18 and 40 wt% hexadecane)	170.43	EG	161.07	[107]
8.	PEG 1000	187.3	EG	141.7	[108]
9.	PEG 6000	190.08	EG	145.14	[109]
10.	LA	141.9	DT	57.4	[110]

1.3.9. Applications of PCMs

PCM nanocapsules or microcapsules expand the range of PCM applications due to their unique characteristics, which include greater energy alterations, thermal and chemical stability, and a suitable solid-to-liquid phase transition [111]. PCM capsules reduce lethality and protect the core component from the environment while integrating liquid and solid PCMs with polymers

and other basic materials in a secure and effective way. Some of the prospective applications of PCM microcapsules are as illustrated in **Figure 1.20**.

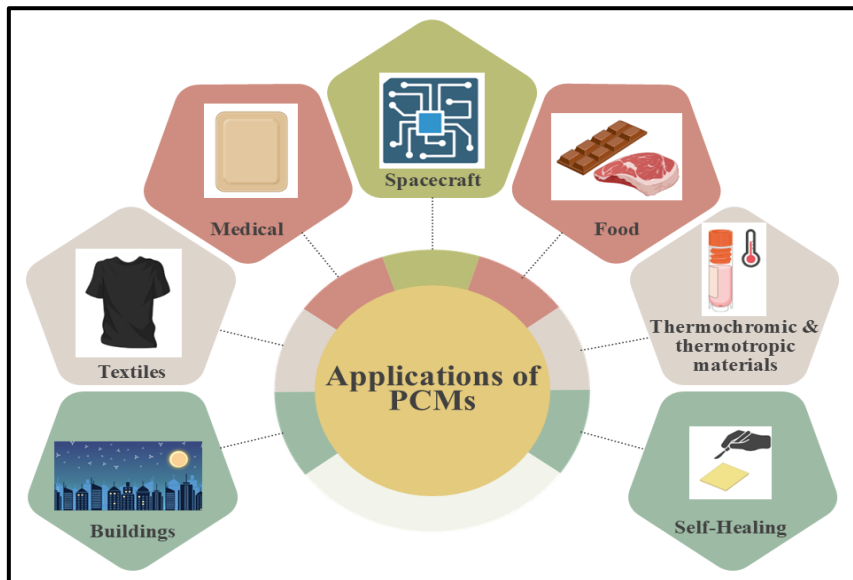


Figure 1.20: Applications of PCMs in different sectors

1.3.9.1. Buildings

The building sector (commercial and residential) consumes about 115 EJ of energy worldwide in 2010, according to estimates from the International Energy Agency. This accounted for 32% of the world's energy consumption [112]. 32–33% of the energy utilized in buildings was used for heating and cooling purposes. Therefore, any improvement in this sector's efficiency can lower environmental pollution and have a significant impact on the world's energy demand. Integrating the idea of thermal mass—which provides inertia against temperature fluctuations—into building designs is one method to boost the efficiency of heating and cooling. For the same mass of structures, PCMs with a high TES density close to the thermal comfort temperature range are perfect for optimizing thermal inertia. MPCMs and NPCMs are integrated into gypsum boards, flooring, panels, wallboards, drywalls, concrete, insulation panels, ceilings etc. Even though direct impregnation (i.e. PCM without encapsulation), is less expensive, there are concerns about the unprotected PCM's long-term stability and its detrimental effects on building materials. For instance, high alkalinity affects the stability of

PCM such as fatty esters and fatty alcohols in concretes containing calcium hydroxide. Building materials are adversely affected by inorganic PCM due to its corrosive nature. Organic PCM materials are flammable and may emit harmful fumes upon combustion. Furthermore, as the temperature rises above the PCM melting point, leakage problems arise due to the porous nature of the building materials like mortar that include PCM. The mechanical strength of concrete may also be weakened by direct PCM impregnation. Attempts to employ MacroPCM were not very effective due to the low thermal conductivity of PCM. The PCM crystallized around the edges and hindered efficient heat transfer when it came time to recover the heat from the liquid phase. MPCM provides a solution to these problems because it is leak-proof and resistant to ignite. Microencapsulation of PCM boosts its compatibility with building materials, optimizes its long-term stability, and also resolves the conductivity concerns [70]. Salihi et al. [57] developed an energy-efficient mortar infused with MPCMs to raise TES capacity and enhance the indoor thermal performance of building envelopes. CaCO_3 was used as the shell material to produce MPCMs under controlled circumstances. The following are the main conclusions of this study: (i) Testing the MPCMs-enhanced mortar in a semi-arid region showed that it might increase building envelope thermal efficiency, with an average maximum temperature drop of 1.6 °C inside the test cell. (ii) The MPCMs-enhanced mortar effectively stores and releases thermal energy through both sensible and latent heat methods, with LHS makes a considerable contribution (23.9%) to the overall energy storage capacity.

1.3.9.2. Textiles, Clothes and Footwear

PCM capsules are employed in textiles that regulate body temperature. In addition to indoor clothing like pillowcases, blankets, mattresses and duvets, it is utilized for the protection against extremely cold temperatures in outdoor apparel including gloves, parkas, boots, vests, ear warmers, snowsuits, hunting clothing, trousers and ski wear [113]. Additionally, PCM-containing textiles aid in preventing overheating. Encapsulated PCM can be embedded into fabric in two different methods. PCM capsules were directly embedded within fiber or were coated on the surface of fabric [31]. **Table 1.8** represents the overview of the PCM applications across diverse textile industry sectors as reported by various researchers.

Table 1.8: PCMs applications in different textile industry sectors

S.No.	Material	Synthesis Method	Fabric	Fabrication	Application	Ref.
1.	Paraffin, Copper oxide (CuO)-doped polyurea	Interfacial polymerization	Cotton	Coating	Intelligent textiles, such as spacesuit, mountaineering wear, medical textiles, and other technical textiles	[114]
2.	Trimethylolethane hydrate, MF-UF	In-Situ polymerization	Polyester	Knife-over-roll coating	Smart textiles	[115]
3.	Cellulose nanofiber-stabilized paraffin emulsion	Pickering emulsion	Polyester	Spray Coating	Thermal regulating textile	[116]
5.	ESE and a Eu^{3+} -doped $\text{CaCO}_3/\text{Fe}_3\text{O}_4$	Pickering emulsion-templating in-situ precipitation method	Polyester	Paste-coating	Bifunctional applications: thermal regulation and fluorescent recognition in advanced textiles	[117]
6.	N-octadecane, melamine-formaldehyde resin and single layer graphene oxide	-	Viscose fiber	Wet Spinning	For underwear garments fabrics and filling storage sheet	[118]
7.	PEG1000 and Polyamide 6	Composite	Nanofiber	Coaxial electrospinning	Sensitive thermal management applications	[119]
8.	Octadecane, Pectin/SA and Alginate/SA	Composite	Polyester	Silk screen printing technique.	For pillows and mattresses or compressed sheets	[120]
9.	ESE, Aerogel	Composite	Woven Fabric	SV-MATIS coating machine	Firefighter's protective garment	[121]
10.	Paraffin, PMMA	-	Cotton	Screen Printing Method	Hospital Bed Sheet	[122]

1.3.9.3. Medical Field

PCM is regarded as a promising material for several biomedical applications demanding thermal protection, like specific bandages or burn wound dressings. Numerous PCMs have been documented for usage in the biomedical area, including microencapsulated PCMs for medication storage, delivery, and thermal protection of tissues around tumours during

cryosurgery [123], [124]. Temperature-regulated textiles are beneficial for burn treatment, and heat/cool therapy because they can maintain the skin's temperature within the appropriate range [125].

1.3.9.4. Spacecraft Applications

New spacecraft system applications can take advantage from the latest developments in PCM research and development. In the field of heat rejection and removal, spacecraft can benefit from high thermal conductivity materials, high heat transport systems such as capillary heat pipes, loop heat pipes, fixed conductance heat pipes, and passive coatings with low absorptivity to emissivity. Salt hydrate-based PCMs are more appropriate for use in spacecraft transportation [36]. PCM's applications in aeronautical technology include:

- Optimize the efficiency of the radiator and fluid-loop systems
- Nano/Microsatellites
- Onboard power generation by employing thermal energy
- Architecture for universal thermal control of spacecraft
- Electronic components functioning in cyclical conditions
- Accurate dimensional stability

Rostamian et al. [126] concentrated on developing microcapsules for temperature regulation of satellite electronic boards at a critical temperature of 55 °C. They successfully produced a series of microcapsules with eutectic LA and SA as the core and a MF shell using an in-situ polymerization procedure. The MPCM with the highest encapsulation ratio was picked to control the electronic board temperature in order to assess the performance of the produced microcapsule. According to their findings, the MPCM-based heat sink caused a 74%, 133%, 220%, and 100% delay in attaining the critical temperature when operating at constant electric power levels of 4, 6, 8, and 10 W.

1.3.9.5. Food Industry

PCMs have been tested in the food sector as heat storage and conveyance systems for packaging applications, chilling storage units, and heat processing sections [111]. Yadav et al. [127] employed emulsion polymerization technique to nanoencapsulate the eutectic PCM of n-dodecanol and cetostearyl alcohol with PMMA shell. The resulted NPCM with the core: shell ratio of 1.75:1 demonstrated the higher enthalpy of 134.0 J.g⁻¹, with an encapsulation ratio of

69.5%. Therefore, the prepared nanocapsules powder was used to analyze the thermal buffering test of eutectic PCM and NPCM inside a temperature-controlled packaging (TCP) box. A thermal buffering test was employed to examine the power-charging and discharging capabilities of NPCMs. The 90 g powder nanocapsules used for the charging/discharging test were evenly dispersed throughout the six low-density polyethylene packets that were attached to the box's interior wall. The packets' dimensions were 80 mm × 80 mm × 80 mm, with a thickness of 1.6 mm. When the chocolate-containing box was exposed to an ambient temperature of 30 ± 2 °C, it was seen that the polyethylene packets containing NPCM (90 g of total) provided thermal buffering to the chocolate in the TCP box (total 160 g) for 65.21 minutes.

1.3.9.6. Thermochromic and Thermotropic Materials Applications

Reversible thermochromic microcapsules find extensive applications in textiles, inks, color indicators, cement, luminous thermos-sensors and intelligent coatings. Thermochromism refers to the reversible change in color of a material in response to temperature variations [128], [129]. Thermochromic systems are classified as direct or indirect, depending on whether the color change is caused by direct thermal stimulation or by temperature-induced changes in the surrounding environment. Indirect thermochromic systems are multicomponent assemblies include developer, leuco dye and solvent in a certain ratio, whereas direct systems consisting of liquid crystals and molecular rearrangements. In such systems, the solvent acts as a phase-change medium, and the color transition temperature is governed by its melting and crystallization behavior [130]. Thermochromic MPCMs are commonly synthesized via in-situ polymerization, with crystal violet lactone, bisphenol A, and 1-tetradecanol forming the core components [131]. Chromogenic materials also show strong potential in solar control glazing applications [132], [133]. Compared to thermochromic systems, thermotropic materials based on light reflection and scattering offer improved solar regulation by autonomously switching from transparent to light-scattering states at a threshold temperature, thereby effectively reducing overheating in buildings and solar thermal collectors [36].

1.3.9.7. Self-Healing

One of the most intriguing applications for EPCMs is self-healing. Self-healing composites may overcome concealed damage, micro-cracking, and the most severe restrictions of polymeric structural materials. To encourage healing, an epoxy matrix is mixed with a chemical

catalyst and an encapsulating healing ingredient. Isocyanate and amine are stabilized using an inverse Pickering emulsion. The amine core microcapsules are produced by the interfacial polymerization of the isocyanate and amine, which are subsequently separated, dried, and redispersed in epoxy [41]. Li et al. [134] adopted a solvent evaporation process to produce a series of microcapsules with PMMA as the shell material and polyetheramine as the core material and a liquid curing agent. The resultant microcapsules demonstrated excellent thermal and curing agent storage stability. The highest healing efficiency of 93.50% was achieved with microcapsules containing 15 wt% epoxy. Thereby, the microcapsules carrying liquid curing agent can be used effectively to generate epoxy-based self-healing composites. Hettiarachchi et al. [135] used two alternative methods to produce CaCO_3 microcapsules to encapsulate the EPX healing agent and hardener: the soft-template method (ST- CaCO_3) and the in situ emulsion method (EM- CaCO_3). The healing agent ARALDITE 506 was loaded into microcapsules of EM- CaCO_3 and ST- CaCO_3 , which were then integrated into a polymer matrix (EPX) to form thin EPX composite coatings that exhibit self-healing property and serve as a barrier against metal corrosion. The EPX composite coatings that were developed with 20 (w/w%) and 50 (w/w%) ST- CaCO_3 demonstrated superior healing capabilities. Therefore, it was observed that ST- CaCO_3 microcapsules performed better than EM- CaCO_3 . Furthermore, the EPX/ CaCO_3 coatings displayed outstanding self-healing characteristics by filling the spaces between the scratch surfaces.

1.4. Significant Findings from Literature

The literature demonstrates considerable progress in the synthesis of EPCMs using a wide variety of core-shell combinations, synthesis techniques, and PCM-to-shell ratios. Several approaches, including emulsion-based polymerization, interfacial polymerization, and in-situ polymerization methods, have been explored to tailor the thermal and structural properties of EPCMs. However, despite the advancements, many reported systems exhibit relatively low encapsulation ratios and efficiencies, primarily due to incomplete shell formation, PCM leakage, or suboptimal material incompatibility, as summarized in **Table 1.9**.

Table 1.9: EPCMs designed by using various core-shell ratios and fabrication techniques

Encapsulated Phase Change Materials						
PCM	Shell	PCM: Shell	Method	Particle Size	Encapsulation Ratio/ Efficiency	Ref.
Caprylic Acid	PMMA	1:1	Suspension Polymerization	3.9 μ m	E _E = 66%	[74]
n-Octadecane	Poly(stearylmethacrylate) with Pentaerythritol triacrylate (PETRA) and divinylbenzene (DVB)	1:1	Suspension Polymerization	5 μ m 21 μ m	E _E = 36.3% E _E = 40.6%	[136]
n-Octadecane	PMMA (with PETRA) 10%TiO ₂ doped PMMA	1:1	Suspension Polymerization	10–20 μ m	E _E = 73.2% E _E = 43.1%	[137]
Paraffin Wax	MF	1:1	In-Situ Polymerization	260–450 nm	E _E = 75%	[138]
Tetradecane	UF	1:1	In-Situ Polymerization	-	E _R = 61.8%	[139]
Paraffin Wax	UF	1:1	In-Situ Polymerization	6.07 μ m	E _R = 66.5%	[140]
ESE	PF	3:6.47	In-Situ Polymerization	0.1~0.15 μ m	84.2; 83.4%	[80]
CA-MA mixture	CuO-UF	1:1	In-Situ Polymerization	-	E _R = 60.9%	[141]
ESE	CuO-doped polyurea	1:1	Interfacial Polymerization	10 -15 μ m	74.9; 74.7%	[114]
Na ₂ HPO ₄ ·12 H ₂ O	SiO ₂	4:1 3:1 2:1 1:1	Interfacial Polymerization	200–350nm	E _R = 35.1% E _R = 38.2% E _R = 48.8% E _R = 27.9%	[142]
Paraffin	PS	-	Emulsion Polymerization	< 1 μ m	E _R = 40%	[143]
ESE	PMMA	1:1	Mini-Emulsion Polymerization	135nm	E _R = 62%	[144]
n-dotriacontane	PS	1:1	Mini-Emulsion Polymerization	168.2 nm	95.0; 61.2%	[145]
n-Octadecane	Poly(ethyl methacrylate) and PMMA	80: 20	Mini-Emulsion Polymerization	140 nm 119 nm	89.5; 88.9% 94.7; 93.6%	[146]
PA	SiO ₂ (pH=11)	1:1	Sol-Gel	183.7nm	83.2; 82.5%	[147]

	pH=11.5 pH=12)			466.4nm 722.5nm	85.2; 84.3% 89.5; 88.3%	
ESE	TiO ₂	60:40 50:50 40:60	Sol-Gel	1.5–2μm	77.9; 77.6% 65.6; 65.2% 49.9; 49.4%	[148]
NaNO ₃	SiO ₂	1:0.5 1:0.25	Sol-Gel	0.2-0.5μm 0.5–1μm	E _R = 15.9% E _R = 18.3%	[149]
NaNO ₃ and KNO ₃	SiO ₂	-	Sol-Gel	1560nm	57.5; 56.8%	[150]

Table 1.10: SSPCMs synthesized by different supporting materials

PCM	PCM Melting Temperature	Supporting Material	Varying content wt%	Maximum PCM loading concentration	Ref.
Paraffin	18 and 28 °C	EP	3,5,7,9,11	5%	[151]
CaCl ₂ ·6H ₂ O- NH ₄ Cl- SrCl ₂ ·6H ₂ O mixture	23.46	EG EP	0-8 (NH ₄ Cl) 0, 0.5, 0.8, 1.0, 1.2, 1.5 (SrCl ₂ ·6H ₂ O)	45% EP 12% EG 95 wt% CaCl ₂ ·6H ₂ O- 4 wt% NH ₄ Cl-1 wt% SrCl ₂ ·6H ₂ O	[152]
Paraffin	41.11	DT	SSPCM incorporated into cement: 10, 15, 20, 30	0.9:1.0	[153]
Paraffin	44	Supporting material: Olefin block copolymer Filler: EG with different mess number-50, 100, 200	EG: 4, 7, 10	10wt% EG with mess number 50	[154]
CA	30.92	Supporting material: DT Filler: Carbon Nanotubes (CNTs)	DT: 42, 44, 46, 48 CNTs: 1, 3, 5, 7	54% CA+ 46%DT (7% CNTs)	[155]
Beeswax	60-62	Multi-walled CNTs (MWCNTs)	-	5% CNTs	[156]
Tetradecylamine Octadecylamine	39.2 55.1	MWCNTs 1 st level oxidation: p-MWCNTs 2 nd level oxidation: a-MWCNTs	pMWCNTs: 3 aMWCNT: 3 cMWCNTs: 0.5, 1, 3, 5, 7	3% cMWCNTs	[157]

		3 rd level oxidation: c-MWCNTs			
CA	30.71	Kaolin	10-30	17.5	[158]
PEG600	5.16			21	
Heptadecane	22.08			16.5	
CA-MA-Stearic acid	22.92	EV, EV/Carbon Composite, EV/Carbon Composite with Acid Treated	-	Eutectic and Supporting matrix is 2:1. Thermal conductivity: > EV/Carbon Composite with Acid Treated	[159]
Sodium nitrate	306.4	EV	Sodium Nitrate to EV is varying from 30: 1 to 5: 1.	Adsorptive capacity of EV to sodium nitrate= 734.6%	[160]

Similarly, SSPCMs developed by using different supporting materials have shown improved shape stability for specific applications; nevertheless, the incorporation of supporting matrices often limits the effective utilization of the PCM phase (**Table 1.10**). These observations highlight that achieving high encapsulation efficiency while maintaining structural and thermal reliability remains a key challenge, thereby justifying the need for further optimization in PCM design and synthesis.

These gaps highlight the significance of producing new and improved PCMs, notably organic-based systems, capable of meeting the demands of pragmatic TES applications. Even though organic PCMs, such as paraffins, possess attractive properties such as chemical stability, non-corrosive nature, high latent heat and negligible supercooling, but their extensive application is still constrained by few serious challenges including low thermal conductivity, seepage during phase transition and insufficient mechanical strength. Therefore, it is imperative to construct sophisticated organic PCM systems by employing strategies such optimal encapsulation and polymer shell design that boost long-term reliability, thermal performance and structural stability. Addressing these problems while retaining the inherent benefits of organic materials is critical for developing reliable, efficient and sustainable next-generation TES systems.

1.5. Research Gaps

Recent literature clearly demonstrates a growing shift toward organic PCMs encapsulated within polymeric shells for TES applications, driven by their chemical stability, processing

flexibility, and application adaptability. However, as highlighted in **Tables 1.9 and 1.10**, the majority of these systems still suffer from low encapsulation ratio and efficiency, revealing a critical disconnect between material selection and application-ready performance. These limitations stem primarily from inadequate shell design and weak interfacial compatibility, which restrict effective PCM confinement under practical operating conditions.

Although polymeric shells are inherently attractive for flexible, lightweight, and application-specific thermal management systems, existing encapsulation strategies largely fail to translate these advantages into high-performance products. Majority of studies emphasize material combinations rather than performance-driven capsule engineering, leaving a significant gap in the optimization of polymer-based shells capable of maximizing PCM utilization while ensuring structural and thermal reliability.

In addition, the slow thermal response associated with the low thermal conductivity of organic PCMs continues to limit their effectiveness in real-world TES and regulation applications. The lack of integrated, application-oriented design approaches, that simultaneously enhance encapsulation efficiency, thermal reliability, and response behaviour, defines critical and timely research gaps. Addressing gaps is essential for advancing organic PCM–polymer shell systems from laboratory concepts to deployable, high-performance TES solutions.

1.6. Research Objectives

The aim of the present work is to **Fabricate and Evaluate the Encapsulated Phase Change Materials for Latent Heat Storage**. Furthermore, the synthesized PCMs were evaluated through thermal characterization to determine their applicability in real-world TES scenarios. The detailed objectives of the present study are summarized as below:

- (1) Fabrication and evaluation of microencapsulated phase change materials as latent heat thermal energy storage systems.
- (2) Design and performance evaluation of nanoencapsulated phase change materials as latent heat thermal energy storage systems.
- (3) Investigation and optimization of synthesis parameters for the development of encapsulated phase change materials with relevance to practical thermal energy storage applications.
- (4) Incorporation of suitable fillers into the synthesized phase change material systems for enhancing thermal conductivity and improving functional performance.

- (5) Development and assessment of shape-stabilized phase change materials with emphasis on structural stability and thermal performance.

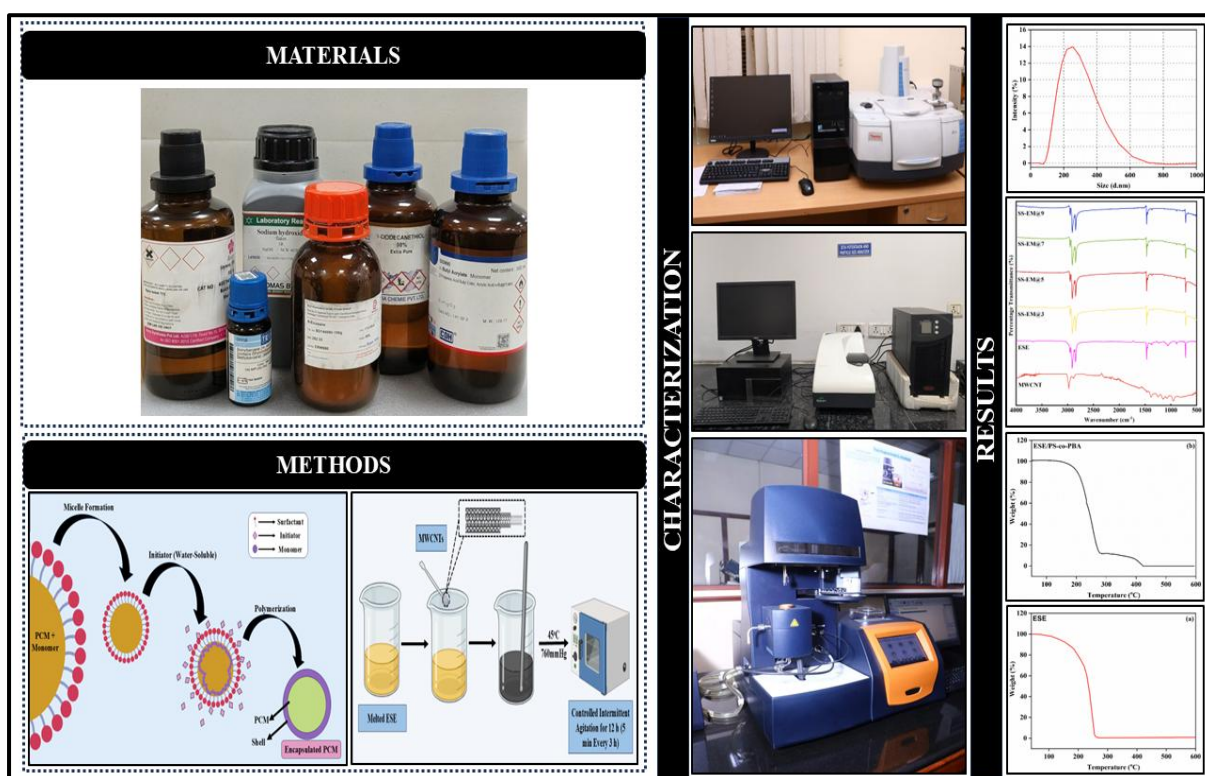
1.7. Overview of the Thesis

The objective of this thesis is the fabrication and evaluation of the encapsulated phase change materials for latent heat storage. The whole thesis is organized in **NINE** chapters. **Chapter 1** of the thesis provides a comprehensive overview of PCMs, followed by a critical review of research contributions reported by various researchers toward the development of different classes of PCMs. This chapter systematically identifies existing research gaps and outlines the latest trends in the field. Based on the detailed analysis of the available literature, the objectives of the present study are clearly formulated. **Chapter 2** presents the experimental methodology, detailing the materials and procedures employed for the synthesis of EPCMs and SSPCMs. The chapter further describes the characterization techniques used to investigate the properties of the synthesized materials, including PSD, surface morphology, thermal and chemical characterization, and thermal stability. Additionally, kinetic models such as Kissinger's method, Augis–Bennett's approximation, and the Mahadevan model, applied to determine the effective activation energy and Avrami theory, employed to analyze the crystallization behaviour of the produced materials are discussed in detail. **Chapter 3** represents the studies on n-Eicosane/polystyrene-co-polybutylacrylate [ESE/Poly(St-co-BA)] MPCMs synthesized through ultrasonicated mini-emulsion technique. **Chapter 4** deals with the detailed analysis of the prepared n-Eicosane/polystyrene-co-polybutylacrylate [ESE/Poly(SMA-co-BA)] nanocapsules and discusses the impact of long alkyl polymer chains on thermal performance and stability. **Chapter 5** emphasizes on the analysis and interpretation of DVB-crosslinked ESE/Poly(St-co-BA) microcapsules, where DVB was incorporated into the oil phase at varying ratios with respect to the monomer for optimizing the thermal stability of ESE/Poly(St-co-BA) microcapsules. This chapter systematically examines the influence of crosslinked shell structure on thermal performance, phase change behaviour and encapsulation parameters highlighting its significance for advanced TES applications. **Chapter 6** addresses the analysis and interpretation of the incorporated ZnATH-(O) NPs into MPCMs (where the polymer shell cross-linked with DVB) aimed at enhancing heat storage capacity. Similarly, **Chapter 7** deals with the evaluation of the integrated FeATH-(O) NPs into MPCMs. These NP dopants utilize anthocyanin (ATH) extract derived from RC that acts as reducing, capping and stabilizing agent which optimizes the thermal behaviour and stability of the prepared MPCMs.

The primary emphasis of these studies is to assess the influence of NPs concentration on the thermal behavior and stability of the microcapsules. **Chapter 8** investigates the tailoring of a series of SSPCMs based on ESE and MWCNTs with varying mass fractions, with emphasis on enhancing thermal performance. **Chapter 9** of the thesis summarizes the overall conclusions derived from the results obtained in all the studies conducted. In addition, recommendations for the future research are provided to forthcoming researchers interested in pursuing similar kind of work on PCMs or extending the study to more advanced levels. This chapter is followed by the **Reference**.

CHAPTER 2

MATERIALS AND METHODS



CHAPTER 2

MATERIALS AND METHODS

2.1 Raw Materials/ Chemicals

In this study, the following raw materials /chemicals were used for the preparation of EPCMs and SSPCMs:

1. Styrene monomer (SM)
2. Butyl Acrylate (BA)
3. n-Eicosane (ESE)
4. Divinylbenzene (DVB)
5. Sodium Lauryl Sulphate (SLS)
6. Multi-walled Carbon Nanotubes Type-5 (MWCNTs)
7. 2,2-Azobisisobutyronitrile (AIBN)
8. Dodecyl Mercaptan (DDM)
9. Liquor Ammonia
10. Stearyl methacrylate (SMA)
11. Zinc Acetate Dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$]
12. Iron (II) Chloride Tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$)
13. Iron (III) Chloride Hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)
14. Hydrochloric Acid (HCl)
15. Anhydrous Ethanol
16. Sodium Hydroxide (NaOH)
17. Tween-80
18. Red Cabbage (*Brassica oleracea var. capitata*) (RC)
19. Muslin Cloth

2.1.1. Chemical Sources and Purity Specifications

The sources and purity grades of the raw materials/ chemicals used for the development of EPCMs and SSPCMs are listed below:

Table 2.1: Sources and purity grade of the raw materials/ chemicals

S.No.	Raw Materials/ Chemicals	Purity (%)	Sources
1.	Styrene monomer	98	Avra Synthesis Pvt. Ltd.
2.	Butyl Acrylate	99	Central Drug House Pvt. Ltd.
3.	n-Eicosane	99	Tokyo Chemical Industry (India) Pvt. Ltd.
4.	Divinylbenzene	>50	
5.	Sodium Lauryl Sulphate	99.5	Sisco Research Laboratories Pvt. Ltd.
6.	Multi-walled Carbon Nanotubes Type-5 (30-50nm OD and 10-30 μ m length)	98	
7.	2,2-Azobisisobutyronitrile	98	Spectrochemicals Pvt. Ltd.
8.	Dodecyl Mercaptan	98	Loba Chemie Pvt. Ltd.
9.	Liquor Ammonia	25	
10.	Stearyl methacrylate	98	Sigma Aldrich
11.	Zinc Acetate Dihydrate	98.5	SD Fine- Chem Ltd.
12.	Iron (II) Chloride Tetrahydrate	≥ 98	Merck
13.	Iron (III) Chloride Hexahydrate	99-102	
14.	Hydrochloric Acid	37	Thermo Fisher Scientific
15.	Anhydrous Ethanol	99.9	
16.	Sodium Hydroxide	96	
17.	Tween-80	-	Thomas Bakers (Chemicals) Pvt. Ltd.
18.	Red Cabbage	-	Purchased from the local market of Rohini, Delhi, India
19.	Muslin Cloth	-	Purchased from the local market of Rohini, Delhi, India

2.2. Research Methodology

The methodology employed to achieve the objectives of the research is divided onto the following sections:

- ❖ Synthesis of microencapsulated and nanoencapsulated phase change materials using mini-emulsion polymerization technique.

- ❖ Optimization of the microencapsulated phase change materials by incorporating the divinylbenzene cross-linker in the polymer shell to enhance the thermal stability.
- ❖ Extraction of anthocyanin from red cabbage.
- ❖ Phyto-fabrication of zinc oxide and iron oxide nanoparticles with anthocyanin extract by using co-precipitation method.
- ❖ Preparation of modified microencapsulated phase change materials by integrating nanoparticles for improved heat storage capacity.
- ❖ Formation of multi-walled carbon tubes-mediated shape-stabilized PCMs for high-efficiency thermal energy storage application.
- ❖ Characterization of the synthesized materials for thermal properties such as melting and crystallization temperatures, amount of heat absorb and release using Differential Scanning Calorimetry.
- ❖ Determination of the thermal stability, morphology, chemical composition and crystalline nature of the prepared materials by Thermogravimetric Analysis, Transmission electron microscopy/ Field-emission scanning electron microscopy, Fourier transform infrared spectroscopy and Powder X-ray Diffraction respectively.

2.2.1. Synthesis of ESE/Poly(St-co-BA) Microcapsules

Mini-emulsion polymerization method was used to obtain the microcapsules. The oil and water phases were each prepared separately. By gradually agitating 0.2 g of SLS into 60 mL of deionized water, the water phase was formed. To prepare the oil phase, a 1:1 ratio of SM to ESE was added. The mass ratio of 1:1 was adopted, to attain an elevated encapsulation ratio and a high latent heat enthalpy. Additionally, 0.04 mL of DDM and 0.1 mL of BA (co-monomer) were added to the oil phase (SM: ESE = 1:1). The oil phase was gradually added into the continuous aqueous phase, then stirred for 30 min at 5000 rpm, and pre-emulsified for 10 min using an ultrasonic cell disrupter at 75% amplitude to obtain the fine emulsion. To persist with the polymerization reaction, the prepared emulsion was then moved to a 250 mL three-neck round-bottom flask equipped with nitrogen inlet, mechanical agitator and condensing reflux unit respectively. 0.05 g of AIBN initiator was added, and the reaction was allowed to proceed for 8 h at 85 °C. The emulsion was cooled down at room temperature over 24 h. Subsequently, the unencapsulated ESE was eradicated from the product by filtering and washing it with hot ethanol twice. At last, the microcapsules were allowed to dry in a vacuum

oven. **Figure 2.1** depicts a schematic representation of the experimental strategy used for ESE/Poly(St-co-BA) microcapsules synthesis.

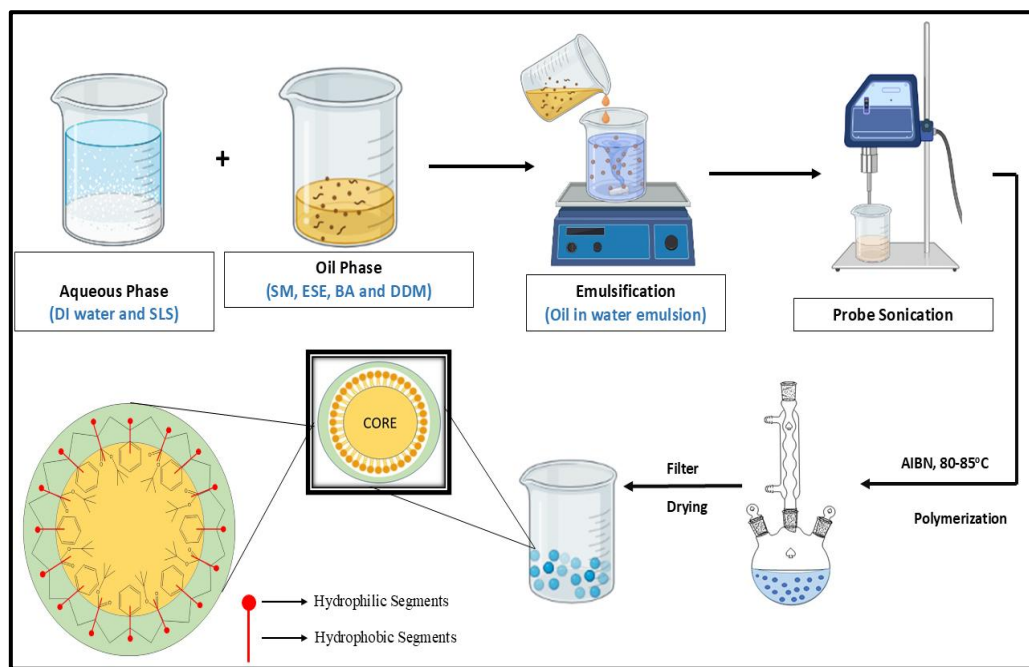


Figure 2.1: An illustration of the experimental approach for ESE/Poly(St-co-BA) synthesis

2.2.2. Synthesis of ESE/Poly(SMA-co-BA) Nanocapsules

ESE/Poly(SMA-co-BA) nanocapsules were produced using the same polymerization process. Typically, an oily mixture is formed by combining 12 mL ESE, 12 mL SMA, 0.2 mL BA, 0.1 mL DDM and 0.1 g AIBN. An aqueous medium was produced through the addition of 144 mL Milli-Q water with 0.2 g SLS and 0.2 mL Tween-80 composite surfactants. Afterwards, the oil phase was steadily mixed into the aqueous phase and stirred at 5000 rpm for 30 min. Miniemulsification was performed for 10 min by sonicating the emulsion at 75% amplitude with a sonifier (Model UP400St, Hielscher, Germany). To prevent thermal polymerization during the sonification process, the emulsion was immersed in an ice bath. Afterwards, the emulsion was transferred in a 500 ml two-neck round bottom flask connected with a stirrer and fitted with a condenser. To eliminate the oxygen, nitrogen purging was done for 30 min. The reaction was conducted for 12 h under the same reaction condition, with the flask submerged

in a water bath at 85 °C. Following the reaction, the latex temperature was gradually brought down to room temperature. **Figure 2.2** displays a schematic illustration of the followed experimental approach for producing ESE/Poly(SMA-co-BA) nanocapsules.

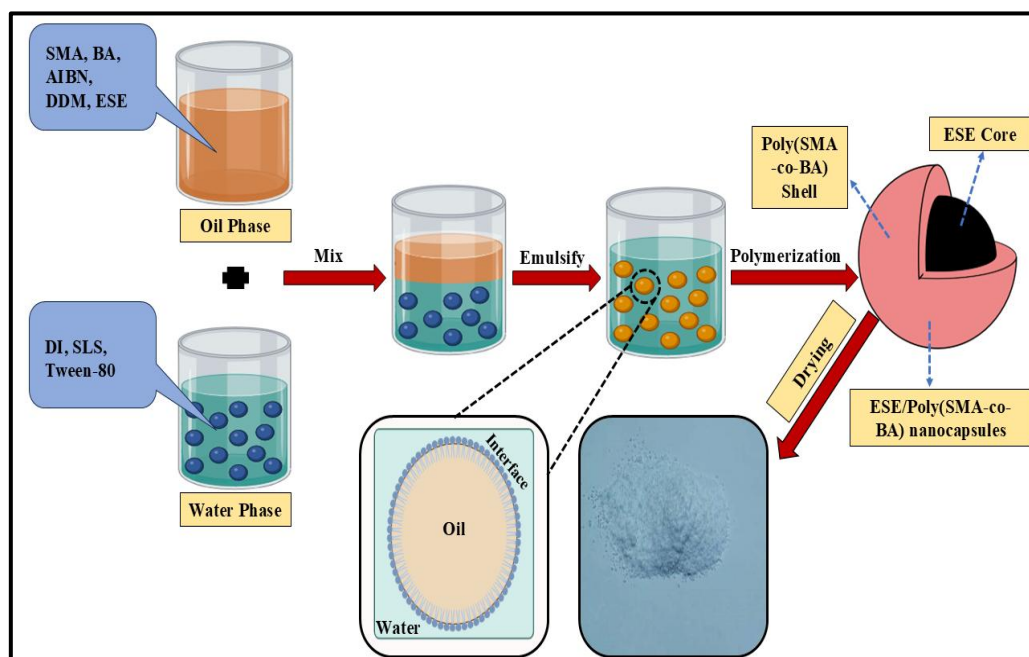


Figure 2.2: An illustration of the experimental approach for ESE/Poly(SMA-co-BA) synthesis

2.2.3. Optimization of MPCMs by Integrating Cross-Linker

In Section 2.2.1, The MPCMs were synthesized successfully using mini-emulsion polymerization technique. Further, the synthesis procedure was optimized by incorporating the varying amounts of DVB cross-linker with respect to monomer in the oil phase. The impact of different concentrations of DVB on the morphology, thermal performance and stability of the synthesized MPCM was investigated in detail. **Figure 2.3** shows the schematic representation of the shell network between the PS, PBA and DVB. The samples with varying amounts of cross-linking agents were prepared, and are presented in **Table 2.2**.

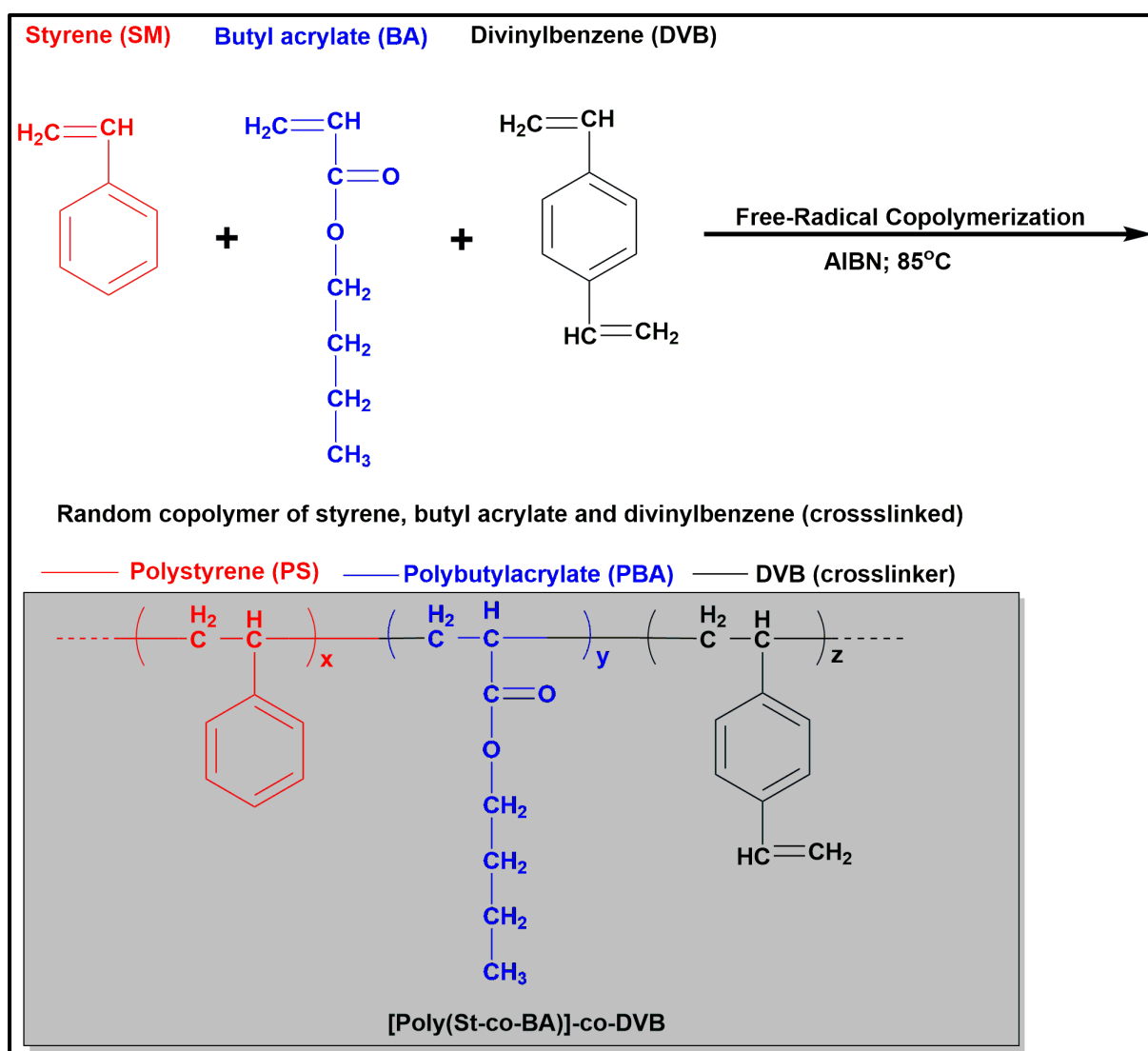


Figure 2.3: Schematic representation of the shell network

Table 2.2: MPCMs prepared with varying amounts of DVB

Sample Code	ESE (mL)	SM (mL)	DVB (mL)	BA (mL)
EPD0.5	5	5	0.025	0.1
EPD1	5	5	0.05	0.1
EPD2	5	5	0.1	0.1
EPD3	5	5	0.15	0.1
EPD5	5	5	0.25	0.1

2.2.4. Extraction of Anthocyanin (ATH) from Red Cabbage (RC)

ATH was extracted from RC (*Brassica oleracea* var. *capitata*) using pure ethanol as the solvent [161]–[163], as illustrated in **Figure 2.4**. The procedure involved cutting and washing of fresh RC using distilled water. Then, excess moisture was removed using a muslin cloth. 100 g of RC were pulverised and mixed with 150 ml of pure ethanol solvent in an Erlenmeyer flask for 36 h at 4 °C to extract phytochemicals. Subsequently, the mixture was filtered, and the resulting filtrate was centrifuged at 4000 rpm for 10 min for further purification. Afterwards, the pH of the mixture was first maintained at 2, using HCl. Then, the mixture was kept in the dark at 4 °C for 36 h. Afterwards, the pH of the solution was adjusted to 7 by adding NaOH, and it was further kept at a temperature of 4 °C for future use.

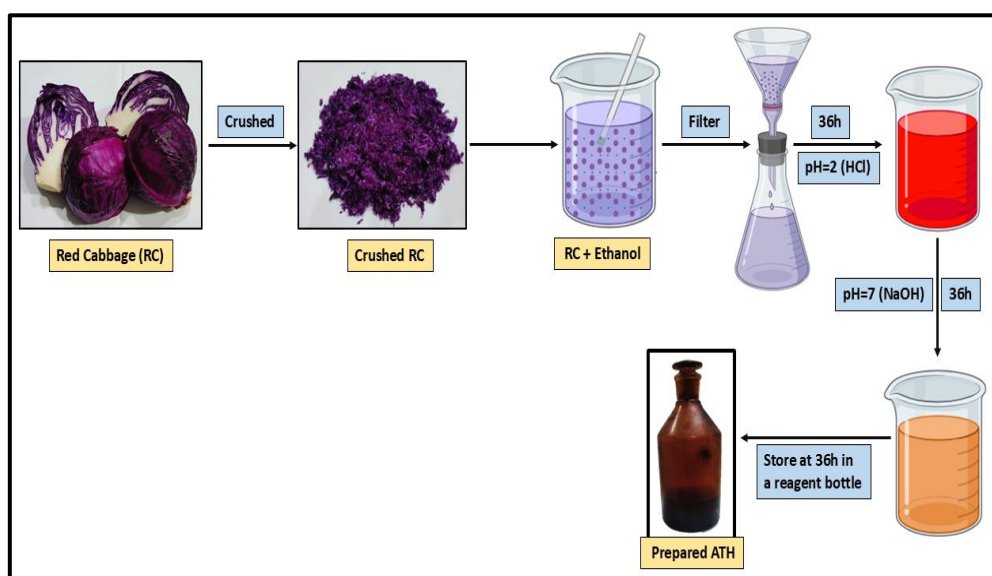


Figure 2.4: Extraction of ATH from RC (*Brassica oleracea* var. *capitata*)

2.2.5. Phyto-Fabrication of Zinc Oxide (ZnO) NPs with ATH Extract [ZnATH-(O) NPs]

The phyto-fabrication of ZnO NPs was carried out using ATH extract, depicted in **Figure 2.5**. Firstly, 1 g of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 50 mL distilled water and stirred for 15 min at room temperature. Afterwards, 5 mL of extracted ATH solution was added and stirred for the next 30 min. At this point, the colour of the solution turned to orange. Additionally, a 1 M NaOH solution was added to the solution in a dropwise manner to maintain its pH at 10, and

the resulting solution was then agitated further for 4 h. The resulting white precipitate were then filtered and rinsed with distilled water and ethanol solvent in a 1:1 ratio. The isolated product underwent a 24 h drying process at 60 °C, followed by a 2 h calcination in a muffle furnace at 450 °C.

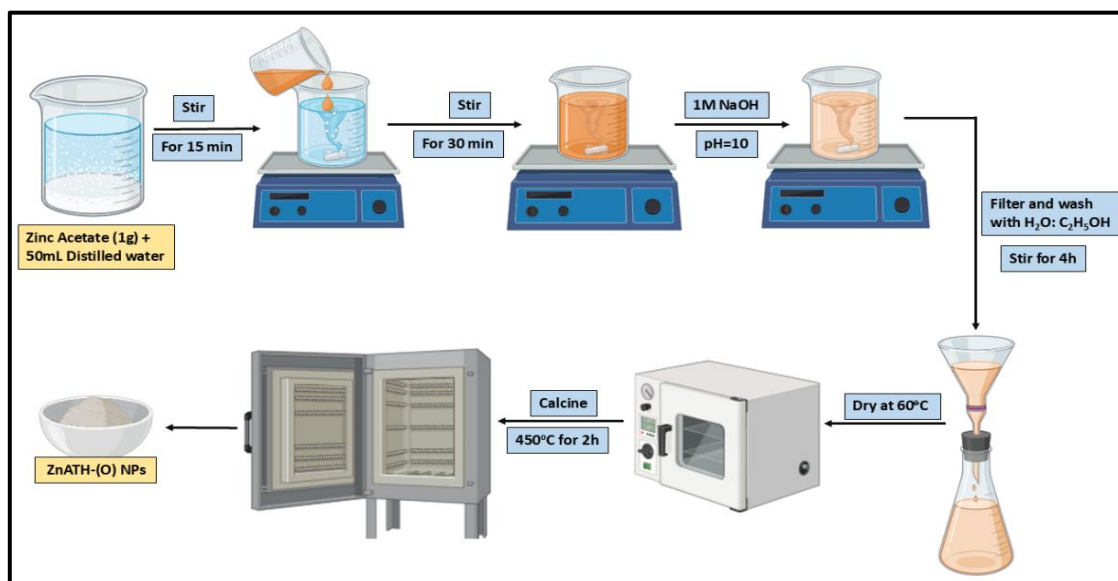


Figure 2.5: Systematic methodology for the preparation of ZnATH-(O) NPs

2.2.6. Phyto-Fabrication of Iron Oxide (FeO) NPs with ATH Extract [FeATH-(O) NPs]

The green synthesis of FeO NPs using ATH extract (FeATH-(O) NPs) was carried out by employing facile co-precipitation method (**Figure 2.6**). 2.72 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.98 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved separately in 10 mL of double-distilled water until a clear solution was obtained. Then, both the solutions were mixed, and 30 mL of double-distilled water was subsequently added. Further, 5 mL freshly prepared ATH solution was added and stirred magnetically for 30 min. The pH of the mixture was maintained at 10, by dropwise addition of ammonium hydroxide ($\text{NH}_3 + \text{H}_2\text{O}$) until a brown to dark black color was obtained, and the resultant mixture was further agitated for 4 h at 85 °C. Finally, the black-colored precipitates were filtered, washed with a water-ethanol mixture to remove unreacted impurities and further dried in a hot air oven at 60 °C for 18 h. The obtained precipitates were further calcined in a muffle furnace for 2 h at 450 °C and then ground to obtain fine black-colored FeATH-(O) NPs.

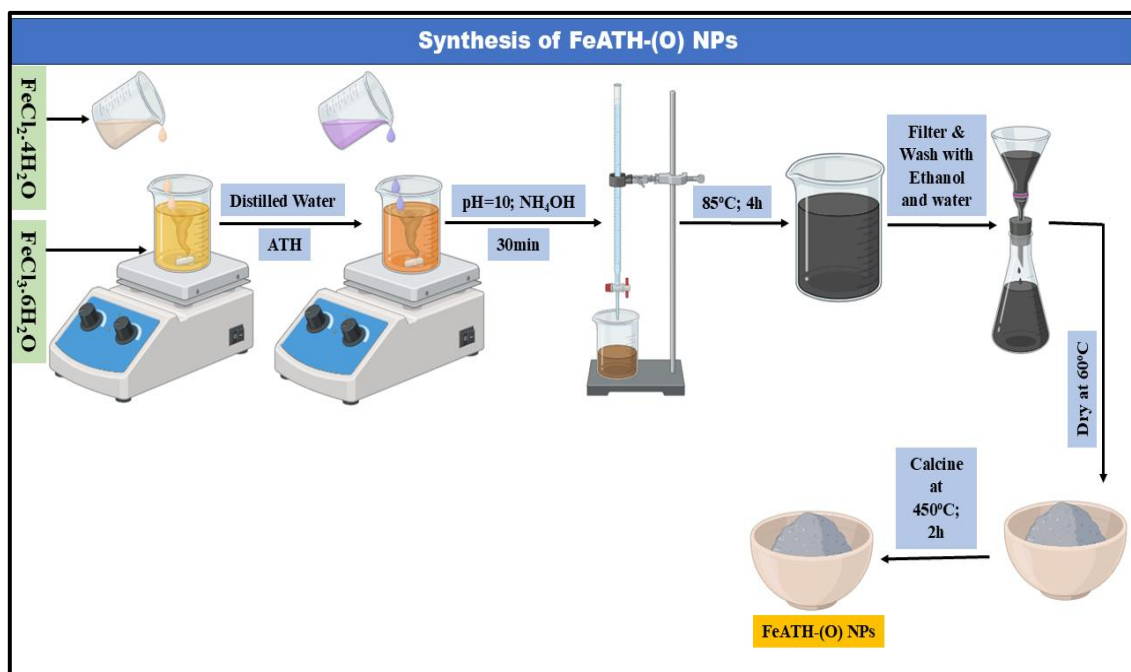


Figure 2.6: Systematic methodology for the preparation of FeATH-(O) NPs

2.2.7. Preparation of Modified MPCMs by Integrating ZnATH-(O) and FeATH-(O) NPs

The doped PCMs were prepared using a direct-synthesis approach using ESE as the base material and additive NPs as illustrated in **Figure 2.7**. The NPs were added into the ESE at distinct weight fractions to formulate the experimental samples for the investigation. For the synthesis of doped PCMs, the ESE was heated above its melting point with constant stirring. The NPs were gradually incorporated in portions until the desired concentrations were reached. The mixtures were then homogenized at 120 °C for 40 min using a high-speed homogenizer at 6,000 rpm to ensure uniform dispersion of the dopants within the molten paraffin. After that, an ultrasonic bath was used for 1 h at 90 °C to improve dispersion and complete the doping procedure.

To produce the modified MPCMs similar polymerization technique was employed where the doped ESE was surrounded by a hybrid polymer shell composed of polystyrene-co-polybutylacrylate [Poly(St-co-BA)], with 0.5wt% of DVB (w.r.t monomer) serving as a cross-linking agent to improve structural stability.

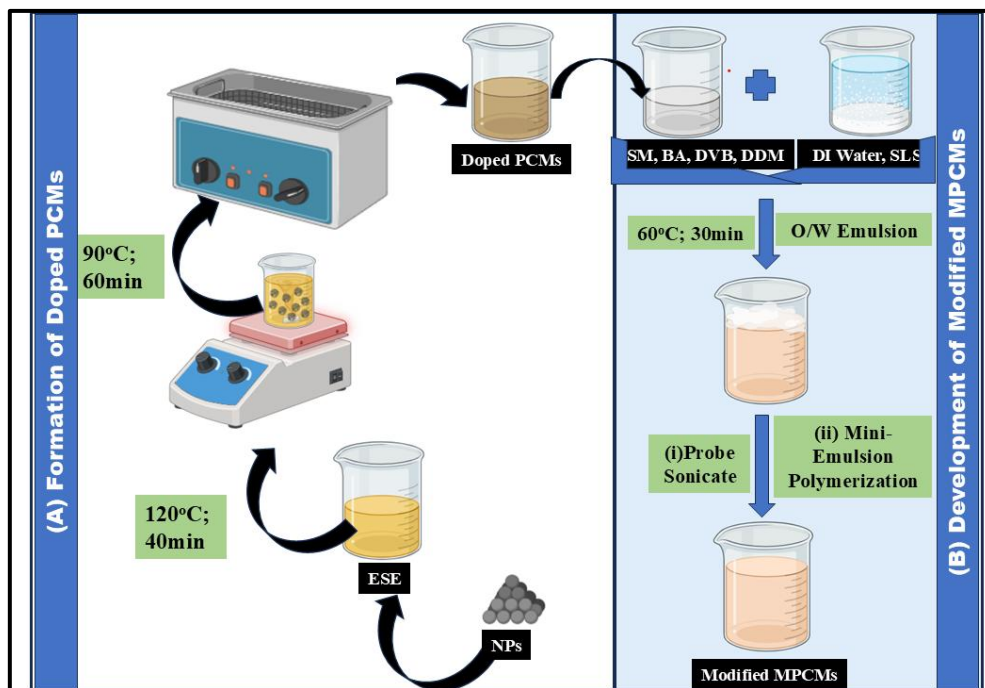


Figure 2.7: Schematic representation of modified MPCMs synthesized by mini-emulsion polymerization technique

2.2.8. Development of Shape- Stabilized ESE/MWCNT Composites

Using ESE as the primary base fluid, four sets of ESE/MWCNT composite materials were produced by loading MWCNTs for mass fractions of 3, 5, 7, and 9%. The precise procedure followed is (**Figure 2.8**): Four beakers were filled respectively with 9.7, 9.5, 9.3, and 9.1 g of ESE liquid. Subsequently, 0.3, 0.5, 0.7, and 0.9 g of MWCNTs were added to each beaker respectively, and stirred with a glass rod for 5 min. Afterwards, the prepared four samples were positioned in a vacuum drying oven set at 45 °C to induce the vacuum adsorption effect. Four groups of ESE/MWCNT PCMs with varying MWCNTs mass fractions were formed by agitating the samples for 5 min after every 3 h. The total vacuum adsorption time was 12 h, and the pressure in the vacuum oven was kept at 760 mmHg.

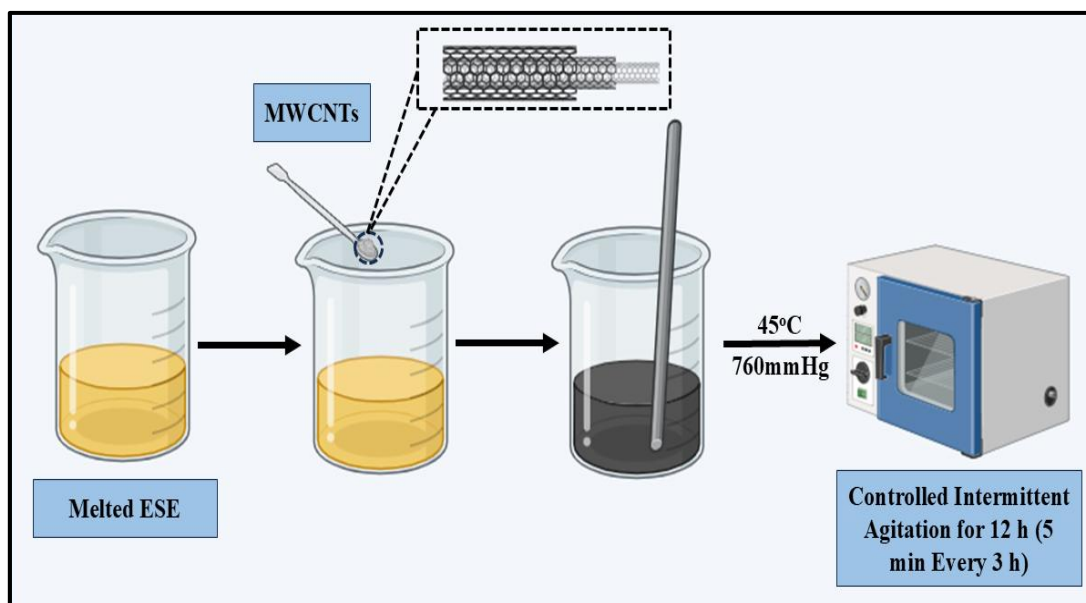


Figure 2.8: An experimental approach for the synthesis of ESE/MWCNT composites

2.3. Characterization of the Synthesized MPCMs, NPCMs and SSPCMs

2.3.1. Differential Scanning Calorimetry (DSC) Analysis

The thermal performance of the produced materials, including melting and crystallization temperatures and their corresponding enthalpies, was examined using Perkin Elmer, DSC8000 as shown in **Figure 2.9**. Each sample weighed around 5.0 mg and was loaded into an aluminium crucible. Then the samples were subjected to follow a cycle of heating and cooling at temperature range between $-5\text{ }^{\circ}\text{C}$ and $80\text{ }^{\circ}\text{C}$. A steady N_2 flow rate and a continual temperature ramp of $10\text{ }^{\circ}\text{C}.\text{min}^{-1}$ were maintained in the furnace. The samples were examined three times, and the average values were recorded.



Figure 2.9: Differential scanning calorimetry (Perkin Elmer, DSC8000)

2.3.1.1. Encapsulation Ratio, Encapsulation Efficiency and Thermal Storage Capacity of the Synthesized EPCMs

Two vital factors, namely the encapsulation ratio (E_R) and encapsulation efficiency (E_{ES}), are employed to describe the phase change performance of EPCMs which can be derived from DSC data using equations (2.1) and (2.2) [164]:

$$E_R = \frac{\Delta H_{(m)EPCM}}{\Delta H_{(m)PCM}} \times 100\% \quad (2.1)$$

$$E_{ES} = \frac{\Delta H_{(m)EPCM} + \Delta H_{(c)EPCM}}{\Delta H_{(m)PCM} + \Delta H_{(c)PCM}} \times 100\% \quad (2.2)$$

$\Delta H_{(m)PCM}$ and $\Delta H_{(m)EPCM}$ denote the melting enthalpies of pristine PCM and EPCM, respectively; $\Delta H_{(c)PCM}$ and $\Delta H_{(c)EPCM}$ represent the crystallization enthalpies of the pristine PCM and EPCM, respectively. The encapsulation ratio indicates the PCM encapsulation within the capsules, whereas the loading content refers to the dry weight percentage of the core material. It is comprehensible that not all capsules can perform the role of PCMs since phase transitions often do not transpire within small-sized capsules due to the confinement of molecular motion. On the contrary, the encapsulation efficiency represents the effective performance of the PCM inside the EPCM for heat energy storage and thermal regulation.

Furthermore, the encapsulation efficiency is inferred from the enthalpies associated with the melting and crystallization processes.

The thermal storage capacity (C_{es}) of the EPCM, representing its ability to store thermal energy during the phase transition, may be determined from the DSC measurements using equation (2.3):

$$C_{es} = \frac{E_{ES}}{E_R} \times 100\% \quad (2.3)$$

2.3.1.2. Kinetics of Non-Isothermal Crystallization Analysis

For PCM, crystallization has been identified as a key step for storing the thermal energy throughout the transition of phase from a disordered to an ordered state. Both regional environments and foreign substances have a significant impact on this process. Anticipatedly, PCMs crystallization behaviours will be affected by encapsulation within the polymer shell. It becomes essential to profoundly investigate the kinetics of PCM crystallization, as the energy storage capacity of a PCM is highly influenced by its crystallization behaviours throughout the transition process. In order to fully comprehend the temperature dependence of the crystallization rate during the phase transition, the non-isothermal crystallization kinetics of the pure PCM and EPCMs were thoroughly examined. Additionally, equation (2.4) can be used to determine the correlation between the relative crystallinity (X_T) of PCM and EPCMs with temperature (T) respectively [165].

$$X_T = \frac{\int_{T_0}^T \left(\frac{dH_C}{dT} \right) dT}{\int_{T_0}^{T_\infty} \left(\frac{dH_C}{dT} \right) dT} X 100\% \quad (2.4)$$

The heat flow rate of DSC scans is represented by (dH_C/dT) , T is an arbitrary temperature, and T_0 and T_∞ are the crystallization onset and endset temperatures, respectively.

2.3.1.2.1. Effective Activation Energy

The nucleation activation energy could reflect the degree of crystal nucleation under a non-isothermal crystallization process, providing a better way to examine the impact of the polymer shell on the crystallization behavior of PCM. There are various methods to determine activation energy.

Kissinger's approach is often used to study the crystallization process that is examined by DSC [166]. Equation (2.5) provides the relationship between the peak crystallization temperature (T_p , K), heating rate (β , K.min⁻¹), and activation energy (E_a , KJ.mol⁻¹):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \frac{-E_a}{RT_p} + \text{constant} \quad (2.5)$$

Plotting $\ln(\beta/T_p^2)$ versus $1000/T_p$ provides the value of activation energy. The value is determined by the curve's slope.

Another approach to calculate activation energy was proposed by the approximations of Augis and Bennett, using the equation (2.6), as follows [167]:

$$\ln\left(\frac{\beta}{T_p}\right) = \frac{-E_a}{RT_p} + \text{constant} \quad (2.6)$$

Activation energy is given by the $\ln(\beta/T_p)$ against $1000/T_p$ slope. To calculate the value of activation energy, Mahadevan put forth an approximation of the Kissinger formula. As indicated by the equation (2.7) [168]:

$$\ln(\beta) = \frac{-E_a}{RT_p} + \text{constant} \quad (2.7)$$

This approximation ($\ln\beta$) is plotted against $1000/T_p$, and the slope of the curve gives the value of the activation energy.

2.3.1.2.2. Avrami Theory

The Avrami equation could potentially be utilized for determining the crystal growth process, which would more effectively describe the non-isothermal crystallization process. This approach uses the equation (2.8) to determine the order of crystallization (n) from the (χ) volume fraction of the precipitated crystals at a constant heating rate (β , °C.min⁻¹) [165]:

$$\frac{d\{\ln[-\ln(1-\chi)]\}}{d[\ln(\beta)]} = -n \quad (2.8)$$

The value of n can be ascertained by calculating the slope of the curve, that is obtained when $\ln(\beta)$ is plotted against $\ln[-\ln(1-\chi)]$.

2.3.1.3. Mixture Rule of Shape- Stabilized ESE/MWCNT Composite

The theoretical enthalpy of ESE/MWCNT can be computed using the following equation [169]:

$$\Delta H_{\text{ESE/MWCNT}} = A_{\text{ESE}} \cdot \Delta H_{\text{ESE}} \quad (2.9)$$

Where, $\Delta H_{\text{ESE/MWCNT}}$, A_{ESE} , ΔH_{ESE} are the calculated latent heat of the ESE/MWCNT composites, mass percentage of ESE in the composite and latent heat of ESE, respectively.

2.3.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed to evaluate the thermal stability and mass-loss behavior of the prepared materials using a thermal analyzer (TA, TGA5500), as presented in **Figure 2.10**. The samples were placed in platinum crucibles and heated from 30 to 800 °C at a constant heating rate of 10 °C min⁻¹ under an inert N₂ atmosphere. The variation in sample mass as a function of temperature was recorded to assess the thermal decomposition behavior and thermal stability of the materials. The observed mass loss was primarily associated with the evaporation of volatile components, followed by thermal decomposition of the material at higher temperatures. All measurements were performed in triplicate, and the average values were reported.



Figure 2.10: Thermogravimetric analyzer (TA, TGA5500)

2.3.3. Fourier Transform Infrared Spectroscopy Analysis (FTIR)

A Thermo Scientific, Nicolet iS50 Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) assembled with an ATR Miracle diamond crystal was employed to analyze the functional groups of the synthesized EPCM and SSPCM materials. The powder sample remained in contact with the ATR apparatus's diamond eye (1.8 mm) when the clamping equipment was securely anchored. Each sample was scanned 32 times in the wavenumber range of 500 to 4000 cm^{-1} at a resolution of 4 cm^{-1} in order to record the spectrum.



Figure 2.11: FTIR spectrophotometer (Thermo Scientific, Nicolet iS50)

2.3.4. Powder X-Ray Diffraction (PXRD) Analysis

A PXRD with $\text{CuK } \alpha$ radiation (Rigaku SmartLab) was used for crystallographic investigation of the synthesized products. The XRD patterns were recorded at 298 K within the 2θ range of 10° to 80° with step size of 0.02° , and a scanning rate of 1.0 s per step.



Figure 2.12: Powder x-ray diffractometer (Rigaku SmartLab)

2.3.5. Dynamic Light Scattering (DLS)

Using DLS method (DLS, Malvern Zetasizer Nano ZS, UK), the particle size distribution (PSD) and the average diameter of the developed EPCM and NPs were assessed. To prevent the suspended particles from aggregating, the particles were dissolved in ethanol and homogenized using ultra-sonication. For each observation, a set of three scans were executed to record the PSD and particle size.



Figure 2.13: Malvern zetasizer nano ZS

2.3.6. Field-Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM)

The surface morphology and shape of EPCM, NP and SSPCM were explored with the help of FE-SEM (JEOL, JSM-7610F PLUS) with Energy Dispersive X-ray spectroscopy and TEM (Philips, Morgagni 268D). The samples were sputter-coated with a thin layer of gold for FE-SEM analysis in order to improve surface conductivity and image resolution. For TEM analysis, the particles were ultrasonically dispersed in an appropriate solvent, and a drop of the suspension was positioned onto a copper grid coated with carbon, then allowed to dry under ambient conditions, and afterwards imaged accordingly.



Figure 2.14: Field-emission scanning electron microscopy (JEOL, JSM-7610F PLUS)

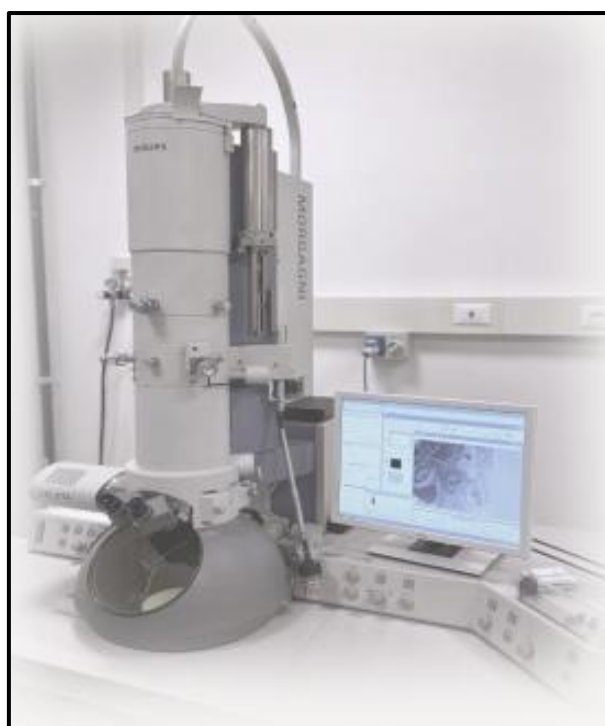


Figure 2.15: Transmission electron microscopy (Philips, Morgagni 268D)

2.3.7. Infrared Thermography Analysis (IFT)

The thermal response of the synthesized MPCMs was evaluated using a FLIR E96 infrared thermographic camera to monitor the temperature distribution and leakage behavior of the samples as a function of time.



Figure 2.16: FLIR E96 infrared thermographic camera

2.3.8. Leakage Test

The total mass of the SSPCM samples on the filter paper was weighed and recorded. The samples were placed in a vacuum drying oven, and the vacuum pressure and temperature were adjusted to 760 mmHg and 60 °C, respectively. After 12 h of vacuum drying, the samples were removed and reweighed. The mass ratio of PCM to supporting matrix corresponding to the minimum mass difference was considered the ideal ratio, and the mass difference between the samples before and after drying was regarded as the amount of PCM leakage during the phase transition process. The criteria of leakage was shown in Table 2.3.

$$\text{Leakage Percentage} = (\text{Initial mass} - \text{Final mass}) / \text{Initial Mass} \times 100 \quad (2.10)$$

Table 2.3: Leakage Criteria [170]

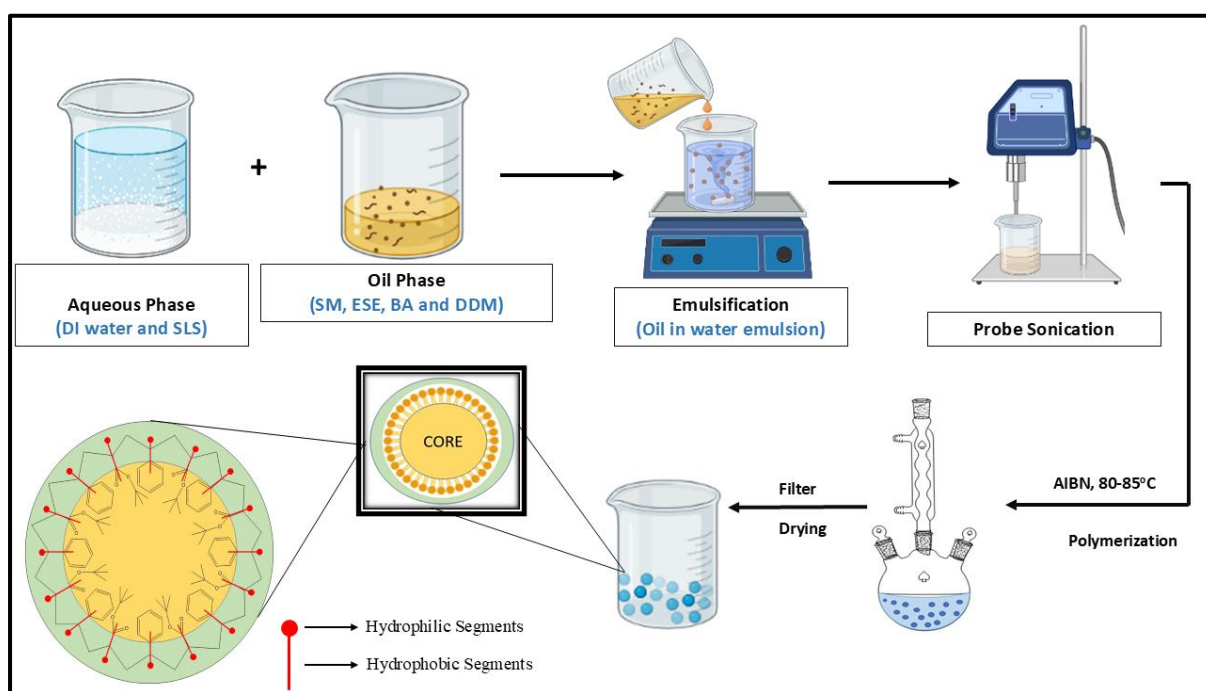
Leakage Percentage (L%)	Phenomenon	Conclusion
$L\% \leq 10$	Trace amounts	Stable
$10 < L\% \leq 30$	A little bit leakage	Basically, remained stable
$30 < L\% \leq 50$	Moderate leakage	Unstable
$L\% > 50$	Severe leakage	Extremely unstable

2.3.9. Thermal Reliability Test

Thermal reliability of the synthesized EPCMs was determined by examining their ability to sustain latent heat energy over numerous phase transitions. After the samples underwent several thermal cycles, DSC analysis was performed in order to investigate into any deviations in their thermal properties. The procedure adopted here has been comprehensively reported in an earlier study [171]. Specifically, two distinct water baths that served as hot and cold sinks were used to run the thermal cycling between 0 and 60 °C. The hot water bath was kept above the PCM's melting temperature, while the cold-water bath was kept below the crystallization temperature, with ice cubes added periodically to maintain the appropriate low temperature. After being sealed in appropriate glass containers and heated in the hot bath for 15 min to attain the melting temperature, the synthesized samples were moved to the cold bath for 15 min to allow solidification below the crystallization temperature. This heating-cooling process comprised one cycle, which was performed up to 100 times.

CHAPTER 3

MICROENCAPSULATION OF PHASE CHANGE MATERIALS: DESIGN TO DEVELOPMENT



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CHAPTER 3

MICROENCAPSULATION OF PHASE CHANGE MATERIALS: FROM DESIGN TO DEVELOPMENT

3.1. Introduction

The enhanced properties of PCMs are gaining more attention in both industrial and domestic areas; however, their phase transition poses certain challenges, such as low thermal conductivity-induced thermal hysteresis, absorption of atmospheric moisture or water loss via evaporation, supercooling, inadequate heat transfer during the charging and recovery procedures, PCM seepage and its reduction etc. Due to these problems, pure PCMs are typically not advised to use directly in the TES applications. To overcome these problems, the microencapsulation technology was developed, in which a polymer material serves as the shell and PCMs are encased, or entrapped, inside it. This technology has many advantages, including high heat transfer rate, protect PCMs from the environment, regulate volume variations during phase conversion, boost physical strength of the core PCMs and increase heat transfer area [74]. This study reports the synthesis and characterization of MPCMs for the pertinence of LHS. The ESE/Poly(St-co-BA) microcapsules were synthesized by encapsulating ESE with a shell made of Poly(St-co-BA) via employing ultrasonic-assistant mini-emulsion polymerization technique.

ESE was chosen as the core material, as it has a melting point of approximately 38.9 °C, a significant amount of latent heat, and the ability to be employed in thermal insulation, thermo-regulated foam, fibers, textiles or building materials. Furthermore, Poly(St-co-BA) is used as a shell material to encapsulate PCMs, where PS forming the main polymer shell around the ESE and PBA serving as the copolymer. PS forms the protective shell around the PCM core, offering thermal insulation, mechanical strength, chemical stability, and processability, ensuring efficient energy storage and durability. Whereas copolymer PBA enhance these benefits by providing tailored properties, improved thermal and mechanical stability, controlled release rates, and superior barrier protection against environmental factors. Together, they provide high-performance MPCMs that are appropriate for a wide range of applications including electronics to construction. The resulted ESE/Poly(St-co-BA) microcapsules were

characterized for their particle size distribution, surface morphology, thermal and chemical properties, thermal stability.

3.2. Results and Discussion

3.2.1. Thermal Performance of ESE/Poly(St-co-BA) Microcapsules

The DSC thermograms of the ESE and ESE/Poly(St-co-BA) samples recorded in the temperature range of -5 °C to 100 °C at a scan rate of 10 °C.min⁻¹ are presented in **Figure 3.1 (a-d)**. The DSC analysis was utilized to assess the critical thermal characteristics, including, crystallization (T_c) and melting (T_m) temperature, latent heat associated with the cooling (ΔH_c) and heating (ΔH_m) processes, as well as the stability of the material during the phase transition. **Table 3.1** shows the experimental findings determined by the DSC. Both exothermic and endothermic peaks can be recognized in the DSC curves of ESE and ESE/Poly(St-co-BA), and their phase change behavior is comparable.

Table 3.1: DSC analysis results of ESE and ESE/Poly(St-co-BA)

Sample	Melting Process				Crystallization Process			
	T_{om} (°C)	T_{pm} (°C)	T_{em} (°C)	ΔH_m (J.g ⁻¹)	T_{oc} (°C)	T_{pc} (°C)	T_{ec} (°C)	ΔH_c (J.g ⁻¹)
ESE	35.5	38.9	40.1	239.9	30.9	30.5	29.6	237.7
ESE/Poly(St-co-BA)	35.7	38.9	40.1	220.5	32.3	31.1	30.1	218.6

T_{om} : Onset melting temperature; T_{pm} : Peak melting temperature; T_{em} : Endset melting temperature; ΔH_m : Latent heat of melting; T_{oc} : Onset crystallization temperature; T_{pc} : Peak crystallization temperature; T_{ec} : Endset crystallization temperature; ΔH_c : Latent heat of crystallization

The DSC curve of pure ESE exhibited a single endothermic melting peak [**Figure 3.1 (a)**], but during crystallization process, it showed a bimodal phase transition behavior with two exothermic peaks [**Figure 3.1 (b)**]. Numerous investigations [172]–[174] have revealed that pure ESE typically manifests a rotator phase and requires two phase transitions to complete the crystallization process from nucleated liquid to stable triclinic structure. The first is a liquid-solid phase transition from the homogeneously nucleated liquid phase to the rotator phase; the second is a solid-solid phase transition, related to the structural phase change in the solid ESE, which changes from the heterogeneously nucleated rotator phase to the stable triclinic phase. Consequently, a rotator-triclinic phase transition peak was seen in the DSC curves at a

temperature greater than the crystallization temperature. The rapid heat evolution during the rotator-triclinic phase change is responsible for the prominent exothermic peak of pure, which was skewed towards higher temperatures [175].

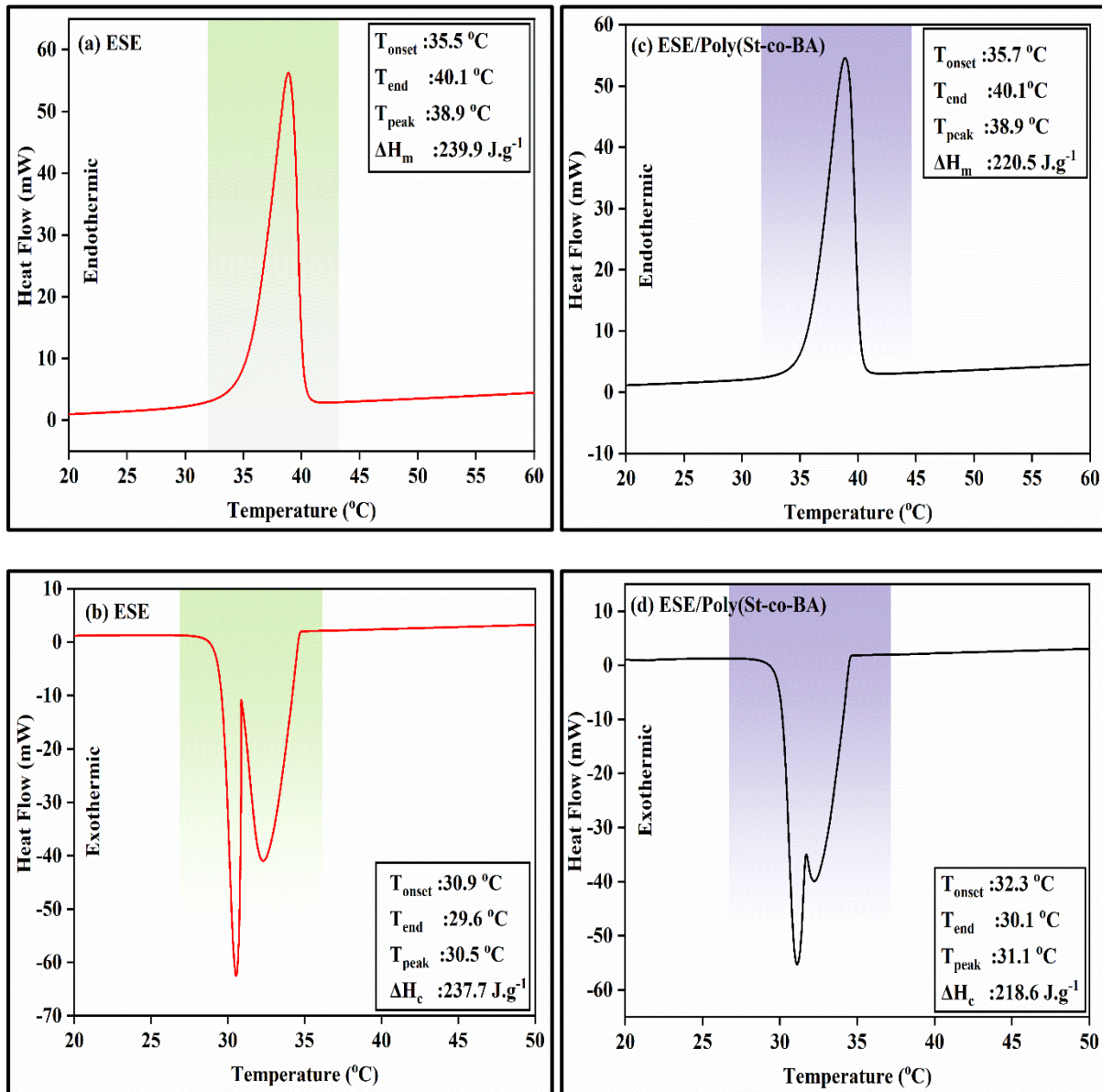


Figure 3.1: DSC curves of (a,b) ESE and (c,d) ESE/Poly(St-co-BA) respectively

The melting and crystallization temperature of ESE were found to be 38.9°C and 30.5°C respectively. The recorded latent heat of crystallization was 237.7 J.g^{-1} , while its latent heat of fusion was 239.9 J.g^{-1} respectively. In contrast, the microcapsules possess a melting

temperature of 38.9 °C with a latent heat of fusion of 220.5 J.g⁻¹ and a crystallization temperature of 31.1 °C, with an adequate latent heat of 218.6 J.g⁻¹. The resulting microcapsules show a decrease in latent heat because of the polymer shell [147].

From the obtained results, it is confirmed that the developed ESE/Poly(St-co-BA) exhibits exceptional heat storage capabilities and have ample potential for use in TES applications such as intelligent textile applications [114], solar applications [176], thermo-responsive coatings [177], waste heat recovery applications and building applications [178].

3.2.1.1. Phase Change Performance of ESE/Poly(St-co-BA) Microcapsules

The phase change performance index provides the calculated figures for the encapsulation ratio, encapsulation efficiency, and thermal storage capacity of ESE/Poly(St-co-BA) that determine the effective performance of ESE inside the polymer shell [164]. Using equations (2.1, 2.2 and 2.3), each phase change performance metric was determined.

The encapsulation ratio of ESE in this investigation was determined 91.9% and encapsulation efficiency was recorded as 91.6%. The ESE/Poly(St-co-BA) had shown 99.6% thermal storage capacity, indicating that the ESE has been enclosed in the proper shape and size, producing a material that can stably store and release energy even at the phase transition temperature or above without undergoing any material deformation.

3.2.1.2. Kinetics of Non-Isothermal Crystallization Analysis

ESE and ESE/Poly(St-co-BA) microcapsules crystallization curves at different cooling rates of 5, 10, 15, and 20 °C.min⁻¹ are shown in **Figure 3.2 (a) and (b)** respectively, to illustrate the exothermic behavior during crystallization, under non-isothermal conditions. Additionally, equation (2.4) can be used to determine the correlation between the relative crystallinity (X_T) of ESE and ESE/Poly(St-co-BA) with temperature (T) respectively, and the resulting graphs are shown in **Figure 3.2 (c) and (d)** [165].

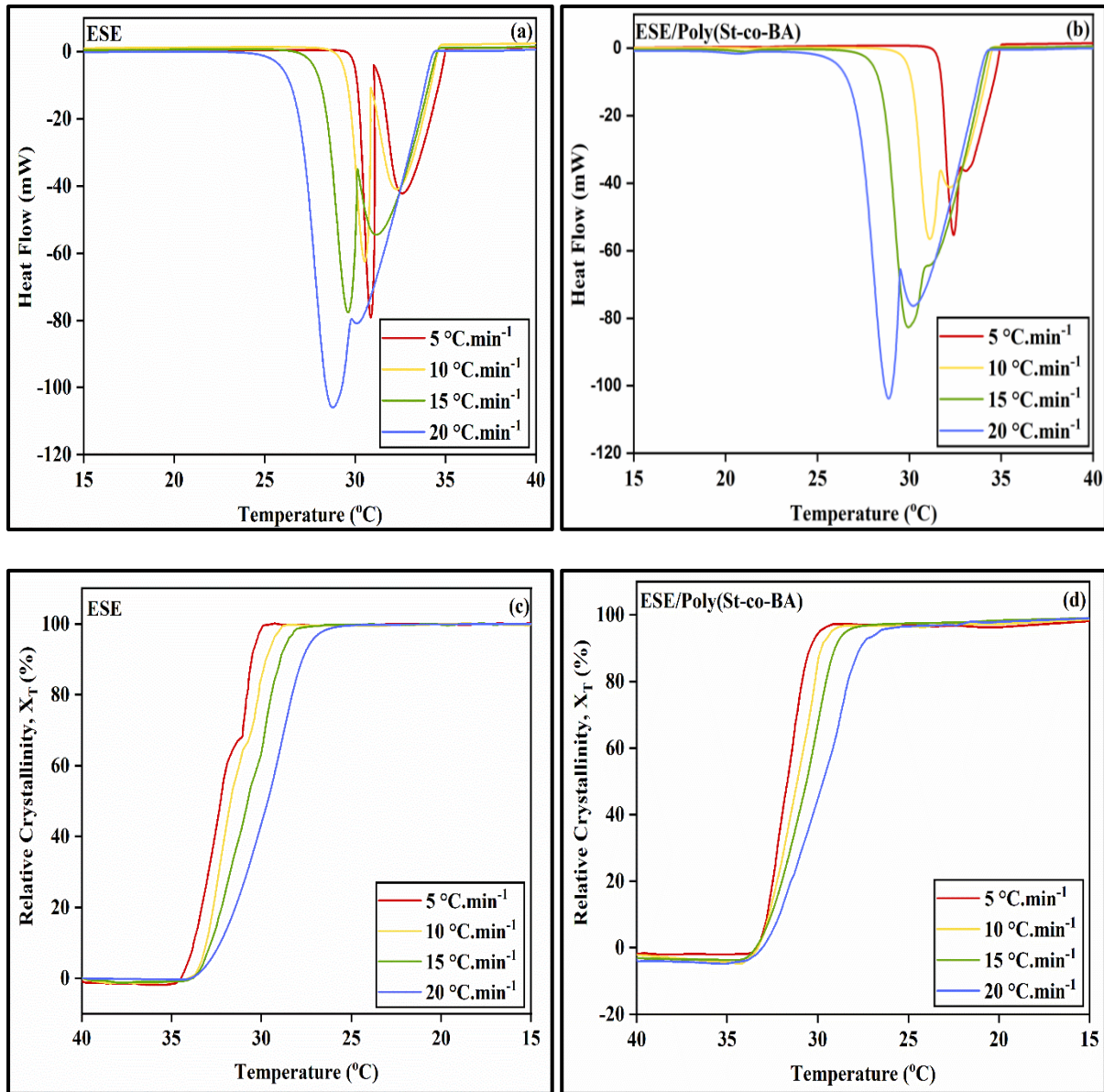


Figure 3.2: Non-isothermal crystallization DSC thermograms of (a) ESE and (b) ESE/Poly(St-co-BA); Plot of relative crystallinity (X_T) vs. temperature (T) for (c) ESE and (d) ESE/Poly(St-co-BA) at different cooling rates of 5, 10, 15, 20°C.min⁻¹

The exothermic peaks of ESE and ESE/Poly(St-co-BA) were found to move toward lower temperatures when the cooling rate increased, as shown in **Figures 3.2 (a) and (b)**. This phenomenon is caused by an acceleration of the overall crystallization rate, even though the motion of ESE was somewhat affected by the lower temperature. Moreover, at different cooling rates, the peak crystallization temperature values of ESE are slightly distinct from that of

ESE/Poly(St-co-BA), suggesting that the Poly(St-co-BA) shell had minimal influence on the ESE crystallization process. It was evident from **Figure 3.2 (c) and (d)** that relative crystallinity of ESE and ESE/Poly(St-co-BA) was developed with the drop in temperature. At the equivalent relative degree of crystallinity, the crystallization temperatures fall with an increased cooling rate. Additionally, the molecular chains diffuse more readily at a lower cooling rate and have good fluidity, which enables samples to have higher crystallinity at an elevated temperature.

3.2.1.2.1. Effective Activation Energy

In a non-isothermal environment, the activation energy generally represents the energy barrier for the phase transition in ESE. Notably, activation energy is made up of two components: the energy required to form critical-size crystal nuclei, known as nucleation activation energy, and the energy required to transit the molecular segments of ESE across the phase boundary, known as transport activation energy. The nucleation and mobility process of ESE molecules are correlated with the activation energy. The activation energy of ESE/Poly(St-co-BA) was found to be lower than that of ESE, as determined by the different models using equations (2.5, 2.6, 2.7) [**Figure 3.3 (a) to (f)**] and **Table 3.2** summarizes the activation energy values.

The difference in the activation energies suggests that ESE/Poly(St-co-BA) crystallize more readily due to a lower energy barrier caused by the heterogeneous nucleation. As previously mentioned, the heterogeneous nucleation provided by Poly(St-co-BA) has the potential to lower the nucleation activation energy and facilitates the crystallization of ESE molecules.

Table 3.2: Values of the crystallization activation energy as determined using various models

Sample	Method to find activation energy (KJ.mol ⁻¹)		
	Kissinger Model	Augis and Bennett approximation	Mahadevan Model
ESE	-23.7	-21.1	-18.4
ESE/Poly(St-co-BA)	-16.1	-13.7	-11.2

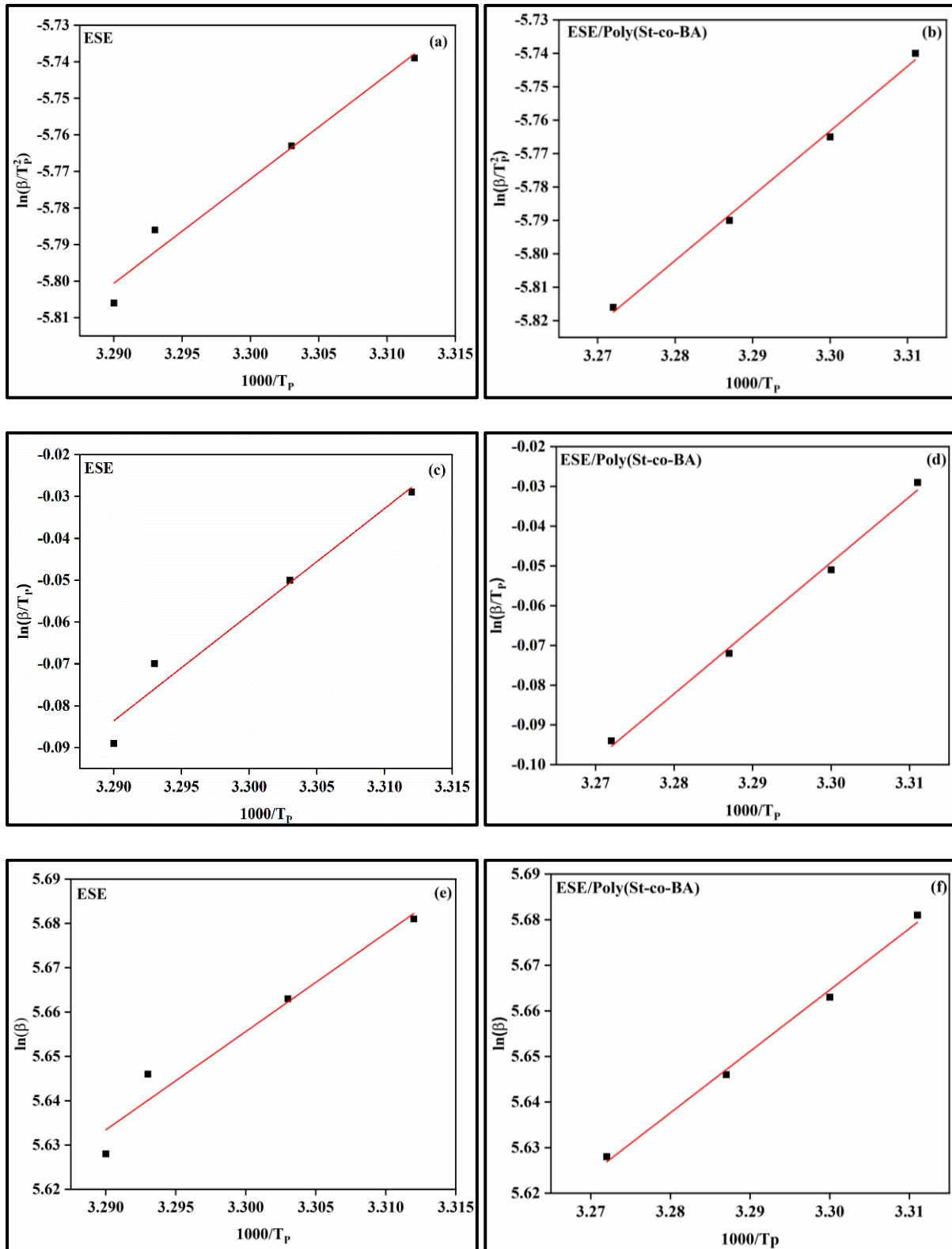


Figure 3.3: Nucleation activation energy plots of ESE and ESE/Poly(St-co-BA) using (a,b) Kissinger's method, (c,d) Augis–Bennett approximation, and (e,f) Mahadevan method respectively

Conversely, the Poly(St-co-BA) shell can boost the transport activation energy and impede the free mobility of ESE molecular chains. Nonetheless, the nucleation effect of ESE/Poly(St-co-BA) molecules outweighs the hindering effect of its molecular chain mobility in the ESE/Poly(St-co-BA). The Poly(St-co-BA) polymer shell skeleton can provide a large number of heterogeneous nucleation sites for ESE to crystallize. Consequently, the adverse impact was successfully mitigated. This finding implies that the phase transition kinetics of ESE in the encapsulated state were facilitated by the Poly(St-co-BA) shell encapsulation.

Another possible reason for the enhanced ESE crystallization performance is that the modification treatment or encapsulation might have increased the van der Waals forces on the shell's surface, and enhancing its ability to initiate the nucleation process. This suggests that the ESE/Poly(St-co-BA) microcapsules were more favorable for lowering the nucleation barrier and stimulating ESE nucleation, which in turn improved the ESE/Poly(St-co-BA) crystallization behavior.

3.2.1.2.2. Analysis Based on the Avrami Theory

For ESE and ESE/Poly(St-co-BA), the order of crystallization (n) is determined by employing equation (2.8) and listed in **Table 3.3**. The value of n can be ascertained by calculating the slope of the curve, that is obtained when $\ln(\beta)$ is plotted against $\ln[-\ln(1-\chi)]$, as depicted in **Figure 3.4**.

Table 3.3: Avrami index data of ESE and ESE/Poly(St-co-BA)

	B	$\ln(\beta)$	Partial Area (a)	Total Area (A)	$\chi=a/A$	$\{\ln[-\ln(1-\chi)]\}$	n
ESE	5	1.6	-24.8	-1752.1	0.01	-4.2	1.1
	10	2.3	-62.5	-1754.7	0.04	-3.3	
	15	2.7	-41.1	-1057.9	0.04	-3.2	
	20	3	-89.2	-1342.4	0.07	-2.7	
ESE/Poly(St-co-BA)	5	1.6	-24.2	-1162.4	0.02	-3.9	0.8~1
	10	2.3	-37.2	-874.3	0.04	-3.1	
	15	2.7	-58.6	-1129.1	0.05	-2.9	
	20	3	-68.3	-1176.1	0.06	-2.8	

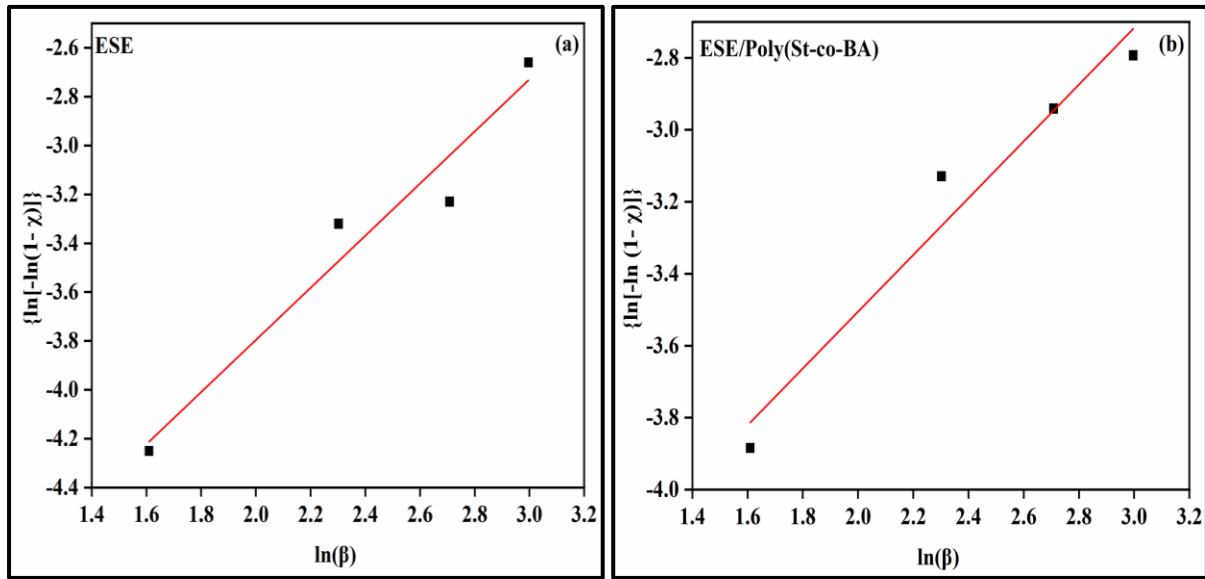


Figure 3.4: Plot of $\{\ln[-\ln(1-\chi)]\}$ vs. $\ln(\beta)$ for (a) ESE and (b) ESE/Poly(St-co-BA) at different temperatures

The value of n for the ESE is 1.1, which denotes surface nucleation and one-dimensional (1-D) growth from the outside in. As, a wide range of growth shapes are attributed to the Avrami index, n (ranging from 1 to 3), from spherical to rod-like geometries, consequently, needle-like nucleation growth is seen in ESE. The value of Avrami index for ESE/Poly(St-co-BA) i.e. 0.8~1. This suggests that encapsulating the ESE and raising the crystallization temperature did not appreciably alter the crystallization mechanism and had no impact on the crystal growth geometric dimension.

3.2.2. Thermal Stability of ESE/Poly(St-co-BA) Microcapsules

The thermal stability of the materials at intense heat and temperature was measured using the TGA. An inert nitrogen environment was used for the analyses. The one-step weight loss trend of ESE is depicted in **Figure 3.5 (a)**, where it degrades at a temperature of about 75 °C at first and loses all of its weight at 265 °C. ESE have a steep TGA curve because their constituent components are alkanes, which have a lower decomposition temperature.

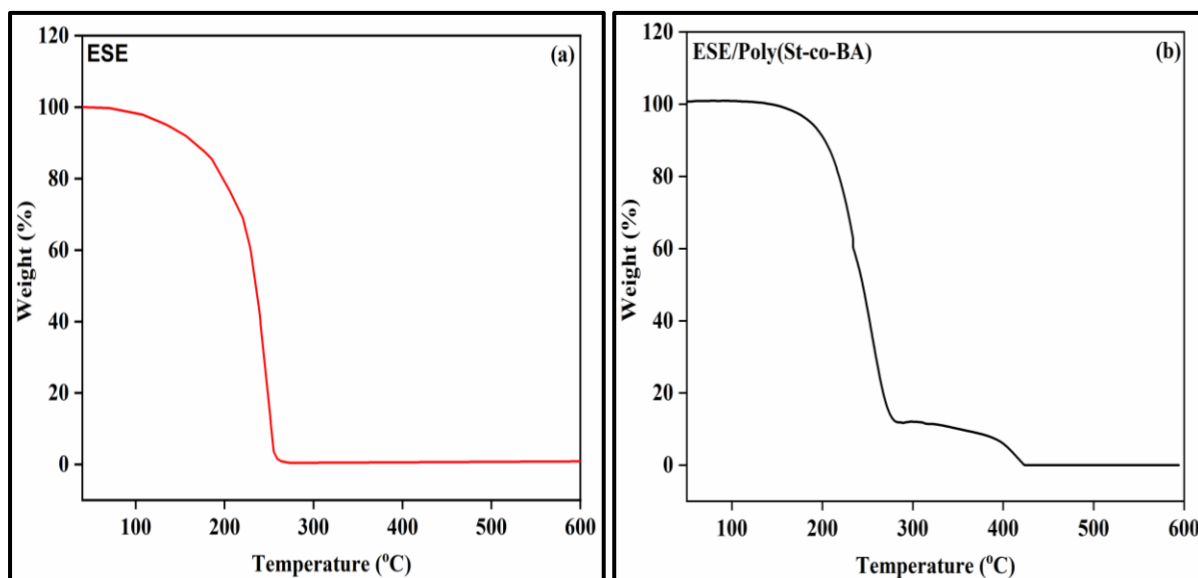


Figure 3.5: TGA analysis curve of (a) ESE and (b) ESE/Poly(St-co-BA)

As illustrated in **Figure 3.5 (b)**, the TGA curve displays a two-step deterioration trend for ESE/Poly(St-co-BA). The first step begins at about 151°C which corresponds to the disintegration of ESE, whose initial decomposition temperature is greater than ESE as a consequence of the crosslinked polymer shell's protection. Further, the degradation of the polymer shell material occurred at 279 °C. ESE/Poly(St-co-BA) are completely degraded at the 424 °C. As, can be seen from the two-step degradation in the ESE/Poly(St-co-BA), the microencapsulation has increased the thermal stability of the ESE, as it encapsulates, which has improved the leakage control, thermal resistance, and durability at high temperatures. It is an ideal result, and the produced microcapsules can be utilized for the moderate temperature range applications, like, photovoltaic panels, textiles, and buildings etc.

3.2.3. FTIR Analysis of ESE/Poly(St-co-BA) Microcapsules

FTIR spectra of ESE and ESE/Poly(St-co-BA) microcapsules are illustrated in **Figure 3.6 (a) and (b)** respectively, depicting its chemical properties. The spectrum of ESE displayed a peak at 716 cm^{-1} , which is associated with the in-plane rocking vibration of the methylene group. On the other hand, the stretching vibration of the C-H bond in ESE of methyl and methylene groups is attributed to the peaks of 2847 cm^{-1} , 2912 cm^{-1} , and 2958 cm^{-1} respectively. Similarly, the C-H bending vibration is observed at the 1472 cm^{-1} peak [144]. The C-H stretching peaks of Poly(St-co-BA) and ESE overlapped in the ESE/Poly(St-co-BA) spectrum.

Subsequently, the presence of Poly(St-co-BA) was examined to verify the precision of the reaction by examining the resultant ESE/Poly(St-co-BA) spectrum. The C-O and C=O stretching vibration of the PBA co-monomer of the Poly(St-co-BA) shell is associated with two prominent peaks at 1218 cm^{-1} and 1732 cm^{-1} respectively. However, the PS of Poly(St-co-BA) polymer shell was analogous to the peaks at 3026 and 1601 cm^{-1} , which corresponds to the C–H and C=C of Ph stretching respectively.

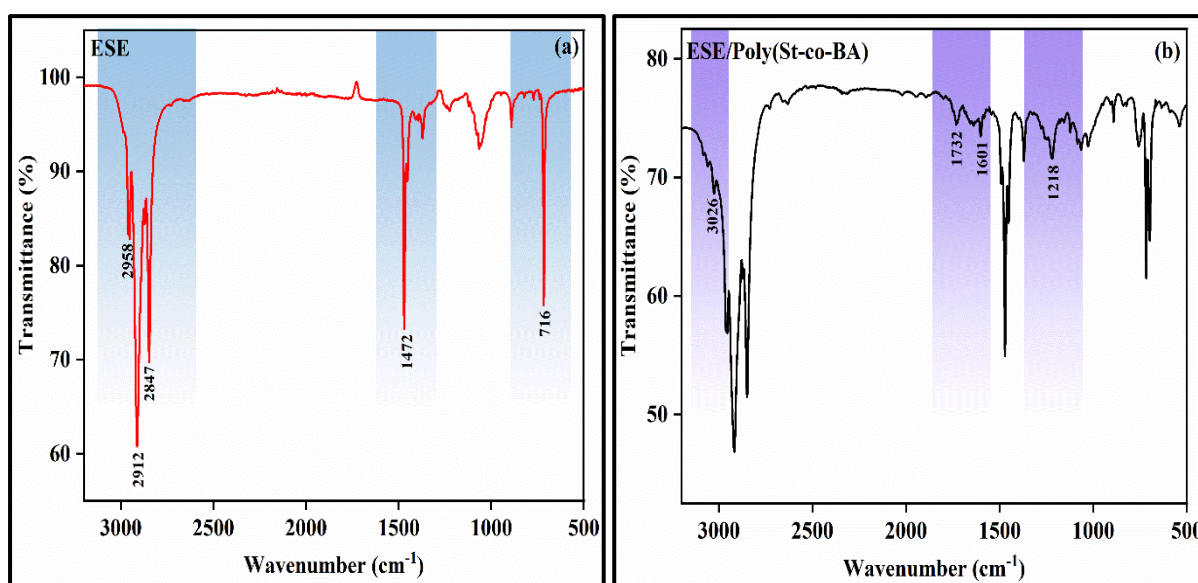


Figure 3.6: FTIR spectra of (a) ESE and (b) ESE/Poly(St-co-BA)

3.2.4. PXRD Analysis of ESE/Poly(St-co-BA) Microcapsules

PXRD pattern of ESE and ESE/Poly(St-co-BA) are shown in **Figure 3.7 (a) and (b)**. On the basis of XRD data, a series of diffraction peaks of ESE presented at $2\theta = 10.4^\circ, 13.9^\circ, 17.4^\circ, 19.3^\circ, 19.8^\circ, 20.9^\circ, 22.5^\circ, 23.5^\circ, 24.8^\circ, 25.6^\circ, 35.1^\circ, 39.8^\circ, 42.3^\circ, 44.5^\circ$ were indexed as (003), (004), (005), (010), (011), (012), (013), (105), (-101), (110), (0010), (0-22), (0012), (207) reflection planes of triclinic crystal phase, respectively. These distinctive diffraction peaks, as seen in **Figure 3.7 (a)**, are entirely consistent with those indexed by the standard PDF card No. 45-1543, indicating that the pure ESE possesses a conventional triclinic crystalline structure in the solid state [172], [179].

The parental ESE was encapsulated with the polymer shell of Poly(St-co-BA). These polymer shells are amorphous in nature and shows broad peak in between 15-25°. The XRD patterns of the synthesized microcapsules contain all the crystalline peaks of ESE and a wide amorphous peak of the Poly(St-co-BA) polymer shell. As confined in the polymer shell of the microcapsules, these diffraction peaks show that the crystalline properties of ESE were well preserved and that its crystal structure remains unchanged. As a result, there is only physical interaction between the ESE core and the Poly(St-co-BA) shell materials during the encapsulation process, which plays a crucial role in determining the stability, functionality and efficiency of the encapsulated product [145], [180], [181].

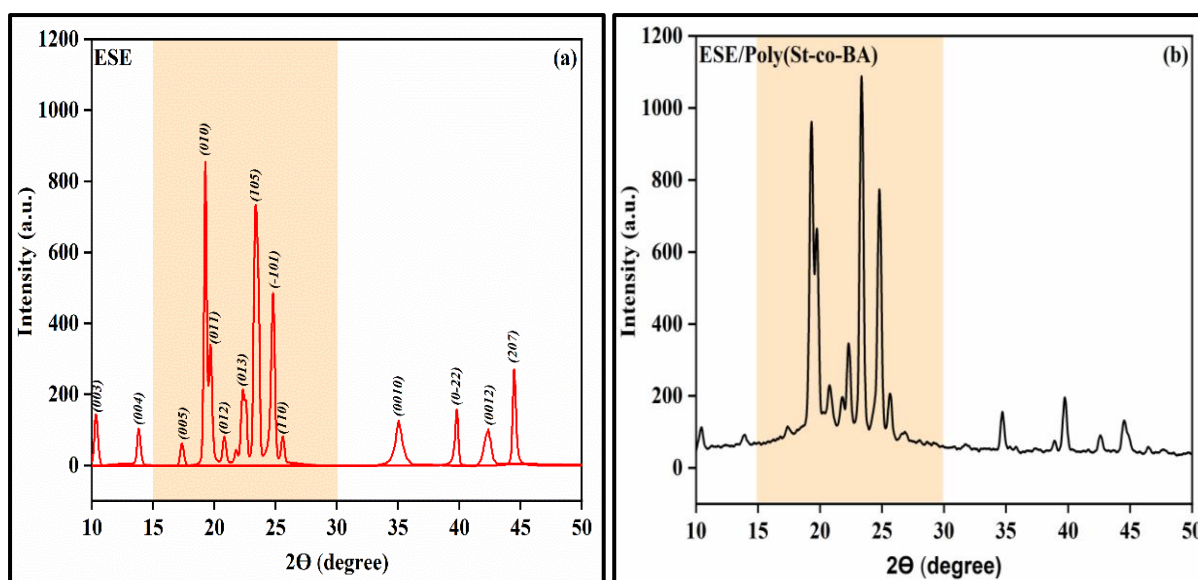


Figure 3.7: PXRD pattern of (a) ESE and (b) ESE/Poly(St-co-BA)

3.2.5. PSD and Morphology of the ESE/Poly(St-co-BA) Microcapsules

The ESE/Poly(St-co-BA) PSD is shown in **Figure 3.8**. The z-average diameter of the ESE/Poly(St-co-BA) was 0.2 μm , and the PSD in volume exhibits particle sizes with unimodal dispersion that span 0.1 to 0.7 μm . The agitation rate regulates the average diameter of the microcapsules. Accelerating the stirring rate lead to a finer emulsion and a decrease in the average diameter of the microcapsules [182].

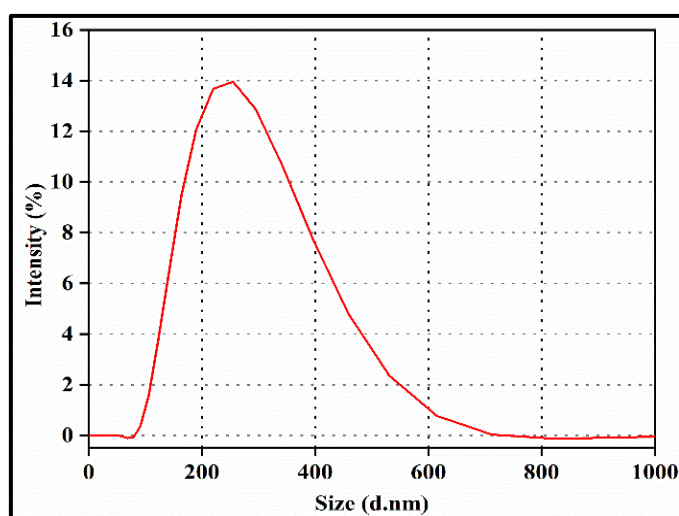


Figure 3.8: PSD of ESE/Poly(St-co-BA)

The TEM image of the ESE/Poly(St-co-BA) is shown in **Figure 3.9**. The ESE/Poly(St-co-BA) microcapsules have smooth and compact surfaces. It was observed that the majority of the microcapsules exhibit a typical spherical profile, where a dark portion representing the Poly(St-co-BA) shell, while the pale portion displayed the encapsulated ESE core.

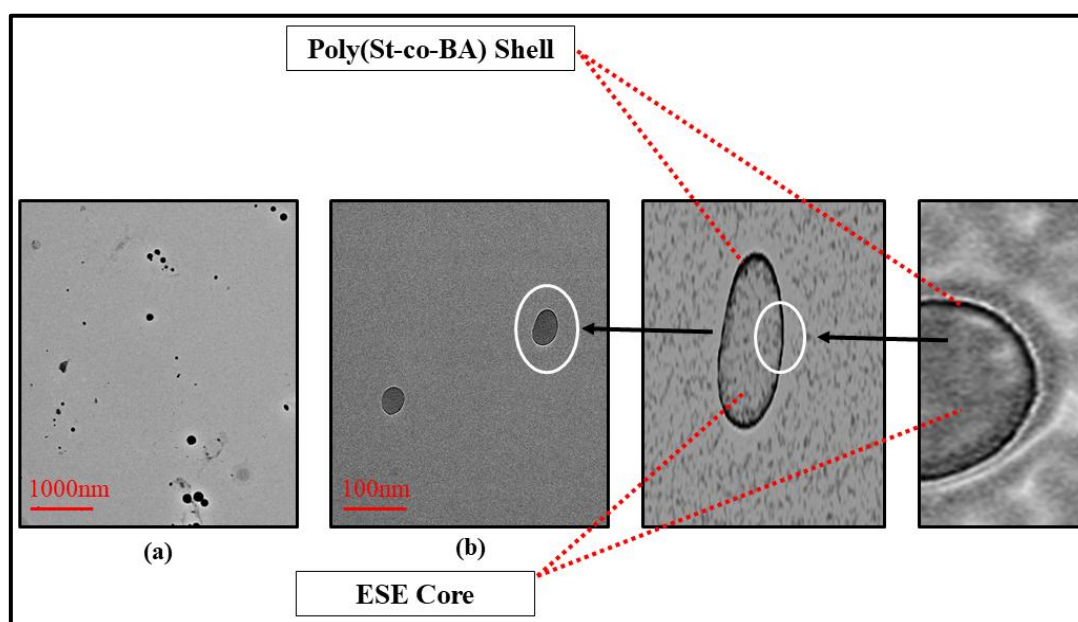


Figure 3.9: TEM micrographs of ESE/Poly(St-co-BA), captured at different positions and different resolutions: (a) 1000nm and (b) 100nm

The diameter of the prepared microcapsules has been calculated by employing image J software. The ESE/Poly(St-co-BA) exhibit diameter ranging from 0.18 to 0.21 μm , which is consistent with the result findings of the particle size analyser [145], [147], [180].

3.2.6. Study on Stability of the Synthesized ESE/Poly(St-co-BA) Microcapsules

In this work, the diffusion-oozing circle test was used to assess the stability of the microcapsules [183]. The microcapsules were planted on the filter paper and left for 3 h at 60 $^{\circ}\text{C}$ in the oven. After that, the sample leakage was assessed using the percentage of the test area. The initial state ESE and ESE/Poly(St-co-BA) is depicted in **Figure 3.10 (a)**. After heating for 3 h at 60 $^{\circ}\text{C}$, the ESE got liquified, while the ESE/Poly(St-co-BA) maintain its structural integrity, as no leakage was observed on the corresponding filter paper [**Figure 3.10 (b)**]. These findings demonstrate that the resulted microcapsules have possessed exceptional thermal stability.

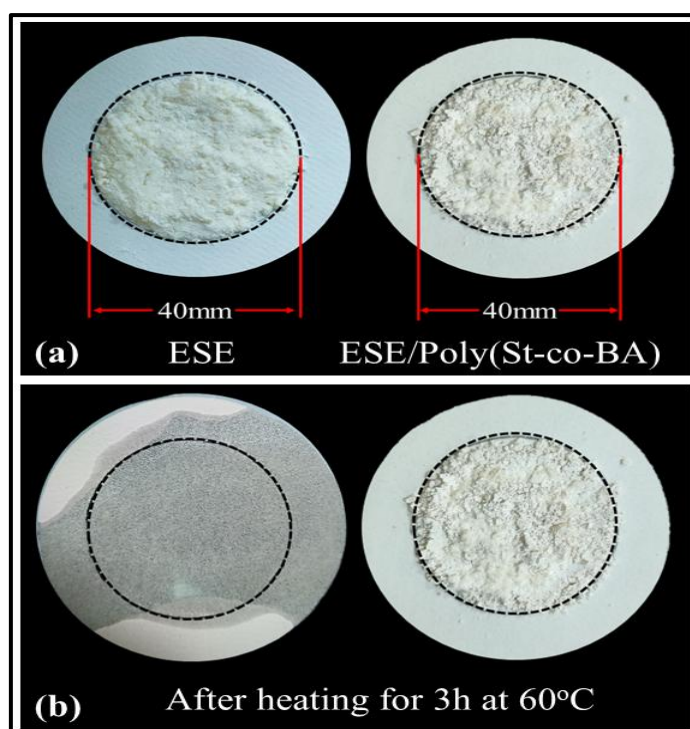


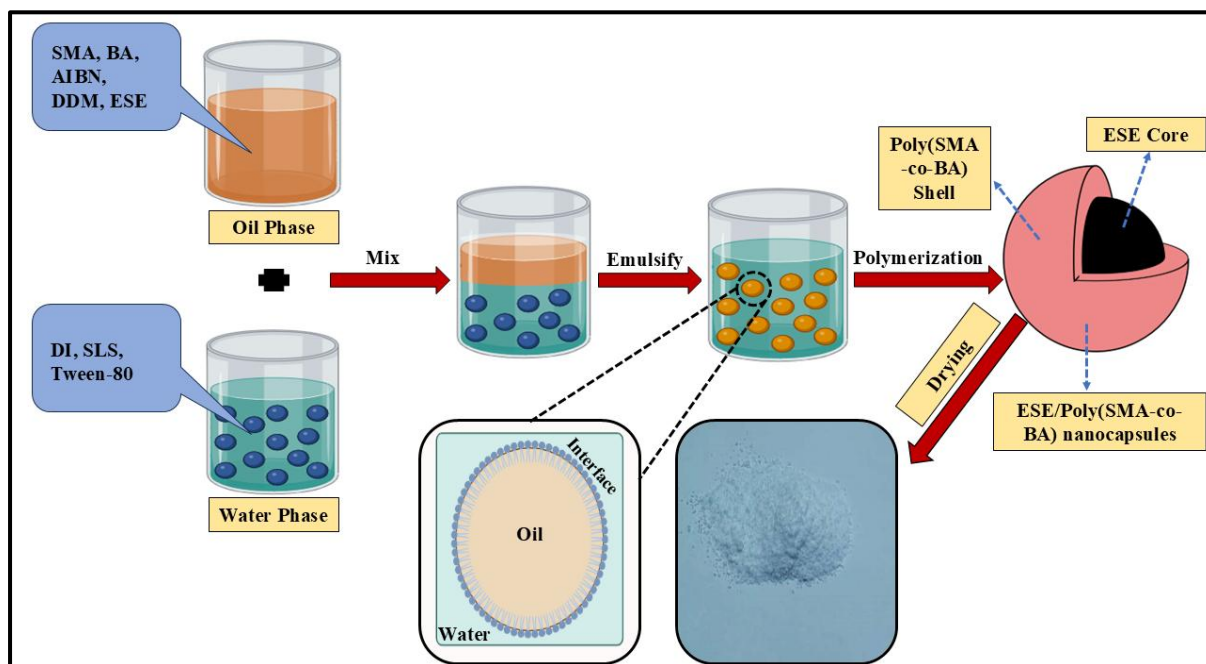
Figure 3.10: Diffusion-oozing circle test-based photographic image of ESE and ESE/Poly(St-co-BA)

3.3. Significant Findings

The fabrication and evaluation of MPCMs, as envisaged under Objective 1, were systematically investigated for their application in LHTES. Accordingly, ESE/Poly(St-co-BA) microcapsules, consisting of ESE as the phase change core encapsulated within a Poly(St-co-BA) polymeric shell, were successfully synthesized via the mini-emulsion polymerization method. Tests have been performed to measure their properties. The prepared ESE/Poly(St-co-BA) are suitable as LHTES material, as demonstrated by the DSC results having 91.9% encapsulation ratio, 91.6% encapsulation efficiency and 99.6% thermal storage capacity, having melting and crystallization temperature of 38.9 and 31.1 °C respectively and their corresponding latent heat equals to 220.5 and 218.6 J.g⁻¹. The activation energy of ESE/Poly(St-co-BA) is lower than that of ESE, as determined by the different models which represents that ESE/Poly(St-co-BA) crystallize more readily due to a lower energy barrier caused by the heterogeneous nucleation. The findings from the analysis of the Avrami index i.e. $n=1.1$ for ESE and $n=0.8\sim 1$ for ESE/Poly(St-co-BA), demonstrated that encapsulating ESE did not significantly change the geometric dimensions of the crystal development, as the crystallization mechanism remained consistent before and after encapsulating ESE. According to the TGA study, the synthesized ESE/Poly(St-co-BA) microcapsules have good thermal stability and degrade in two steps. FTIR results have confirmed that the prepared ESE/Poly(St-co-BA) microcapsules contain all the characteristic peaks of ESE and Poly(St-co-BA). The XRD patterns of the synthesized microcapsules contain all the crystalline peaks of ESE and a wide amorphous peak of the Poly(St-co-BA) polymer shell. The TEM and PSD results have confirmed the uniform spherical geometries, along with the smooth and compact surfaces of the synthesized ESE/Poly(St-co-BA), with a mean particle diameter of approximately 0.2 μm . The synthesized ESE/Poly(St-co-BA) can effectively be used for the TES purposes, by integrating them in potential areas like HVAC systems, electronics cooling, food and textile industry, cold-chain management, medical applications, and greenhouses to provide the most stable environment for the plant growth.

CHAPTER 4

SYNTHESIS AND DESIGN OF NANOENCAPSULATED PHASE CHANGE MATERIALS: AN EMBRYONIC INCEPTION



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CHAPTER 4

SYNTHESIS AND DESIGN OF NANOENCAPSULATED PHASE CHANGE MATERIALS: AN EMBRYONIC INCEPTION

4.1. Introduction

A novel NPCM, ESE/Poly(SMA-co-BA) was produced via a mini-emulsion polymerization reaction of polystearyl methacrylate-co-polybutylacrylate [Poly(SMA-co-BA)] polymer shell around ESE, which served as the core material. The present study builds upon previous research on microencapsulation with a PS shell by investigating nanoencapsulation with a PSMA shell to improve PCM thermal stability. The rigid aromatic structure of the PS shell resulted in significantly lower thermal stability, while the long alkyl polymer chain shell optimizes both thermal stability and interfacial compatibility. Furthermore, a reduced particle size in nanoencapsulation raises the surface area-to-volume ratio, improving heat transfer rates and resolving the problem of low thermal conductivity. Nanoencapsulation enhances the dispersion of PCMs, reduces leakage, and offers superior protection against environmental factors. Additionally, the structural alterations caused by long alkyl polymer chains promote phase change behaviour, augment durability, and extend operational efficiency, rendering nanoencapsulation a more effective and reliable solution for advanced TES applications.

A key innovation of this study is the inclusion of PSMA, which incorporates long alkyl polymer chains into the shell structure, substantially enhancing the nanocapsules' compatibility, stability, and thermal regulation qualities. These long alkyl chains facilitate to form crystalline areas within the polymer matrix, which affects the thermal transitions of the NPCMs. Furthermore, the highly hydrophobic nature of these long chains reduces moisture absorption, resulting in enhanced thermal stability and extended endurance in a variety of environmental conditions. In addition to the structural benefits of PSMA, PBA serves as a copolymer, boosting mechanical flexibility, toughness and diminishing the chances of nanocapsule rupturing during the heating cycle. Its elastomeric nature reinforces the polymer shell, resulting in high encapsulation efficiency and long-term durability. The amalgamation of PSMA's crystalline long alkyl chains and PBA's flexibility results in a strong and versatile encapsulation system with superior thermal stability, mechanical resilience, and controlled release qualities. The

thermal and chemical properties, overall thermal stability, surface morphology and particle size distribution of the synthesised ESE/Poly(SMA-co-BA) nanocapsules were also investigated. The combination of a long alkyl polymer chain and an elastomeric copolymer shell results in a novel and highly efficient encapsulation strategy, making these nanocapsules suitable for a wide range of applications, which includes energy-efficient building materials, electronic cooling systems and textiles.

4.2. Results and Discussion

4.2.1. Thermal Performance of ESE/Poly(SMA-co-BA) Nanocapsules

Figure 4.1 (a-d) depicts the DSC thermogram for the ESE and ESE/Poly(SMA-co-BA) samples. **Table 4.1 (a) and (b)** display the experimental outcomes derived from the DSC analysis. The DSC plots of ESE and ESE/Poly(SMA-co-BA) exhibit both exothermic and endothermic peaks, and the shaded region shows the prominent peaks of the materials. The melting and crystallization temperatures of ESE were determined using DSC thermograms and were found to be 38.9 °C and 30.5 °C, respectively. The observed latent heat of fusion was 239.9 J.g⁻¹, while the latent heat of crystallization was 237.7 J.g⁻¹ [**Figure 4.1 (a) and (b)**]. The ESE/Poly(SMA-co-BA) nanocapsules exhibit a melting temperature of 37.4 °C, accompanied by a latent heat of 224.6 J.g⁻¹ and a crystallization temperature of 25.1 °C, with a latent heat of crystallization of 191.7 J.g⁻¹ [**Figure 4.1 (c) and (d)**]. The observed decrease in latent heat is attributed to the presence of the Poly(SMA-co-BA) polymer shell [147]. The findings confirm that the synthesized ESE/Poly(SMA-co-BA) has remarkable heat storage capabilities and substantial potential for use in TES applications, including waste heat recovery, solar energy systems, building materials, smart textiles and thermo-responsive coatings.

Table 4.1 (a): DSC analysis results of endothermic process in pure ESE and ESE/Poly(SMA-co-BA) nanocapsules

	T _{om} (°C)	T _{pm} (°C)	T _{cm} (°C)	ΔH _m (J.g ⁻¹)
ESE	35.5	38.9	40.1	239.9
ESE/Poly(SMA-co-BA)	32.6	37.4	38.6	224.6

Table 4.1 (b): DSC analysis results of exothermic process in pure ESE and ESE/Poly(SMA-co-BA) nanocapsules

	T_{oc} (°C)	T_{pc} (°C)	T_{ec} (°C)	ΔH_c (J.g ⁻¹)
ESE	30.9	30.5	29.6	237.7
ESE/Poly(SMA-co-BA)	27.9	25.1	20.0	191.7

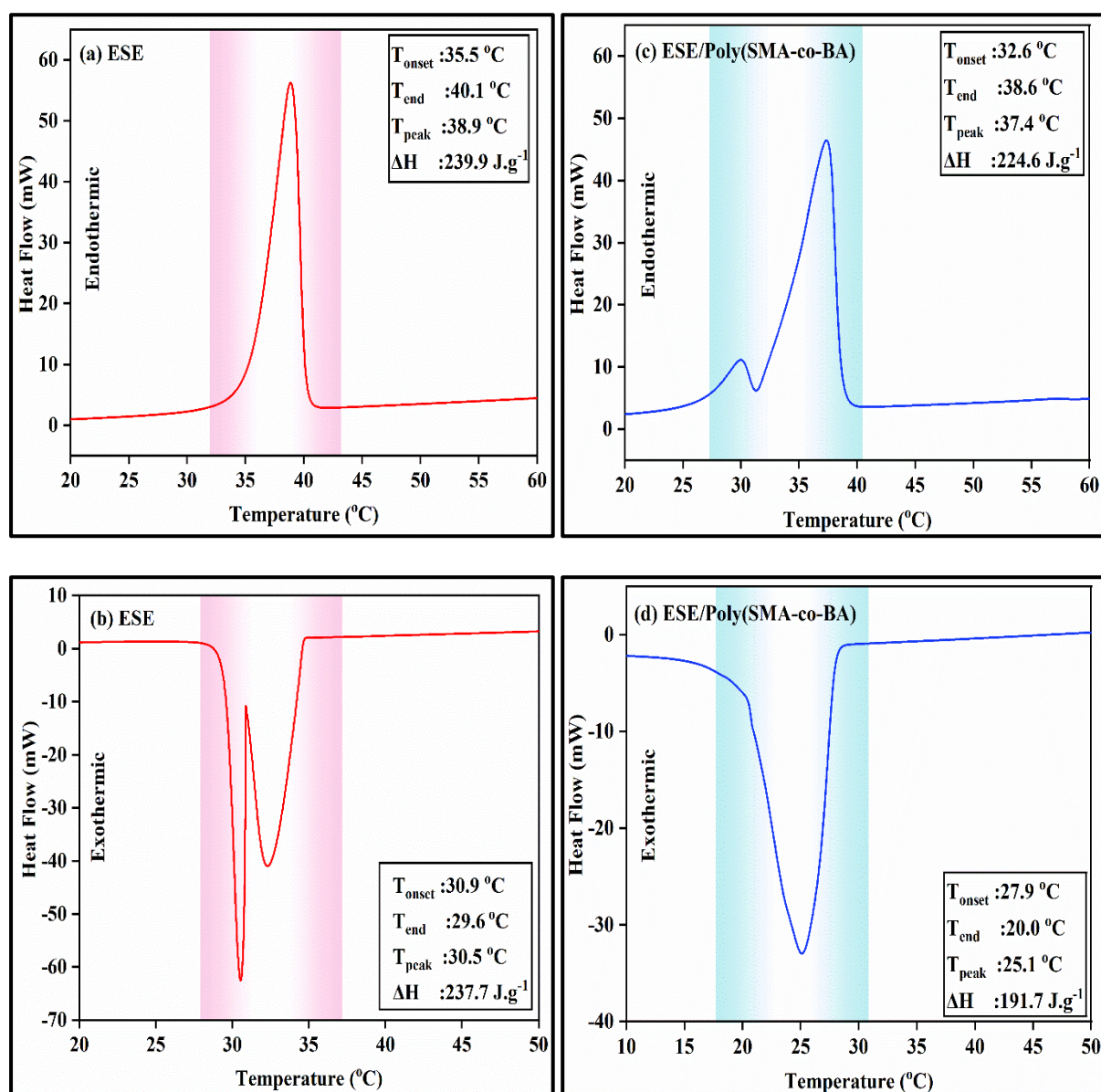


Figure 4.1: DSC thermograms of the (a,b) ESE and (c,d) synthesized ESE/Poly(SMA-co-BA) nanocapsules

4.2.1.1. Effect of Long-Alkyl SMA Polymer Shell Crystallinity on the NPCMs Thermal Behaviour

From Figure 4.1, it was found that the DSC thermogram of pristine ESE contains a single sharp endothermic peak at 38.9 °C and a double sharp exothermic peak at 30.5 °C and 32.3 °C, respectively. On the contrary, the DSC thermogram of NPCMs shows dual endothermic peaks at 30 °C and 37.4 °C and a single exothermic peak at 25.1 °C. This drastic change is due to the dominant nature of the long alkyl side chain of methacrylate towards the thermal transition to a great extent [184]. At a lower temperature, the first endothermic peak of the NPCMs is seen, which is associated with the melting of PSMA's crystalline stearyl side chains from the polymer shell Poly(SMA-co-BA) (**Figure 4.2**) [185]–[188]. The long alkyl side chains in PSMA, a semi-crystalline polymer, have the ability to crystallize independently to form ordered domains inside the polymer matrix. It is important to note that the primary methacrylate backbone remains intact when these side chains melt. Instead, this transition represents the thermal softening or reorganization of the crystalline side-chain regions that can occur without jeopardising the enclosing shell's structural integrity. The melting of the ESE is represented by the second endothermic peak. This peak appears broader and slightly shifted when compared to bulk ESE; this behaviour is ascribed to restricted molecular mobility, confinement effects, and interfacial interactions between the core and shell [136]. These parameters alter the melting dynamics of the PCM, resulting in a less abrupt transition.

In contrast to the two distinct crystallization peaks seen in pure ESE, the NPCM displayed a single broad exothermic peak throughout the cooling cycle. The overlapping crystallization events of the PSMA shell and the paraffin core, which take place in comparable temperature ranges, are most likely the cause of this combined peak [189]. The broad exothermic response is facilitated by the independent crystallization of PSMA, which is stimulated by the reorganization of its side chains, whereas the multi-step crystallization of paraffin that is usually observed in its bulk form is limited by nano-confinement within the shell [190], [191]. The produced NPCMs are compared to other encapsulated PCMs with the shorter and longer alkyl polymer shells in **Table 4.2**.

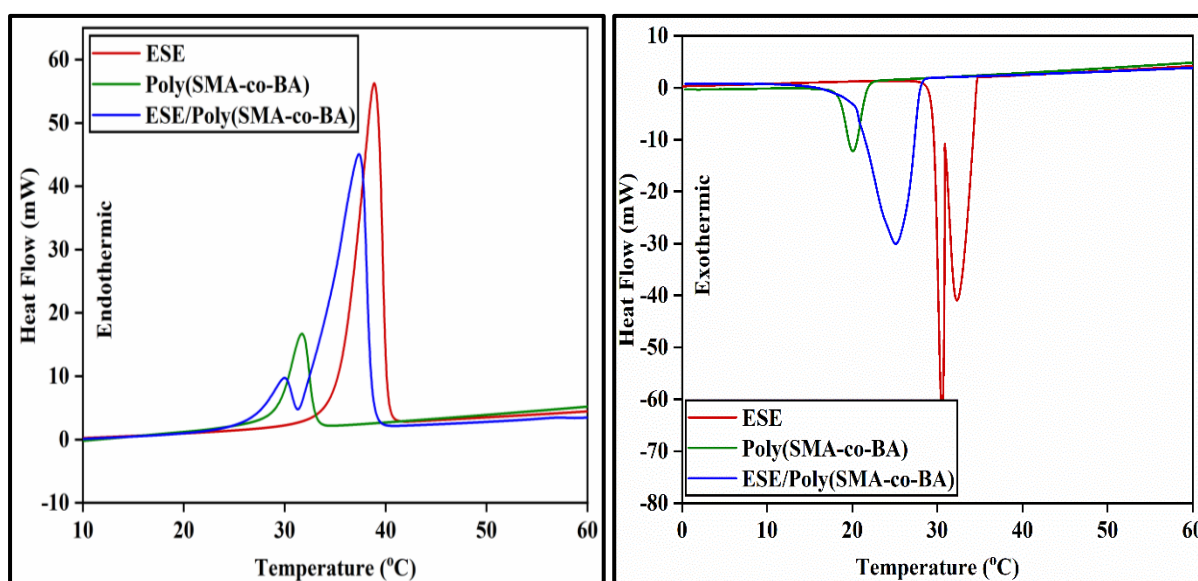


Figure 4.2: Endothermic and exothermic DSC thermograms of the ESE, Poly(SMA-co-BA) and the prepared ESE/Poly(SMA-co-BA)

Table 4.2: Comparative study of the prepared NPCMs with the shorter and longer alkyl methacrylate polymer shell

Shell	PCM	PCM:Shell	ΔH_{m-EPCM} (J.g ⁻¹)	ΔH_{c-EPCM} (J.g ⁻¹)	E_r/E_s (%)	Ref
PMMA	Paraffin	1:1	64.9	66.4	$E_{ES}=52.9$	[77]
	ΔH_m : 122.4 J.g ⁻¹	3:4	62.3	63.9	50.9	
	ΔH_c : 125.7 J.g ⁻¹	3:5	62.2	64.4	50.0	
		1:2	60.3	61.7	48.1	
PMMA/SiO ₂	Paraffin	-				[192]
10.5:3	ΔH_m : 121.0 J.g ⁻¹		70.0	71.0	$E_{ES}=57.4$	
11.5:2	ΔH_c : 124.5 J.g ⁻¹		57.5	57.5	46.9	
12.5:1			53.5	53.5	43.6	
13.5:0			62.1	62.4	50.7	
PMMA	Nonadecane	2:1	43.6	49.4	-	[193]
	ΔH_m : 230.7 J.g ⁻¹	1:1	61.9	63.7	-	

	ΔH_c : 223.8 J.g ⁻¹	1:2	139.2	142.4	$E_R=60.3$	
PMMA	ESE ΔH_m : 202.5 J.g ⁻¹ ΔH_c : 193.4 J.g ⁻¹	1:1	124.7	119.1	$E_R=62$	[144]
PBMA-co-DVB	Octadecane (C ₁₈) ΔH_m : 216.0 J.g ⁻¹ ΔH_c : 216.4 J.g ⁻¹ Butyl stearate (BS) ΔH_m : 104.0 J.g ⁻¹ ΔH_c : 108.1 J.g ⁻¹	(C ₁₈) 1:1 (BS) 1:1 (C ₁₈ :BS=1:1) 1:1 (C ₁₈ :BS=1:1) 2:1	87.9 37.4 40.3 93.1	90.5 37.6 42.1 91.9	$E_{ES}=41.2$ 35.3 33.7 71.3	[194]
(i) PBMA-co-PBA (ii) PBMA-co-PBA-co-PMAA (iii) PBMA-co-PMAA (iv) PBMA-co-PAA	Octadecane ΔH_m : 223.1 J.g ⁻¹ ΔH_c : 227.1 J.g ⁻¹	1:1	(i)116.4 (ii)136.3 (iii)144.3 (iv)141.5	(i)125.5 (ii)130.0 (iii)152.9 (iv)143.0	(i)53.7 (ii)59.2 (iii)66.0 (iv)63.2	[195]
(i) PBMA (with DVB) (ii) PBMA (with PETA)	Octadecane ΔH_m : 223.1 J.g ⁻¹ ΔH_c : 227.1 J.g ⁻¹	1:1	(i)107.1 (ii)126.4	(i)109.4 (ii)123.7	(i)48.1 (ii)55.6	[196]
PU/PBMA (i) With Diethylenetriamine (ii) with Diethylenetriamine and Glycerol (1:1)	Paraffin ΔH_m : 166.0 J.g ⁻¹ ΔH_c : 163.1 J.g ⁻¹	1:1	(i)106.0 (ii)145.2	(i)95.7 (ii)126.7	(i)61.3 (ii)82.6	[197]
PLMA-co-DVB	Octadecane (C ₁₈) ΔH_m : 216.0 J.g ⁻¹ ΔH_c : 216.4 J.g ⁻¹ Butyl stearate (BS)	(C ₁₈) 1:1 (BS) 1:1 (C ₁₈ :BS=1:1) 1:1	67.7 34.3 36.4	67.2 30.7 27.6	$E_{ES}=31.2$ 30.6 24.7	[194]

	ΔH_m : 104.0 J.g ⁻¹ ΔH_c : 108.1 J.g ⁻¹	(C ₁₈ :BS=1:1) 2:1	80.3	81.1	62.2	
PLMA	Octadecane ΔH_m : 223.1 J.g ⁻¹ ΔH_c : 227.1 J.g ⁻¹ Paraffin ΔH_m : 166.0 J.g ⁻¹ ΔH_c : 163.1 J.g ⁻¹	1:1	118.0 76.7	108.9 73.0	E _{ES} =50.4 45.5	[198]
(i) PU/PLMA (ii) PU/PLMA (with TMP) (iii) PU/PLMA (with PETA)	Paraffin ΔH_m : 192.2 J.g ⁻¹ ΔH_c : 191.5 J.g ⁻¹	1:1	(i)102.7 (ii)127.6 (iii)132.3	(i)99.3 (ii)124.7 (iii)127.8	E _{ES} = (i)52.6 (ii)65.8 (iii)67.8	[199]
(i) PSMA (with PETA) (ii) PSMA (with DVB)	Octadecane ΔH_m : 223.1 J.g ⁻¹ ΔH_c : 227.1 J.g ⁻¹	1:1	(i)82.6 (ii)87.9	(i)80.7 (ii)94.8	E _{ES} = (i)36.3 (ii)40.6	[136]
PSMA-co-DVB	Octadecane (C ₁₈) ΔH_m : 216.0 J.g ⁻¹ ΔH_c : 216.4 J.g ⁻¹ Butyl stearate (BS) ΔH_m : 104.0 J.g ⁻¹ ΔH_c : 108.1 J.g ⁻¹	(C ₁₈) 1:1 (BS) 1:1 (C ₁₈ :BS=1:1) 1:1 (C ₁₈ :BS=1:1) 2:1	85.9 36.0 60.3 86.3	99.1 38.7 59.4 90.1	E _{ES} =42.8 35.2 46.1 68.0	[194]
Poly(SMA-co-BA)	ESE ΔH_m : 239.9 J.g ⁻¹ ΔH_c : 237.7 J.g ⁻¹	1:1	224.6	191.7	E _R =93.6 E _{ES} =87.2	This Stud y

PMMA: Polymethylmethacrylate; PBMA: Polybutylmethacrylate; PLMA: Polylaurylmethacrylate and PSMA: Polystearylmethacrylate

4.2.1.2. Phase Change Performance of ESE/Poly(SMA-co-BA) Nanocapsules

The phase-change temperatures and enthalpies of pristine ESE and ESE/Poly(SMA-co-BA) are obtained using DSC thermograms. The pristine ESE exhibits significantly elevated phase change enthalpies, as observed in **Table 4.1 (a) and (b)**. This signifies that the ESE PCM possesses a substantial capacity for LHS and can nearly discharge it as it changes phase. The encapsulation of ESE within the Poly(SMA-co-BA) shell significantly decreased the absolute phase change enthalpies of the nanocapsules. Due to the inert Poly(SMA-co-BA) shell, the latent heat may solely be stored by the phase-changeable ESE core. Consequently, the phase change enthalpies of the synthesized nanocapsules are significantly dependent on the loading of ESE within the nanocapsule. The encapsulation ratio and encapsulation efficiency, are employed to describe the phase change performance of NPCMs and may be derived from DSC findings using equations (2.1 and 2.2) [56], [200].

The synthesized nanocapsules attained an encapsulation ratio of 93.6% and an encapsulation efficiency of 87.2%. Furthermore, the thermal storage capacity of the nanoencapsulated ESE may be ascertained using the findings obtained from DSC measurements by employing equation (2.3) [164]. The nanocapsules were prepared at an ESE/Poly(SMA-co-BA) mass ratio of 1:1 and have a thermal storage capacity of 93.1%, suggesting that nearly all encapsulated ESE may efficiently store latent heat during the phase transition. The ESE has been configured in an appropriate shape and size, resulting in enhancing the material's capability of storing and releasing energy even at or beyond the phase transition temperature without experiencing any material deformation.

4.2.1.3. Kinetics of Non-Isothermal Crystallization Analysis

Figure 4.3 (a) and (b) illustrate the crystallization curves of ESE and ESE/Poly(SMA-co-BA) nanocapsules at cooling rates of 5, 10, and 15 °C.min⁻¹, highlighting the exothermic behaviour during crystallization in non-isothermal conditions. Moreover, equation (2.4) can be determine the correlation between the relative crystallinity (X_T) of ESE and ESE/Poly(SMA-co-BA) with temperature (T), as seen in **Figure 4.3 (c) and (d)** [201], [202].

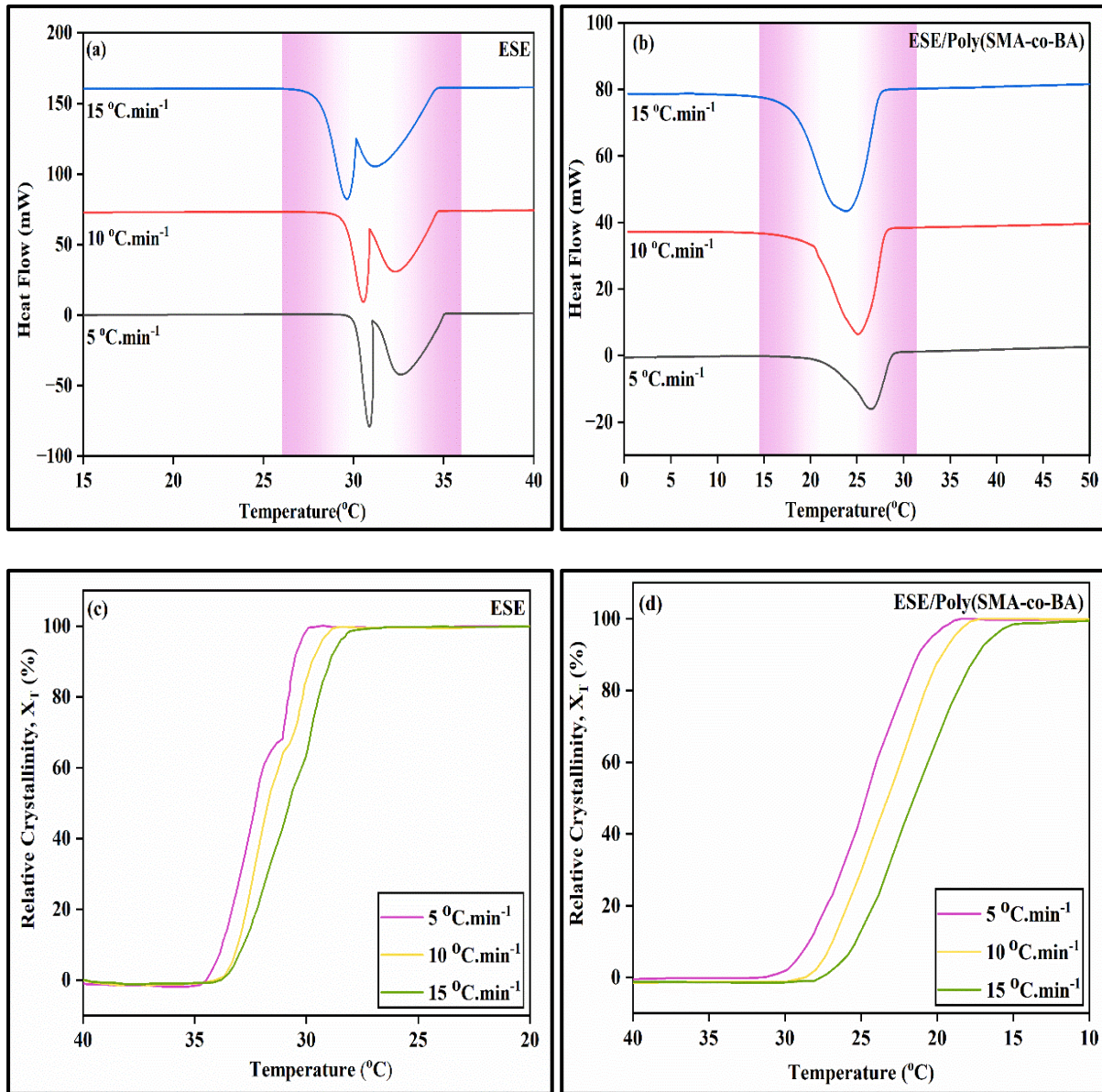


Figure 4.3: Non-isothermal crystallization DSC thermograms of (a) ESE and (b) ESE/Poly(SMA-co-BA); Plot of relative crystallinity (X_T) vs. temperature (T) for (c) ESE, and (d) ESE/Poly(SMA-co-BA) at different cooling rates

The exothermic peaks of ESE and ESE/Poly(SMA-co-BA) were found to move toward lower temperatures when the cooling rate increased, as shown in **Figure 4.3 (a) and (b)**. This effect results from an increased total crystallization rate despite the mobility of ESE being slightly influenced by the reduced temperature. Furthermore, varying cooling rates provide markedly different peak crystallization temperature values for ESE compared to ESE/Poly(SMA-co-

BA), indicating that the Poly(SMA-co-BA) shell exerts a substantial impact on the crystallization process of ESE, as elucidated in Section 4.2.1.1. **Figure 4.3 (c) and (d)** demonstrated that the relative crystallinity of ESE and ESE/Poly(SMA-co-BA) increased as the temperature decreased. At the equivalent relative degree of crystallinity, the crystallization temperatures decrease with an elevated cooling rate. Moreover, the molecular chains diffuse more efficiently at a reduced cooling rate and exhibit enhanced fluidity, allowing samples to attain greater crystallinity at increasing temperatures.

4.2.1.3.1. Effective Activation Energy

The nucleation activation energy may imitate the degree of crystal nucleation during a non-isothermal crystallization process, providing a more efficient method to evaluate the influence of the polymer shell on the crystallization behaviour of ESE. Various methods are available to estimate the activation energy such as Kissinger method, Augis & Bennett approximation and Mahadevan method. **Table 4.3** presents the activation energy values obtained through different methodologies determined by using equations (2.5, 2.6 and 2.7).

The activation energy of ESE/Poly(SMA-co-BA) is inferior to that of ESE, as demonstrated by the different models [**Figure 4.4 (a) to (f)**]. The difference in activation energy indicates that ESE/Poly(SMA-co-BA) crystallizes more rapidly because of a lower energy barrier associated with heterogeneous nucleation. As previously mentioned, the heterogeneous nucleation of Poly(SMA-co-BA) can facilitate the nucleation of ESE molecules and reduce the nucleation activation energy.

Table 4.3: Crystallization activation energy values determined using various models

Sample	Methods to determine activation energy (KJ.mol ⁻¹)		
	Kissinger Method	Augis & Bennett Approximation	Mahadevan Method
ESE	-25.1	-22.6	-20.1
ESE/Poly(SMA-co-BA)	-14.7	-12.2	-9.8

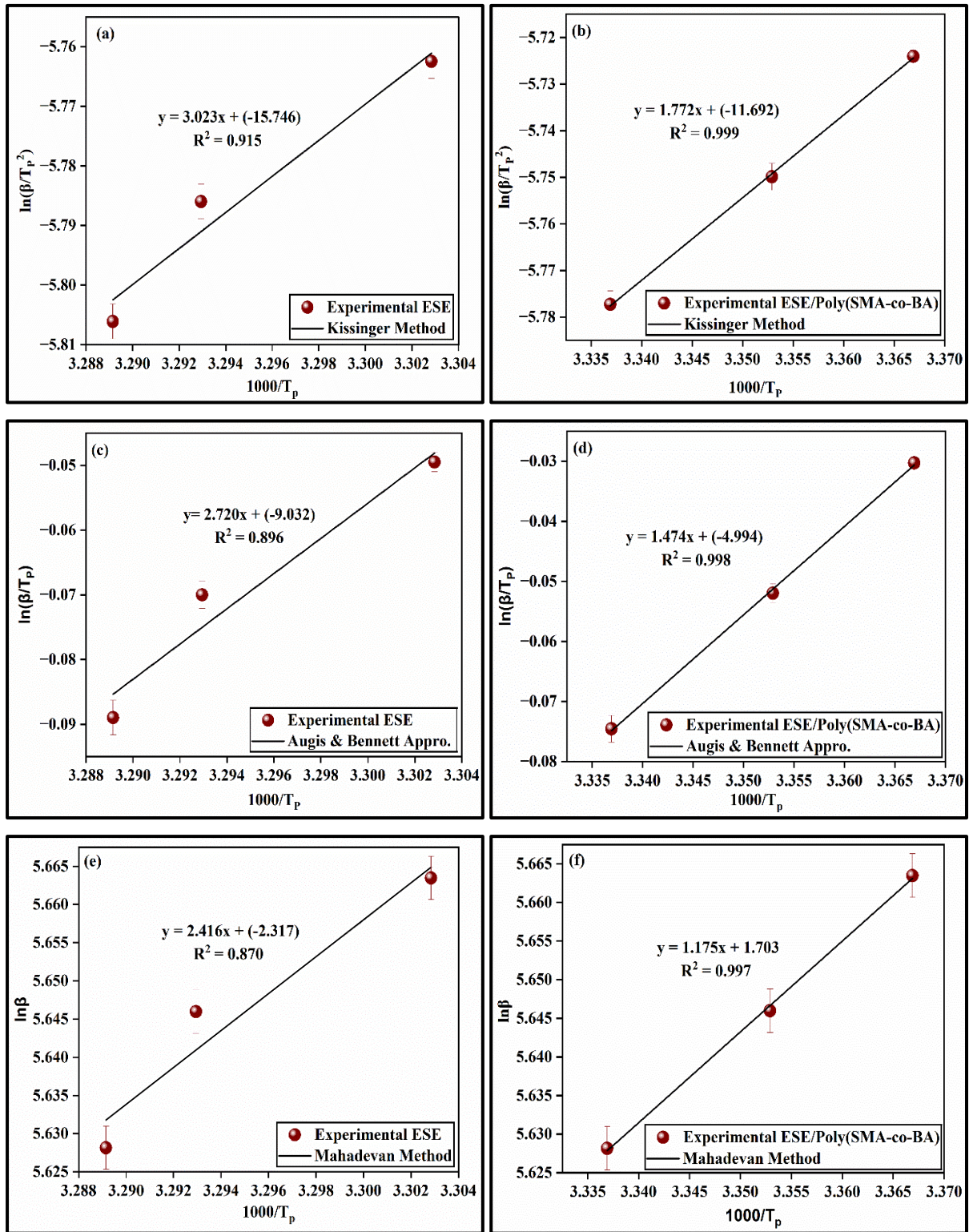


Figure 4.4: Nucleation activation energy plots: (a,b) Kissinger's method $\{\ln(\beta/T_p^2)\}$ vs. $1000/T_p$ for ESE and ESE/Poly(SMA-co-BA); (c,d) Augis and Bennett Approximation $\{\ln(\beta/T_p)\}$ vs. $1000/T_p$ for ESE and ESE/Poly(SMA-co-BA); and (e,f) Mahadevan method $\{\ln(\beta)\}$ vs. $1000/T_p$ for ESE and ESE/Poly(SMA-co-BA)

Conversely, the Poly(SMA-co-BA) shell can augment the transport activation energy and limit the unrestricted movement of ESE molecular chains. Nonetheless, the nucleation activity of ESE/Poly(SMA-co-BA) molecules may exceed the suppressive influence of their molecular chain mobility in ESE/Poly(SMA-co-BA). The Poly(SMA-co-BA) polymer shell structure can provide several heterogeneous nucleation sites for ESE crystallization. Consequently, the adverse impact was successfully mitigated. The research demonstrates that the phase transition kinetics of ESE in its encapsulated form were improved by the Poly(SMA-co-BA) shell.

A probable rationale for the enhanced ESE crystallization capability is that the modification treatment or encapsulation may have increased the van der Waals forces on the shell's surface, hence enhancing its ability to initiate the nucleation process. This suggests that the ESE/Poly(SMA-co-BA) facilitated a reduction in the ESE crystallization nucleation barrier and promoted ESE nucleation, hence improving the crystallization behaviour of ESE/Poly(SMA-co-BA) to great extent.

4.2.1.3.2. Analysis Based on the Avrami Theory

The Avrami equation may be employed to ascertain the crystal growth mechanism, so providing a more accurate representation of the non-isothermal crystallization process. This method uses the subsequent relation to estimate the crystallization order (n) from the volume fraction (χ) of the precipitated crystals at a constant heating rate (β , °C.min⁻¹) utilizing equation (2.8) [203]. The value of n is obtained from the slope of the curve generated by plotting $\ln(\beta)$ against $\{\ln[-\ln(1-\chi)]\}$, as illustrated in **Figure 4.5**.

The results indicated that the value of n for the ESE is 0.9, signifying surface nucleation and one-dimensional growth from the exterior inward. The Avrami index, n (1 to 3), corresponds to different growth morphologies, from spherical to rod-like geometries; thus, needle-like nucleation growth is evident in ESE. The Avrami index for ESE/Poly(SMA-co-BA) is 1.5, signifying a change in crystallization behaviour. This indicates a more complex growth mechanism, maybe including a combination of one-dimensional and two-dimensional growth, or a fluctuation in the nucleation rate [204], [205]. This change in the Avrami index can be influenced by factors such as the properties of the encapsulating material, and the thermal conditions during phase change. Thereby, the encapsulation can alter the crystallization kinetics by providing a confined environment, which affects the nucleation and growth rates of the PCM.

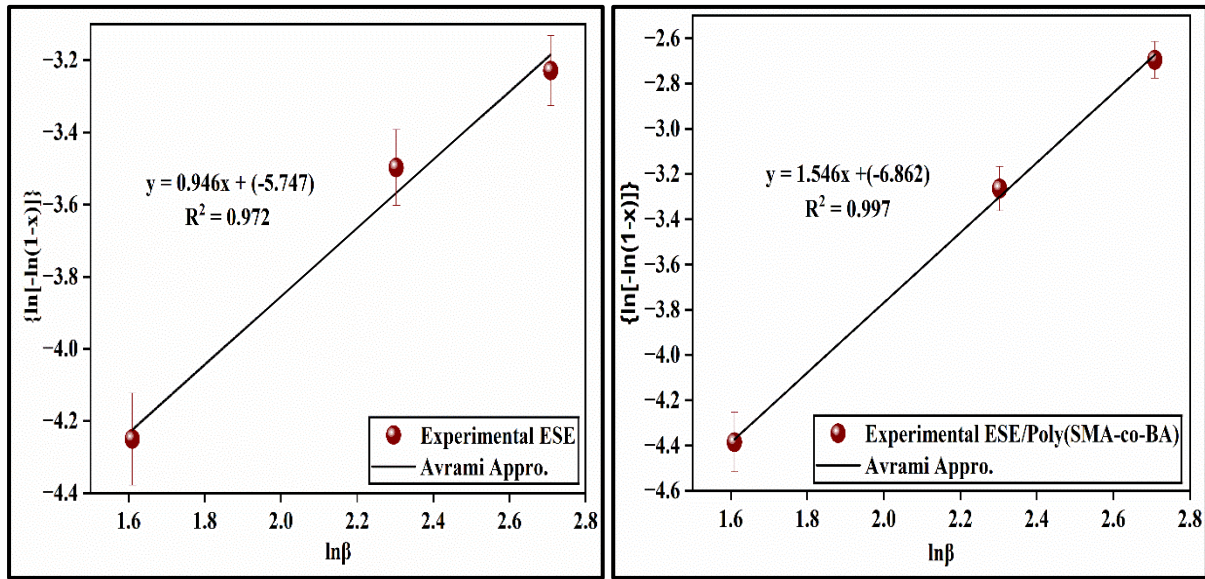


Figure 4.5: Plot of $\{\ln[-\ln(1-\chi)]\}$ vs. $\ln(\beta)$ for ESE and ESE/Poly(SMA-co-BA) at various temperatures

4.2.2. Thermal Stability of ESE/Poly(SMA-co-BA) Nanocapsules

The thermal stability and degradation pattern of the ESE, Poly(SMA-co-BA) and NPCMs are analyzed using TGA and DTG. The thermograms are presented in **Figure 4.6**. The pure ESE undergoes degradation in a singular phase, initiating mass loss at around 75 °C and completely losing its weight at 265 °C. This weight loss may be ascribed to the degradation of the linear alkane chain. Due to ESE being a long-chain n-alkane with a comparatively low breakdown temperature, the mass of pure ESE significantly decreases as the temperature increases [206]. Conversely, ESE/Poly(SMA-co-BA) demonstrated a two-phase deterioration pattern. The initial weight-loss stage (165.6 °C) likely results from the diffusion of n-alkane from the polymer shell, Poly(SMA-co-BA), which may evaporate or breakdown as the temperature increases. The second weight loss phase occurred at a temperature of 299.4 °C due to the disintegration of the Poly(SMA-co-BA) shell. The remaining synthetic NPCM entirely dissipates at a temperature of 600 °C [136], [194]. The TGA data of ESE, Poly(SMA-co-BA) and NPCMs was confirmed by the DTG curves. Furthermore, it is apparent that the initial weight-loss temperature of ESE/Poly(SMA-co-BA) was significantly elevated by 90.6 °C in comparison to the pure PCM. This outcome demonstrated that the Poly(SMA-co-BA) shell effectively protects the core material and inhibits the leakage of the ESE from the nanocapsules.

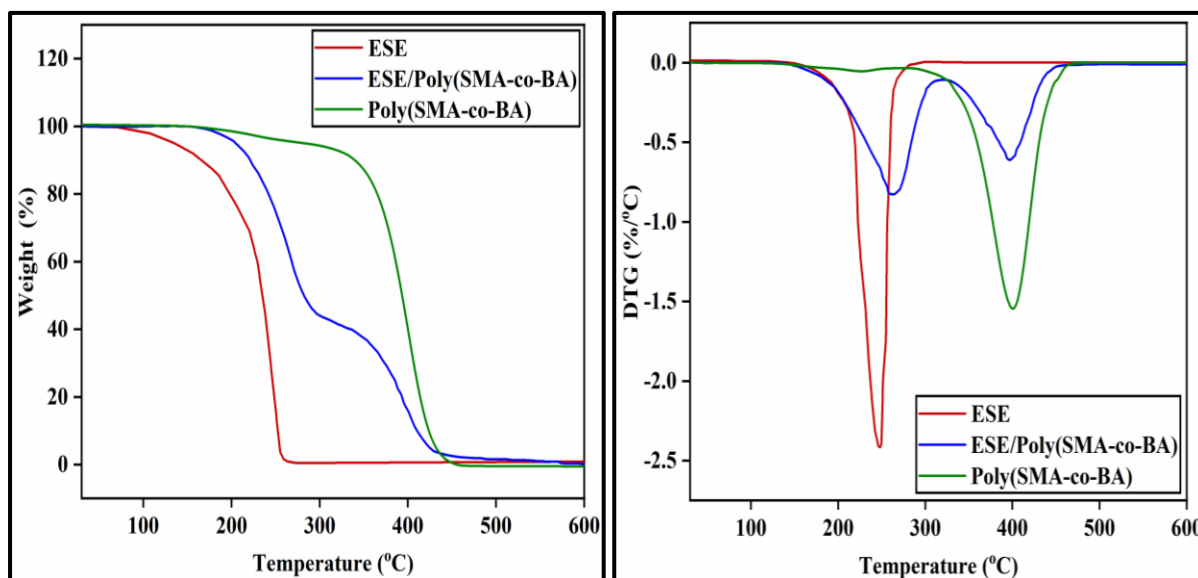


Figure 4.6: TGA and DTG curves of ESE, Poly(SMA-co-BA) and ESE/Poly(SMA-co-BA) nanocapsules

4.2.3. FTIR Analysis of ESE/Poly(SMA-co-BA) Nanocapsules

Figure 4.7 presents the FTIR spectra of ESE, SMA, BA, Poly(SMA-co-BA) and ESE/Poly(SMA-co-BA) nanocapsules. **Figure 4.7 (a)** illustrates the ESE spectrum, which exhibits prominent peaks corresponding to the stretching vibration bands of C–H bonds in methyl and methylene groups at 2958 cm^{-1} , 2916 cm^{-1} , and 2847 cm^{-1} , respectively. The C–H bending vibration is seen at 1468 cm^{-1} , whereas the in-plane rocking vibration of the methylene group is associated with the peak at 716 cm^{-1} [206]. **Figure 4.7 (b)** depicts the FTIR spectrum of SMA, which is dominated by symmetric and asymmetric stretching vibrations in the long ester side groups. The bands at 2922 cm^{-1} and 2852 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2$, respectively. The prominent band at 1723 cm^{-1} is attributed to the C=O stretching vibration, whereas the peak at 1460 cm^{-1} is associated with the bending vibration of $-\text{CH}_2$ groups. Additionally, the peak at 1159 cm^{-1} indicates C–O–C bond vibrations inside the ester group. The characteristic absorption peak at 719 cm^{-1} is ascribed to the extended carbon chain alkyl group $[-(\text{CH}_2)_n-]$, $n > 4$ in SMA [189], [198], [207]. The FTIR spectrum of BA, seen in **Figure 4.7 (c)**, exhibit absorption peaks at 2961 cm^{-1} , 2936 cm^{-1} , and 2876 cm^{-1} corresponding to C–H stretching vibrations. The peak at 1722 cm^{-1} is attributed to C=O stretching, whereas the peaks at 1635 cm^{-1} and 1617 cm^{-1} are associated

with C=C stretching. Furthermore, the peak at 1186 cm^{-1} represents C-O stretching vibrations, characteristic of the BA molecule [208]–[210]. **Figure 4.7 (d)** presents the FTIR spectrum of the polymer shell, shows the absence of C=C absorption peak, which is observed in SMA and BA, confirms that both SMA and BA participated in the polymerization process. The spectrum of the synthesized nanocapsules [**Figure 4.7 (e)**] includes overlapping C–H stretching peaks of Poly(SMA-co-BA) and ESE, along with predominant peaks of SMA and BA, such as the 1732 cm^{-1} (C=O stretching) and 1147 cm^{-1} (C-O stretching) peaks. Along with, the absence of the C=C absorption peak, which confirms the presence of SMA and BA, participated in the formation of ESE/Poly(SMA-co-BA) [211].

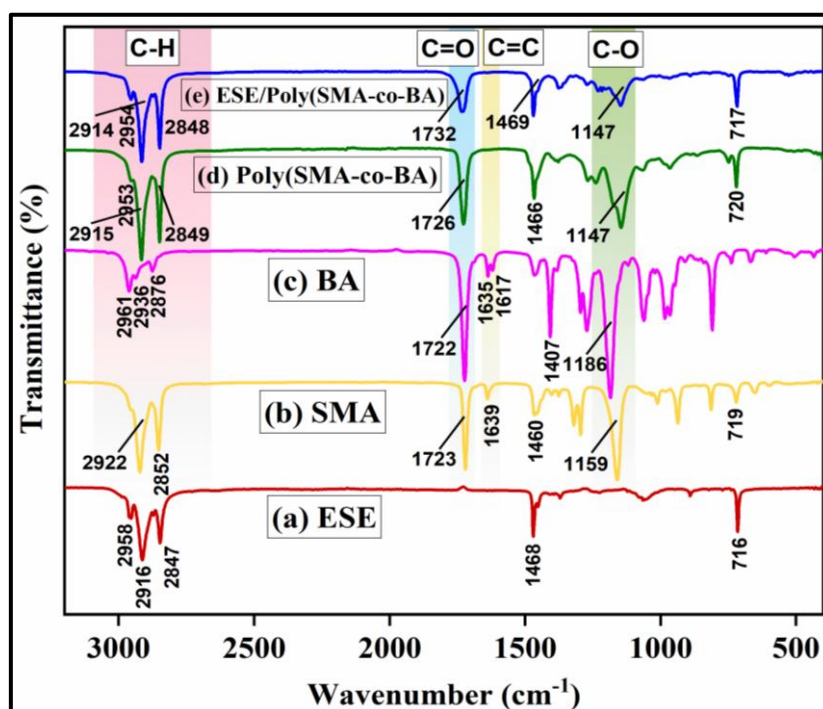


Figure 4.7: FTIR spectra of ESE, SMA, BA, Poly(SMA-co-BA) and ESE/Poly(SMA-co-BA)

4.2.4. PXRD Analysis of ESE/Poly(SMA-co-BA) Nanocapsules

The PXRD patterns of ESE and ESE/Poly(SMA-co-BA) are displayed in **Figure 4.8 (a) and (c)**. According to Varshney et al. [206], the XRD analysis of ESE shows significant diffraction peaks exhibiting various 2θ values that coincide precisely with those listed in the 45-

1543 standard PDF card No. This demonstrates that in the solid form, pure ESE has a distinct triclinic crystalline structure.

The pristine ESE was enclosed within a polymer shell of SMA and a co-polymer shell of BA. The XRD pattern of the ESE/Poly(SMA-co-BA) nanocapsules exhibits all the prevalent peaks corresponding to the highly ordered triclinic phase of ESE, as seen in **Figure 4.8 (c)**. A notable peak at 21.6° , associated with a d-spacing of 0.4 nm in the crystal lattice, was observed. This peak is ascribed to the crystalline configuration of the elongated alkyl chain produced by the SMA polymer shell [212]–[214]. The appearance of this pronounced peak indicates the presence of a metastable face-centered orthorhombic rotator phase, linked to the surface freezing phenomena often seen in n-alkanes contained within nanoscale structures [215], [216]. The literature confirmed that the co-polymer BA shell exhibits the diffraction hump, indicating that the sample is amorphous [217], [218]. In this study, the similar diffraction hump was observed in the range of $13\text{--}28^\circ$, thus confirming the presence of BA in the shell.

To perform quantitative analysis, the deconvolution of the X-ray spectra for ESE and ESE/Poly(SMA-co-BA) is illustrated in **Figure 4.8 (b) and (d)**. The deconvolution was executed by fitting a superposition of Gaussian functions to ascertain the integrated peak areas and refine the peak placements. In the deconvoluted ESE spectra, the three sharp peaks were observed at 2Θ value of 19.8 , 20.8 and 22.4° whereas in the deconvoluted ESE/Poly(SMA-co-BA) spectra, these three peaks were overlapped by the single crystalline peak at 21.6° covering the area within the range of $19.5\text{--}23.9^\circ$. This may be attributed to chemical interaction between the core and the shell.

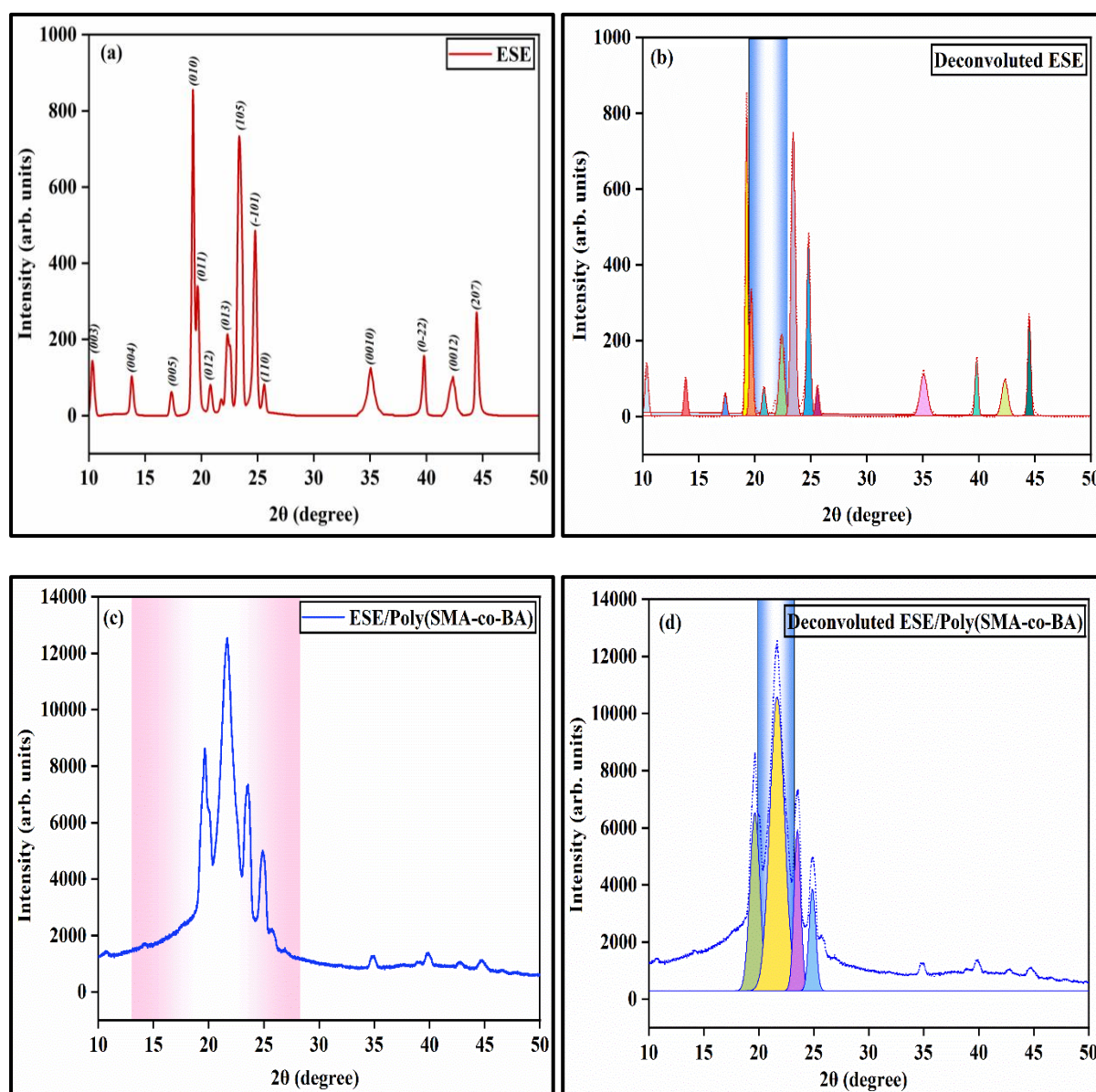
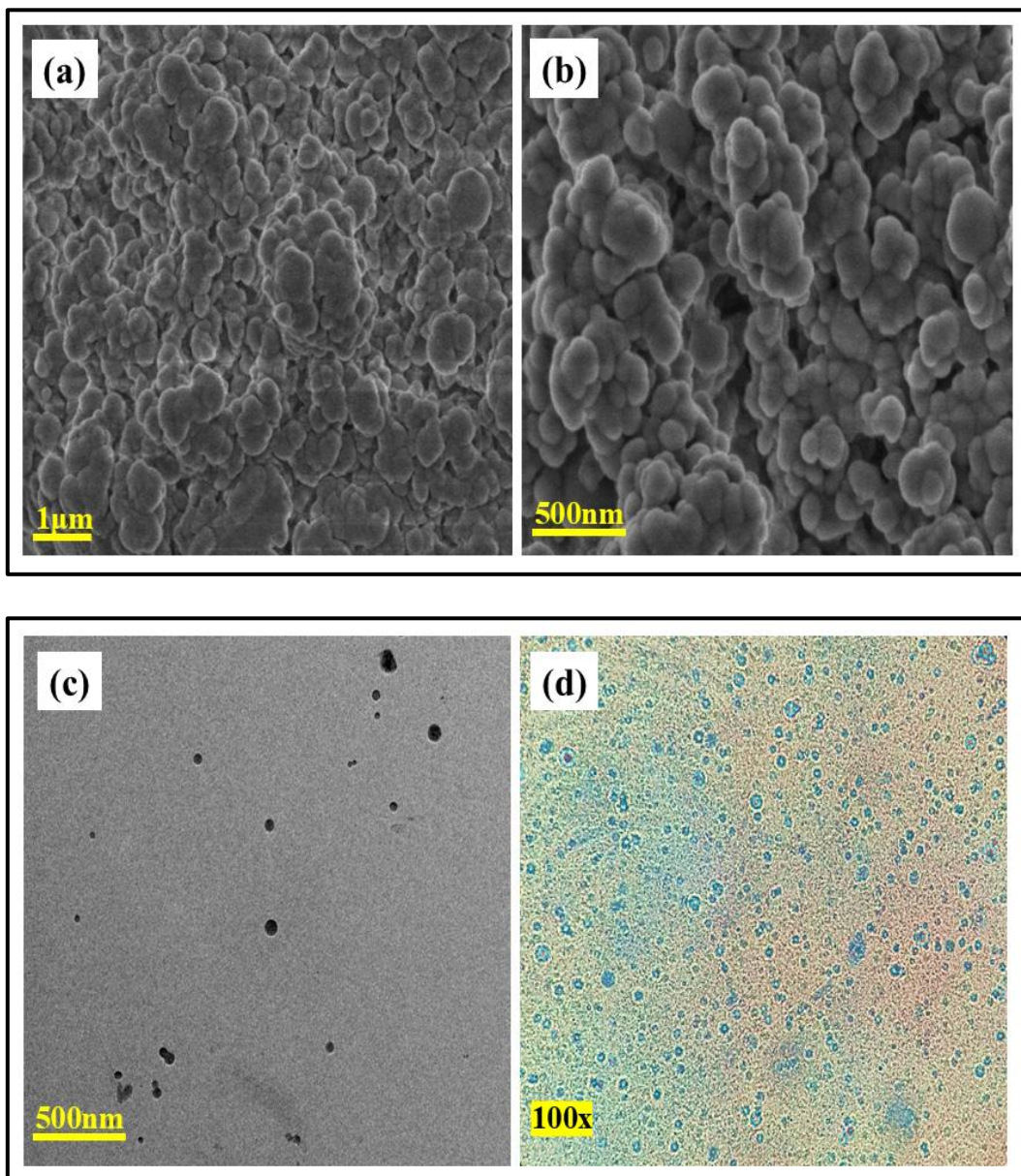


Figure 4.8: PXRD pattern of (a) ESE, (b) deconvoluted ESE, (c) ESE/Poly(SMA-co-BA) and (d) deconvoluted ESE/Poly(SMA-co-BA)

4.2.5. Morphological and PSD Analysis of the Synthesized ESE/Poly(SMA-co-BA) NPCMs

The morphology and particle size of the produced ESE/Poly(SMA-co-BA) nanocapsules were examined using SEM, TEM, POM, and PSD analytical techniques. The acquired SEM/TEM micrographs and POM pictures are displayed in **Figure 4.9 (a-d)**. The micrographs reveal that the nanocapsules have a spherical morphology with a slightly rough and non-uniform exterior

surface. The SEM images indicate that certain regions of the capsules exhibit clustered formations. Conversely, similar structural types were not seen in the TEM and POM images, since the particles were dispersed in an aqueous media before the investigation. Furthermore, based on the scales shown on the SEM, TEM, and POM micrographs, it is clear that the synthesized NPCM was primarily composed of nano-spheres. Consequently, this nano-structured configuration can provide an increased surface area, thereby enhancing the heat transfer rate in latent heat TES systems [193], [219].



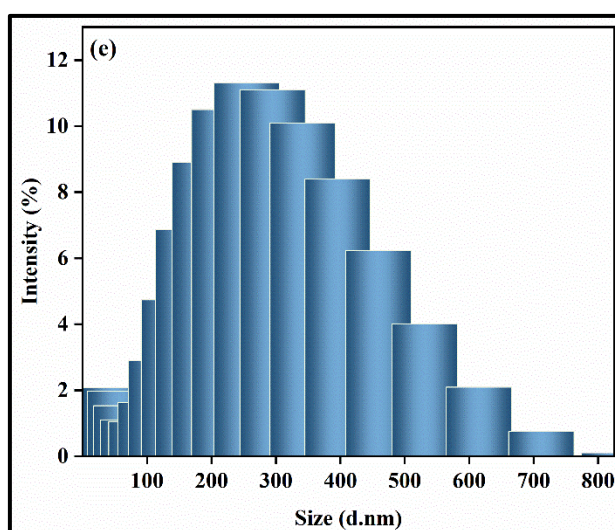


Figure 4.9: (a) & (b) SEM micrographs, (c) TEM micrograph, (d) POM image and (e) PSD of the synthesized ESE/Poly(SMA-co-BA)

The PSD analysis results [Figure 4.9 (e)] indicate that the synthesized nanocapsules exhibit multimodal particle size distributions ranging from 0.4 to 825 nm. Furthermore, the average particle size was determined to be 195.3 nm. The particle size was also determined using Image J software, and the results were consistent with the PSD data.

4.2.6. Thermal Reliability of the ESE/Poly(SMA-co-BA) Nanocapsules

A thermal cycling test was conducted to examine the thermal reliability and chemical stability of NPCMs after numerous cycles of heating and cooling. ESE/Poly(SMA-co-BA) underwent a 100 thermal cycling test. The thermal properties are listed in the Table 4.4, and the DSC thermograms before and after thermal cycling are displayed in Figure 4.10. The melting and crystallization temperatures of the nanocapsules did not significantly alter after 100 cycles. On the other hand, the latent heat value of melting and crystallization decreased by 1.7 and 2.2 J.g⁻¹ respectively. The results demonstrate that the DSC curves before and after the thermal cycles are nearly identical, with only a minor divergence, demonstrating that the NPCMs are extremely thermally stable.

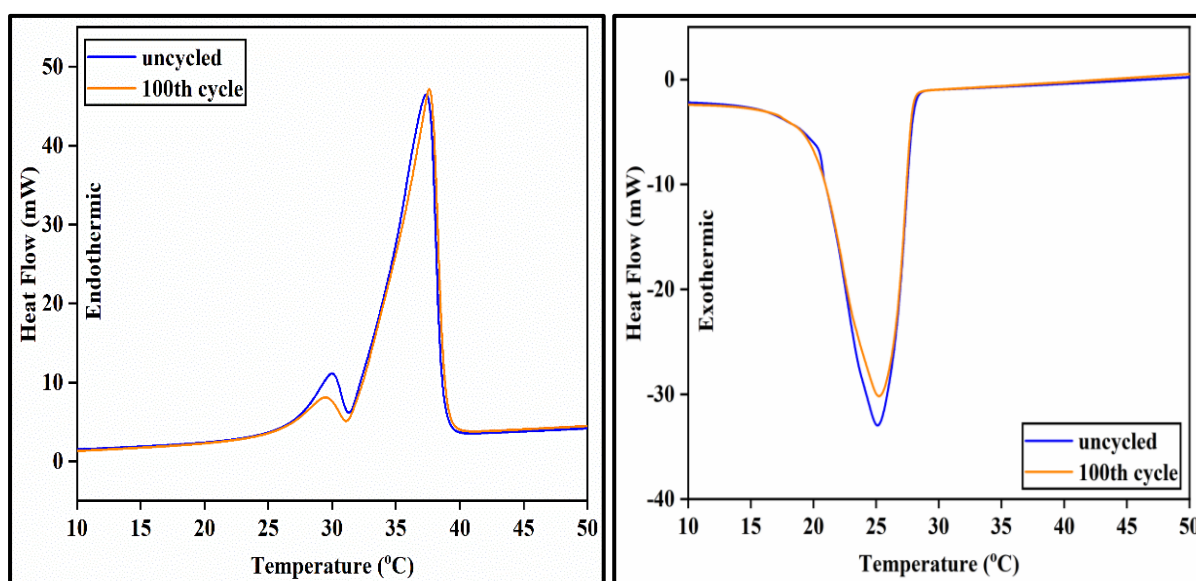


Figure 4.10: DSC thermograms of ESE/Poly(SMA-co-BA) before and after 100 cycles

Table 4.4: Thermal properties of ESE/Poly(SMA-co-BA) with numerous heating and cooling cycles

No. of thermal cycling	Melting Process				Crystallization Process			
	T_{om} (°C)	T_{pm} (°C)	T_{em} (°C)	ΔH_m (J.g ⁻¹)	T_{oc} (°C)	T_{pc} (°C)	T_{ec} (°C)	ΔH_c (J.g ⁻¹)
0	32.6	37.4	38.6	224.6	27.9	25.1	20.0	191.7
100	32.6	37.6	38.8	222.9	27.7	25.2	20.0	189.5

4.2.7. Diffusion-Oozing Circle Test of the Synthesized ESE/Poly(SMA-co-BA) Nanocapsules

The diffusion-oozing circle test was utilized to evaluate the stability of the nanocapsules [183], [206]. The nanocapsules were positioned on filter paper and maintained in an oven at 60 °C for 3 h. Subsequent to this interval, the magnitude of sample leakage was quantified as a percentage of the test area. **Figure 4.11** depicts the initial conditions of ESE and ESE/Poly(SMA-co-BA). Following 3 h of heating at 60 °C, the ESE became liquefied, whereas the ESE/Poly(SMA-co-BA) maintained its structural integrity, with no leakage detected on the associated filter paper. The results demonstrate that the nanocapsules possess exceptional thermal stability.

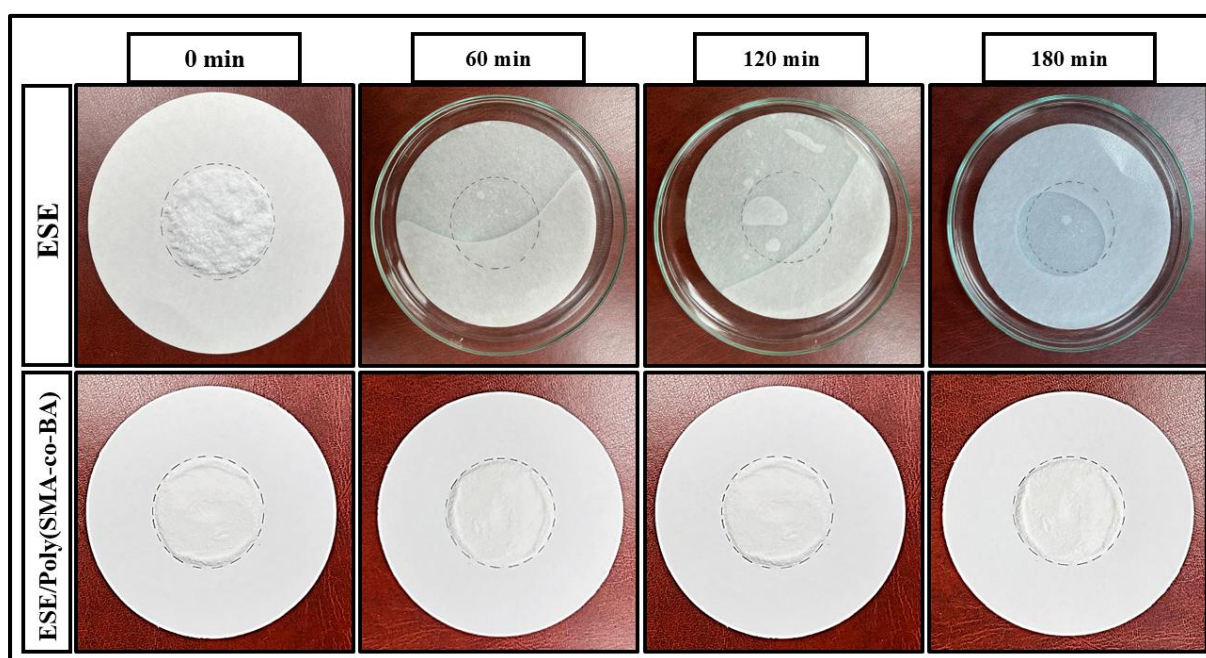


Figure 4.11: Photographic image of ESE and ESE/Poly(SMA-co-BA) from the diffusion-oozing circle test

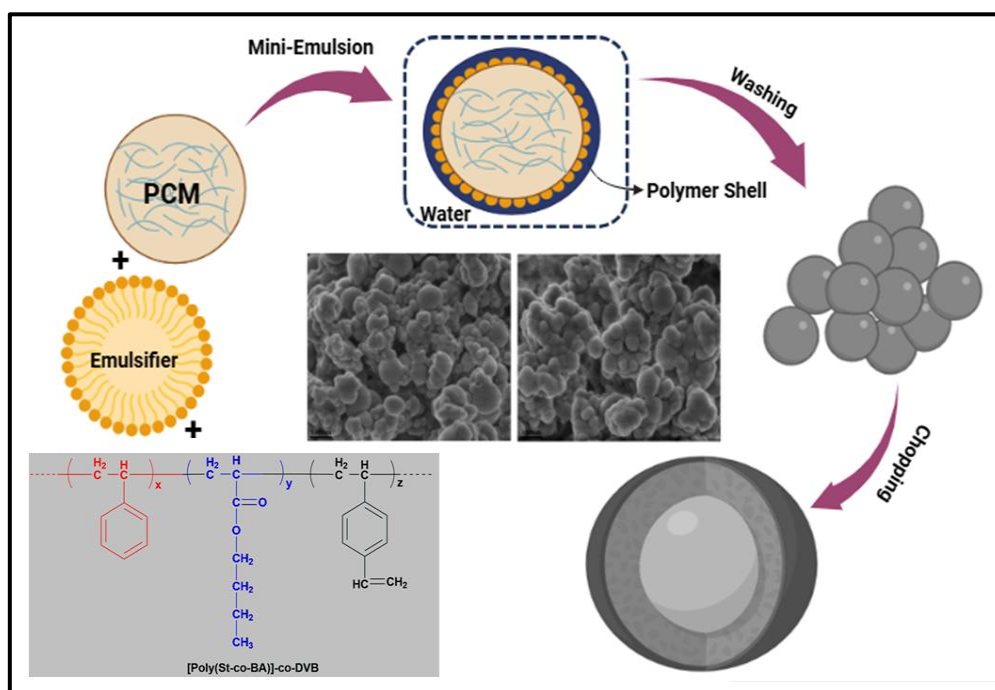
4.3. Significant Findings

The development of ESE/Poly(SMA-co-BA) nanocapsules formed an integral part of the investigations conducted under Objective 2, which encompassed the design and performance evaluation of NPCMs for LHTES. The nanocapsules comprised ESE as the PCM core encased within a Poly(SMA-co-BA) polymeric shell and were developed using mini-emulsion polymerization technique. The produced ESE/Poly(SMA-co-BA) nanocapsules were examined utilizing various characterization techniques. The fabricated ESE/Poly(SMA-co-BA) may serve as a latent heat TES material, as proven by the DSC results, with 87.2% encapsulation efficiency, 93.6% encapsulation ratio and 93.1% thermal storage capacity. The melting and crystallization temperatures of the synthesized nanocapsules are 37.4 °C and 25.1 °C, respectively, and the corresponding latent heat is 224.6 J.g⁻¹ and 191.7 J.g⁻¹. ESE/Poly(SMA-co-BA) has a lower activation energy than ESE, as calculated by various models, indicating that ESE/Poly(SMA-co-BA) crystallizes more quickly due to a reduced energy barrier produced by heterogeneous nucleation. The examination of the Avrami index, $n = 0.9$ for ESE and $n = 1.5$ for ESE/Poly(SMA-co-BA), revealed an abrupt change in crystallization behaviour. It implies a more complex growth mechanism, possibly involving a

combination of one-dimensional and two-dimensional growth, or a change in the nucleation rate. According to the TGA study, the synthesized ESE/Poly(SMA-co-BA) nanocapsules have good thermal stability and degrade in two steps. FTIR results have confirmed that the prepared ESE/Poly(SMA-co-BA) nanocapsules contains all the characteristic peaks of ESE and Poly(SMA-co-BA). The PXRD patterns of the synthesized NPCMs exhibit all characteristic crystalline peaks of ESE. Additionally, the distinct peak at 21.6° signifies the crystalline structure of the long alkyl SMA polymer shell, while the diffraction hump reflects the amorphous nature of the co-polymer shell. The SEM/TEM and POM analysis demonstrated that the produced nanocapsules have a fully spherical morphology, with some clustered formations featuring a rough exterior surface. The PSD study indicated that the diameters of the produced nanocapsules ranged from 0.4 to 825 nm, with a mean diameter of 195.3 nm. The synthesized ESE/Poly(SMA-co-BA) may be efficiently utilized for the purpose of TES by incorporating them into many sectors such as electronic cooling, the food and textile industries, HVAC systems, cold-chain management, medicinal applications, and greenhouses to provide optimal conditions for plant development.

CHAPTER 5

OPTIMIZING THE THERMAL STABILITY OF THE PREPARED MICROENCAPSULATED PHASE CHANGE MATERIALS



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CHAPTER 5

OPTIMIZING THE THERMAL STABILITY OF THE PREPARED MICROENCAPSULATED PHASE CHANGE MATERIALS

5.1. Introduction

In the proceeding chapter, the ESE was successfully microencapsulated in Poly(St-co-BA) polymer shell, using mini-emulsion polymerization technique. But the prepared microcapsules suffer the drawback of being less thermally stable. The produced microcapsules initially losses 87.6% weight loss at the temperature range of 151 °C and 279 °C, which restrict their practical application.

In the present study, the synthesis polymerization procedure was further optimized by incorporating the DVB cross-linker in the Poly(St-co-BA) polymer shell. The addition of DVB, a bifunctional aromatic crosslinker, promotes the mechanical strength and thermal stability of the polymer network. PS, with its aromatic structure, contributes rigidity and thermal resistance to the network, whereas PBA provides flexibility and impact resistance with its softer, rubbery segments. The DVB crosslinker establishes strong covalent bonds between polymer chains, resulting in a stable three-dimensional network. This crosslinking process considerably enhances the structural integrity of the polymer shell, boosting its durability and resilience to high temperatures and mechanical stress. The synergy of PS, PBA, and DVB produces a balanced, durable polymer network that is suited for applications that require both flexibility and thermal durability.

Divinylbenzene (DVB) was specifically chosen as the cross-linking agent due to its bifunctional aromatic structure, which includes two vinyl groups connected to a benzene ring. This structure allows for the development of rigid, thermally stable three-dimensional (3-D) polymer networks. Compared to aliphatic crosslinkers such as 1,4-butylene glycol diacrylate and trimethylolpropane triacrylate, which form more flexible networks with lower thermal and mechanical stability, DVB provides higher rigidity and durability. The trifunctionality of pentaerythritol tetraacrylate gives it a high crosslink density, but it lacks the structural rigidity that DVB's aromatic backbone provides. This study also explores the influence of different

DVB crosslinker concentrations on the properties of the microcapsules, including shell strength, morphology, heat capacity, and thermal stability of the MPCM.

5.2. Results and Discussion

5.2.1. Thermal Performance of MPCMs

DSC analysis was done on each sample to comprehend the variations in thermal properties, such as melting/crystallization temperatures and phase change enthalpies. **Figure 5.1 (a) and (b)** shows enthalpy variation with temperature by the addition of DVB cross-linker. Additionally, **Table 5.1** provides a summary of the DSC analysis results.

The pure ESE (PCM) exhibited an initial onset melting at 35.5 °C, followed by a distinct melting peak observed at 38.9 °C, with an associated phase change enthalpy of 239.8 J.g⁻¹. The DSC thermogram showed two exothermic peaks at 32.3 °C and 30.5 °C, indicating a bimodal solidification behavior during crystallization process that contributed to a total enthalpy of 237.7 J.g⁻¹ [206]. The two exothermic peaks of ESE correspond to the production of the metastable α -form or rotator R1 phase and the stable β -form or triclinic crystalline phase, respectively. The initially induced surface-mediated heterogeneous nucleation gives rise to the rotator phase, whereas the crystalline phase is formed as a result of the subsequent bulk homogeneous nucleation [220].

Table 5.1: Thermal properties of MPCMs prepared at a varied DVB ratio

Sample No.	DVB w.r.t Styrene (%)	Melting Process				Crystallization Process				E _R
		T _{om} (°C)	T _{pm} (°C)	T _{em} (°C)	ΔH_m (J.g ⁻¹)	T _{oc} (°C)	T _{pc} (°C)	T _{ec} (°C)	ΔH_c (J.g ⁻¹)	
EPD0.5	0.5	35.0	38.2	39.8	104.4	32.5	30.9	29.5	98.6	43.5
EPD1	1	34.9	38.8	41.4	139.9	32.5	31.0	29.4	121.9	58.3
EPD2	2	34.8	38.7	41.2	146.7	32.9	30.9	28.6	131.2	61.1
EPD3	3	35.3	38.9	41.5	153.2	34.3	30.8	28.3	142.6	63.9
EPD5	5	35.7	39.4	42.6	170.5	34.4	30.6	27.4	155.6	71.1
EPD7	7	35.3	39.4	42.4	149.7	31.3	29.9	27.5	141.0	62.4

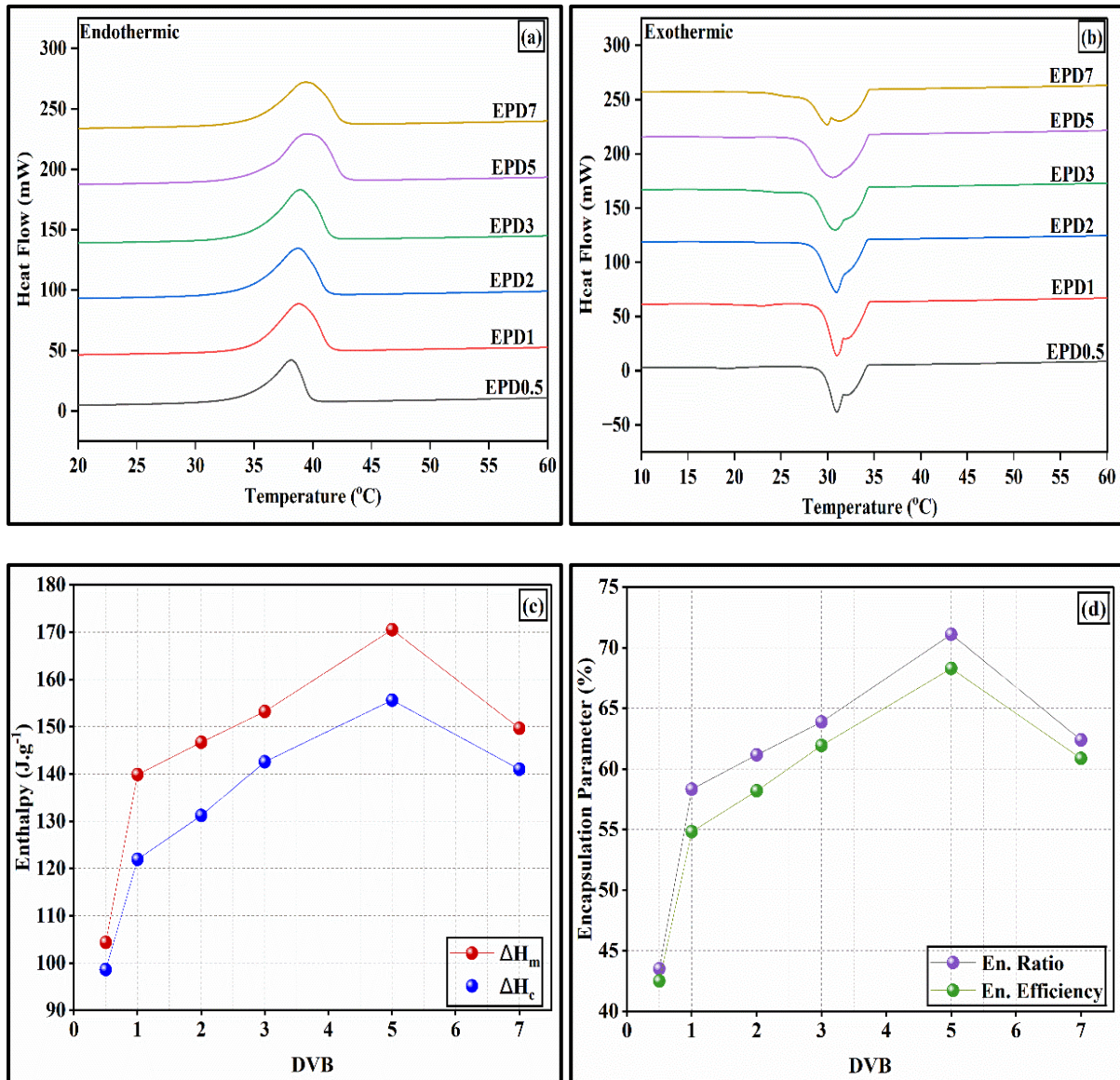


Figure 5.1: (a,b) DSC heating and cooling curves, (c) Phase change enthalpy (ΔH) and (d) Encapsulation ratio and efficiency of the synthesized MPCMs

On the other hand, the melting peak temperatures of the prepared MPCMs (EPD0.5, EPD1, EPD2, and EPD3) stayed almost identical to the pure PCM, but EPD5 showed a discernible elevation. The endothermic melting peak gradually broadened as the crosslinker content increased, as seen in **Figure 5.1 (a)**, suggesting an expansion in the melting temperature range. In particular, the melting range rose from about 4.6 °C for pure ESE to approximately 6.9 °C for EPD5. Additionally, compared to the pure PCM, the latent heat enthalpy of all produced MPCMs was substantially lower. These observations can be ascribed to the cumulative impacts

of confinement effect, thermal resistance imposed by the polymer shell and capsule polydispersity, all of which impede effective phase transition and heat transfer [220]–[222].

Figure 5.1 (b) shows that EPD0.5 and EPD1 have two different exothermic peaks, similar to pure ESE, showing the coexistence of heterogeneous and homogeneous nucleation mechanisms. These peaks, however, became less prominent in EPD2 and EPD3, indicating a further suppression of homogenous nucleation. In the instance of EPD5, the dual peaks fused into a single exothermic peak, indicating a shift toward primarily heterogeneous nucleation. This phenomenon can be attributed to the emergence of a rotator phase, in which the microcapsules' interfacial effects play a major role in governing crystallization. A slight tailing of the exothermic peak toward lower temperatures, resulting in a broadened crystallization range of about 7 °C, further demonstrates the diminished contribution of homogenous nucleation [220], [223], [224]. Overall, this transformation from dual to single crystallization peaks emphasizes the significant impact of microcapsule structure and crosslinking density on the encapsulated PCM's phase transition behavior.

The enthalpy of the MPCM progressively rose as the cross-linker concentration increased from 0.5% to 5%, as shown in Table 5.1 and **Figure 5.1 (c) and (d)**. This trend indicates greater encapsulation efficiency and superior heat storage capacity, which is likely due to the development of a more stable and compact polymer shell that adequately sustains a higher amount of PCM while minimizing leakage during phase transition. However, elevating the cross-linker concentration above 5% resulted in a substantial decrease in enthalpy. This reduction can be ascribed to excessive cross-linking, which causes a denser and more rigid shell structure. Such rigidity may impede the molecular mobility of the PCM, reducing its capacity to perform effective phase transitions. Furthermore, a decline in latent heat may result from a reduction in the encapsulated PCM volume caused by the rise in shell content at higher cross-linker levels [225].

The effective performance of the PCM for latent heat storage was indicated by the proportion of ESE inside the polymer shell. The core percentage (E_R) value ranged from 43.5 to 71.1%, as determined by applying the equation 2.1 to the DSC findings for different MPCM. (Table 5.1). With a focus on their thermal performance, the synthesized ESE MPCMs were compared with previously published other ESE-based encapsulated PCMs with various polymer shells and core:shell ratios, as shown in **Table 5.2**.

Table 5.2: Comparison of produced ESE MPCMs with other reported ESE-based encapsulated PCMs employing different core-shell ratios, polymer shells

S.No.	PCM	$\Delta H_{(m)}$ PCM	Monomer	Cross Linker	Method	Core: Shell	$\Delta H_{(m)}$ MPCM	E_R	Ref.
1.	ESE	247.3	Polyurea Formaldehyde	-	Suspension	1:2	136.2	55.07	[79]
2.	ESE	232.7	Poly(styrene-co- acrylamide)	DVB	Emulsion	-	152.2	65.41	[226]
3.	ESE	-	Poly(methyl methacrylate-co- acrylic acid)	EGDMA	Emulsion	1:1	90.9	32.9	[227]
4.	ESE with Fe_3O_4	250.41	SiO_2 with Cu loading	-	Interfacial Polycondens ation	1:1	150.07	61.48	[164]
5.	ESE	206.38	Polyphenol Formaldehyde	-	In-Situ	3:6.5	173.8	84.21	[80]
6.	ESE+ n- tetracos ane (90- 10%)	265.60	PMMA	EGDMA	Emulsion	1:2 1:1 2:1	86.67 130.67 169.26	32.63 49.20 63.73	[228]
7.	ESE	202.49	PMMA	-	Mini Emulsion	1:1	124.7	61.58	[144]
8.	ESE	276.7	Poly(methyl methacrylate-co- methacrylic acid)	EGDMA	Emulsion	1:1	145.8	52.69	[229]
9.	ESE	227.10	$CaCl_2$	-	Self - Assembly	1:1	86.13	37.93	[230]
10.	ESE	239.87	Poly(St-co-BA)	DVB	Mini- Emulsion	1:1	170.54	71.10	This study

5.2.2. Thermal Stability of MPCMs

Thermal stability is an essential parameter for assessing the energy storage performance and structural durability of microcapsules at high temperatures. TGA was employed to examine the thermal degradation behavior of various MPCMs within the temperature range of 40 °C to 800 °C. The core PCM decomposed in a single step at 75 °C to 265 °C, leaving almost no material remnant, indicating full volatilization. In contrast, an evident two-step degradation pattern was shown by the TGA curve of MPCM that was synthesized without the integration of any cross-linking agent. The initial phase of weight loss, which accounted for 87.6% of the overall mass loss, took place between 151 °C and 279 °C. The second degradation stage, from 279 °C to 424 °C, resulted in an additional 12.4% weight loss. This two-step deterioration entails the disintegration of the core ESE PCM followed by the polymer shell [206].

From **Figure 5.2**, it was observed that the EPD0.5-EPD5 also shows two step degradation. But by the incorporation of DVB, the weight loss percentage of the microcapsules improves as the temperature rise. The weight loss percentage on the first stage are as follows: EDP0.5 (55.2%), EPD1 (53.2%), EPD2 (53.2%), EPD3 (57.5%) and EPD5(62.2%), which is lower than the MPCM produced without DVB. The increased first-stage weight loss arises from the higher PCM encapsulation, while the presence of DVB contributes to improved structural stability of the polymer shell during the subsequent degradation stage. Additionally, at higher temperatures (449–471 °C), the DVB-containing samples retained a small but measurable residue in the range of 2–2.7%, but the ESE and DVB-free MPCM demonstrated full disintegration with no residual mass. This residual mass can be attributable to the presence of thermally stable cross-linked polymeric fragments produced after DVB inclusion. The present study enhances the thermal stability of the synthesized microcapsules by the addition of cross-linker: (1) weight loss percentage reduce; (2) degradation temperature shifted from 424 °C (without DVB) to 471 °C (with 5% DVB); and (3) 2-2.7% residue left.

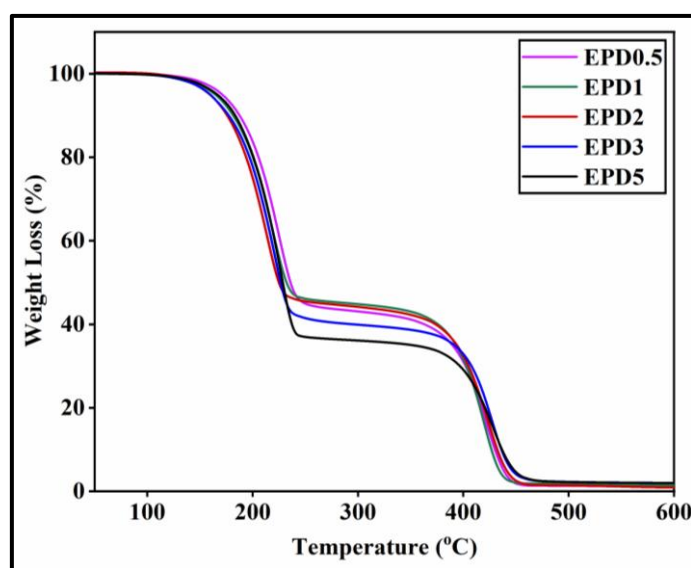


Figure 5.2: TGA curves of EPD0.5, EPD1, EPD2, EPD3 and EPD5

5.2.3. FTIR Analysis of MPCMs

Figure 5.3 (a) and (b) depicts the FTIR spectra of ESE, EPD0.5, EPD1, EPD2, EPD3 and EPD5. The FTIR spectrum of ESE exhibits characteristic peaks at 2958 cm^{-1} , 2912 cm^{-1} , and 2847 cm^{-1} , corresponding to the stretching vibrations of C–H bonds in methyl and methylene groups. The peak at 1472 cm^{-1} is attributed to the bending vibration of the C–H bonds, while the band observed at 716 cm^{-1} corresponds to the in-plane rocking vibration of the methylene ($-\text{CH}_2-$) group [206]. The PS component of the Poly(St-co-BA) shell appears peaks at 3026 cm^{-1} and 1601 cm^{-1} , which signify the C=C and C–H stretching vibrations, respectively. On the other hand, PBA co-monomer within the Poly(St-co-BA) polymer shell shows C=O and C–O stretching vibrations at 1732 cm^{-1} and 1218 cm^{-1} , respectively.

For the cross-linker DVB, the stretching vibration of the benzene ring skeleton was linked to the distinctive absorption peaks in the $1453\text{--}1493\text{ cm}^{-1}$ range. The characteristic peak at 837 cm^{-1} was attributed to the para-substituted position on the benzene ring, and the peaks at 796 cm^{-1} and 716 cm^{-1} were ascribed to the meta-substituted position on the benzene ring. In addition, the peak at 3026 cm^{-1} and the peak in the range of $1027\text{--}1066\text{ cm}^{-1}$ were identified as the stretching and bending vibration of $\text{C}_{\text{AR}}\text{--H}$ respectively. DVB has been polymerized, as evidenced by the strong characteristic peak at 2913 cm^{-1} , which was attributed to the stretching vibration of $-\text{CH}_2$ [231]–[233]. However, the addition of DVB to the microcapsules does not

result in any additional evident peaks in the FTIR spectra. This could be related to the structural similarities between PS and DVB, which cause spectral overlap and obscure individual contributions. The spectral distinction of individual components was further complicated by the notable overlapping of C–H stretching peaks of DVB with the other C–H stretching peaks. These findings highlight the complexity of polymer characterization using FTIR spectroscopy, where closely related chemical structures can influence spectral resolution and peak differentiation.

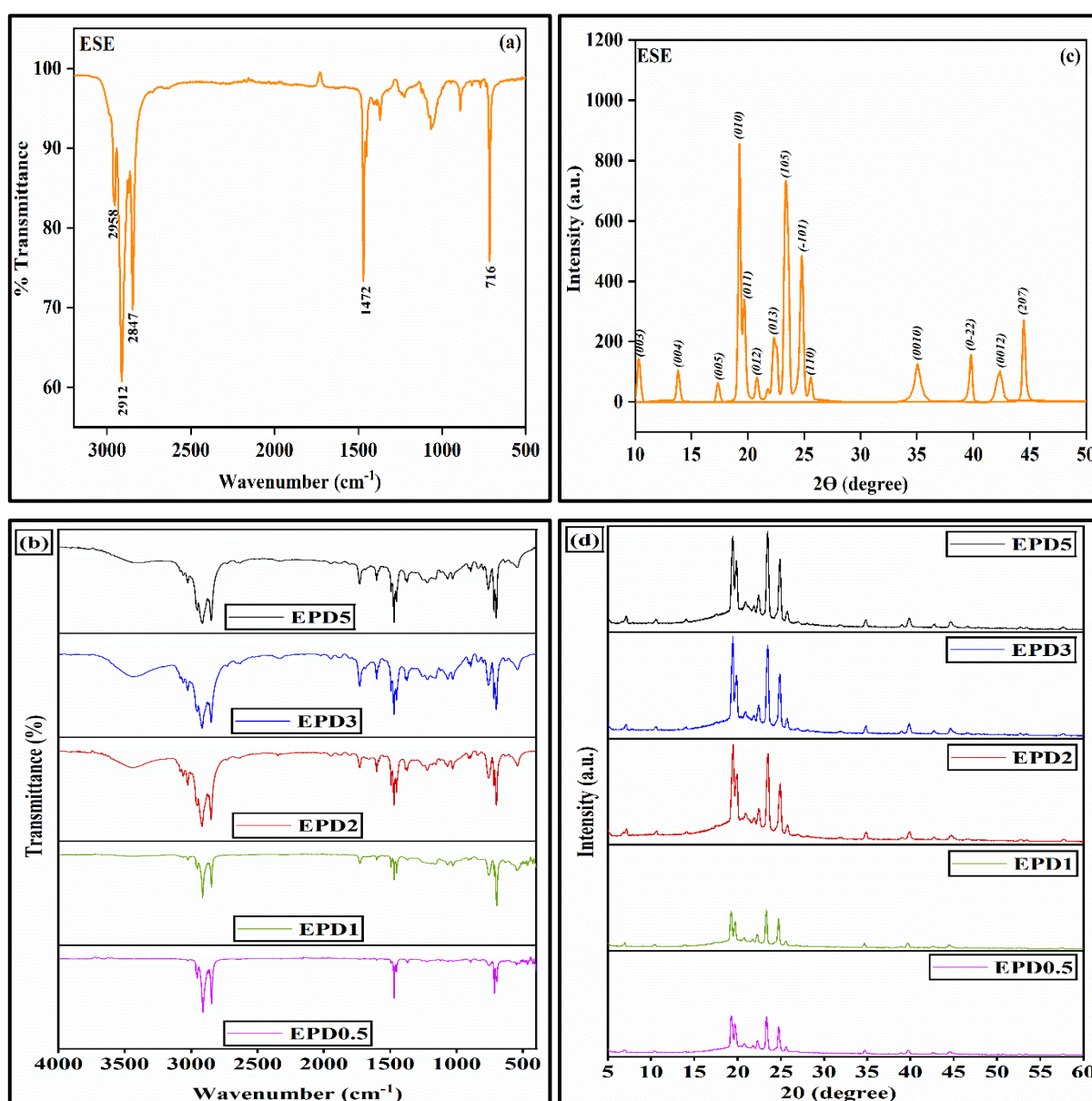


Figure 5.3: (a,b) FTIR spectra and (c,d) PXRD pattern of the pure ESE and the synthesized MPCMs respectively

5.2.4. PXRD Analysis of MPCMs

Figure 5.3 (c) and (d) presents the PXRD patterns of ESE, EPD0.5, EPD1, EPD2, EPD3 and EPD5 microcapsules synthesized with varying amount of DVB crosslinker. The XRD pattern of ESE exhibits a series of characteristic diffraction peaks at 2θ values of 10.38° , 13.87° , 17.39° , 19.27° , 19.79° , 20.85° , 22.45° , 23.46° , 24.82° , 25.62° , 35.08° , 39.80° , 42.33° , and 44.53° , which are indexed to the (003), (004), (005), (010), (011), (012), (013), (105), (-101), (110), (0010), (0-22), (0012), and (207) planes, respectively [206]. As illustrated in Figure 5.3 (c), these discrete diffraction peaks are consistent with the standard PDF card No. 45-1543, demonstrating that pure ESE has a typical triclinic crystalline structure in the solid state.

An amorphous Poly(St-co-BA) polymer shell containing the parental ESE is demonstrated by a broad diffraction peak that ranges from 10° to 30° . A gradual rise in the intensity of this amorphous hump was noticed as increasing amounts of DVB crosslinker was added. The XRD patterns of the produced microcapsules show all of the distinctive crystalline peaks of ESE, as well as a broad amorphous peak associated to the Poly(St-co-BA) polymer shell and DVB crosslinker. Notably, DVB itself shows a broad diffraction pattern in the 2θ range of 10° – 20° , which overlaps with the amorphous region of the polymer shell [234]. This overlap indicates that DVB was homogeneously incorporated into the polymeric network, enhancing the structural integrity of the encapsulation matrix.

The confinement of ESE within the polymer shell preserves its crystalline characteristics, since no significant shifts or variations in peak positions were found. This indicates that the core material and the polymeric shell interact solely physically, confirming that the encapsulation technique does not cause any structural changes in the ESE core. Such interactions are crucial for assessing the thermal stability, functionality, and overall productivity of the encapsulated system.

5.2.5. Morphology and PSD of MPCMs

Figure 5.4 (a-e) presents FE-SEM images of EPD0.5, EPD1, EPD2, EPD3, and EPD5 microcapsules produced with different concentrations of DVB. DVB functions as a crosslinking agent, reinforcing the polymer network through the formation of covalent bonds between polymer chains, leading to a more stable and denser structure of microcapsule polymer shell. As the polymer network is more tightly bound and less prone to deformation, the

increasing crosslinking produces a smoother and more compact surface morphology. As a result, the microcapsules possess better structural integrity, which reduces the possibility of flaws such as shell breaking or surface wrinkles [235].

The encapsulated MPCMs showed a uniform spherical morphology, with particle sizes ranging from 0.16 to 0.22 μm . Notably, an expanded PSD was observed by increasing the amount of DVB from 0.5 to 5%. Such result was observed in other comparative data where the same cross-linker was used [224], [236].

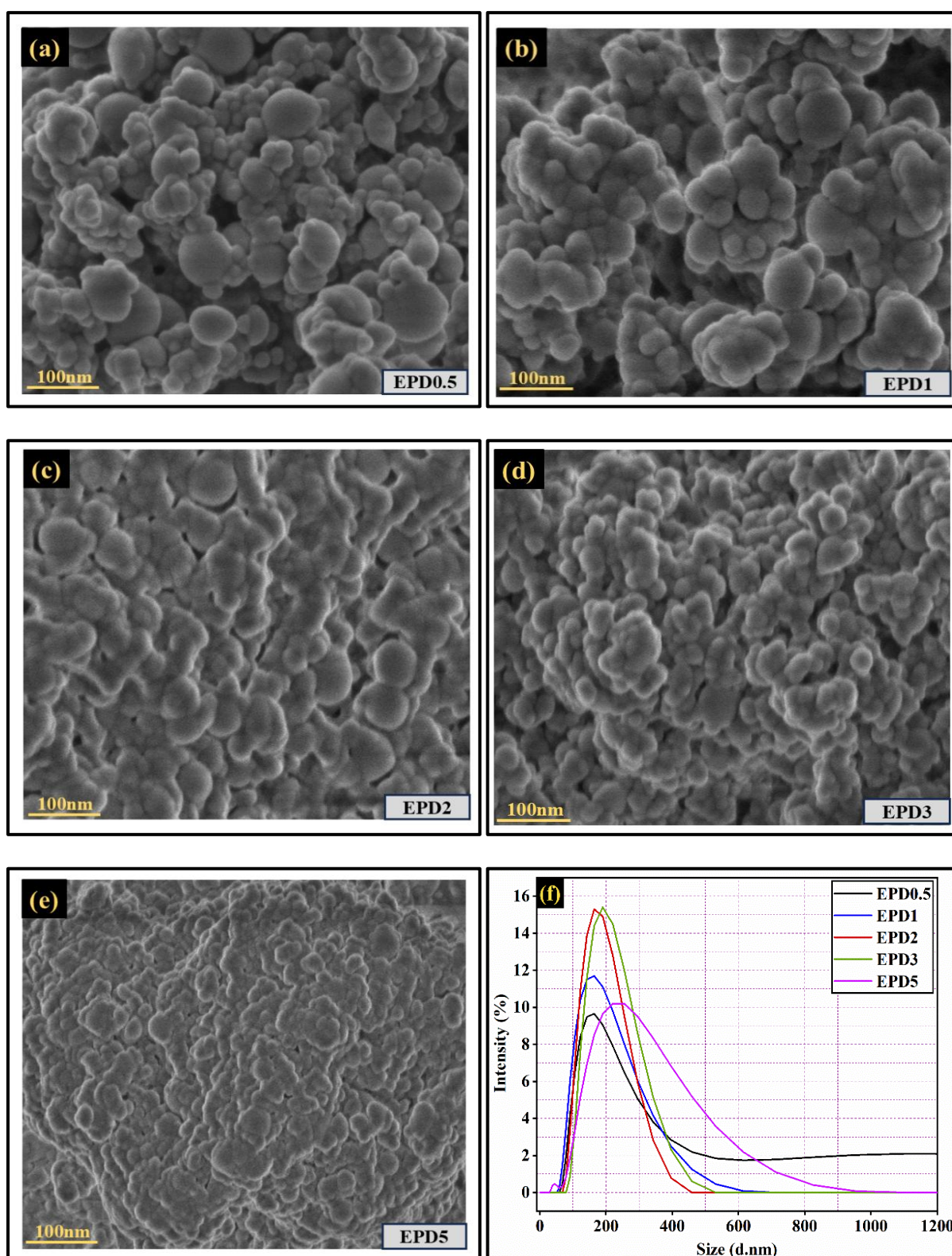


Figure 5.4: FE-SEM images and PSD of the prepared encapsulated PCM by varying the different amount of DVB: EPD0.5, EPD1, EPD2, EPD3 and EPD5

5.2.6. Thermal Reliability of MPCMs

It is crucial that MPCMs maintain their high level of thermal durability even after repeated thermal circulation. To confirm the reliability of MPCMs, thermal cycling tests are performed on EPD5 due to high encapsulation ratio and efficiency. The thermal cycling test is conducted at a temperature range between 0 °C and 60 °C. **Figure 5.5** shows the DSC curves of EPD5 following 50 heating and crystallizing cycles, and **Table 5.3** provides comprehensive data. It is clear that after 50 thermal cycles, the latent heat drops from the initial 170.5 J.g⁻¹ to 169.1 J.g⁻¹, whereas the melting and crystallization temperatures of the MPCMs barely change. These findings demonstrate that MPCMs encapsulated with Poly(St-co-BA) polymer shell crosslinked with 5 wt% of DVB are highly reliable, suggesting that they are appropriate for long-term recycling applications.

Table 5.3: DSC data of EPD5 after 50 thermal cycles

No. of cycles	T _{on} (°C)	T _{pm} (°C)	T _{em} (°C)	ΔH _m (J.g ⁻¹)	T _{oc} (°C)	T _{pc} (°C)	T _{ec} (°C)	ΔH _c (J.g ⁻¹)
0	35.7	39.4	42.6	170.5	34.4	30.6	27.4	155.6
50th	35.7	39.3	42.4	169.1	34.4	30.5	27.4	152.0

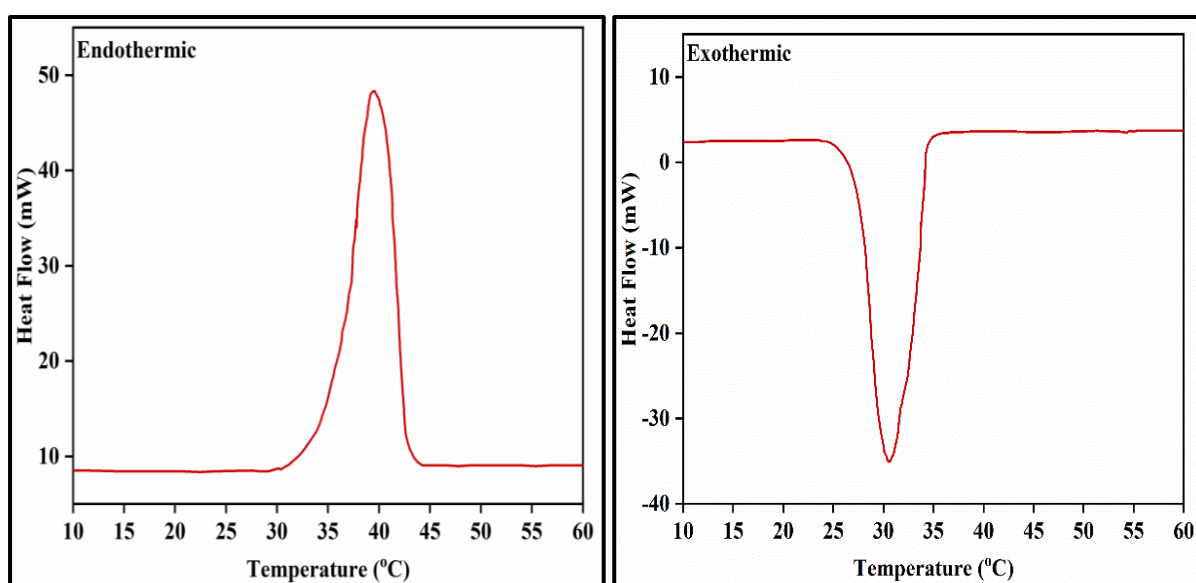


Figure 5.5: DSC curve of EPD5 at 50th cycle of heating and cooling

5.2.7. Exudation Stability (Infrared Thermography Analysis, IFT) of MPCMs

The leakage resistance of the MPCMs was determined using pure ESE as a reference. Samples of pure ESE and microcapsules formed with various DVB ratios were placed in the center of filter paper and heated at 60 °C. Infrared thermographic images were captured at 1-min intervals, and their findings are shown in **Figure 5.6**. The thermographic scale ranged from black and dark blue (coolest regions) to light blue, yellow, and red (hottest regions).

For ESE, rapid heat absorption was observed due to the absence of a protective polymer shell, causing the cool central region to disappear completely within 5 min of heating. In contrast, all DVB-crosslinked MPCMs exhibited improved thermal resistance and delayed heat transfer behaviour due to the presence of the polymer shell, as evidenced by the retention of distinct blue/green regions during heating. This thermal behaviour correlated well with the DSC and PSD analyses. EPD0.5 and EPD1 exhibited crystallization behaviour comparable to pure ESE, indicating the coexistence of homogeneous and heterogeneous nucleation; however, the polymer shell still provided effective thermal buffering and PCM confinement, particularly in EPD1, which retained a noticeable cooler region after 5 min. With further increase in DVB concentration (EPD2 and EPD3), suppression of homogeneous nucleation and improved shell compactness promoted more controlled thermal diffusion and uniform heat distribution.

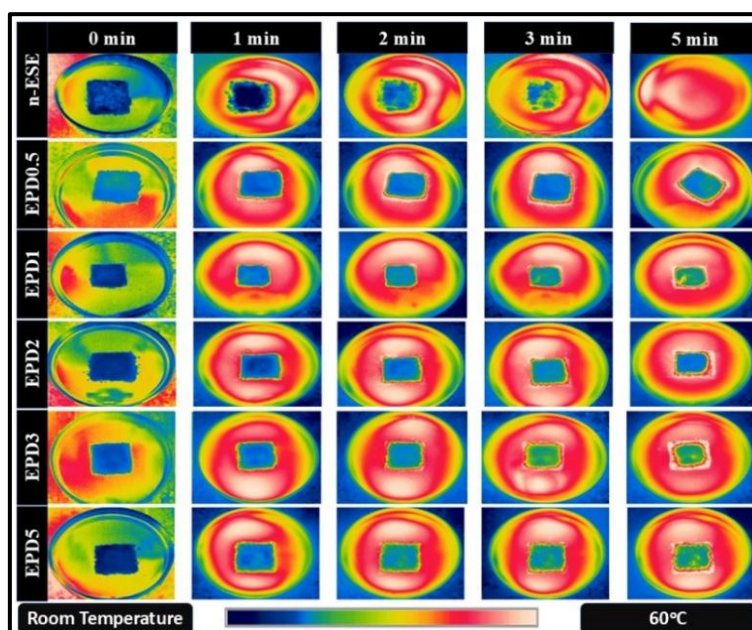


Figure 5.6: IFT images of microencapsulated ESE prepared with different DVB ratios

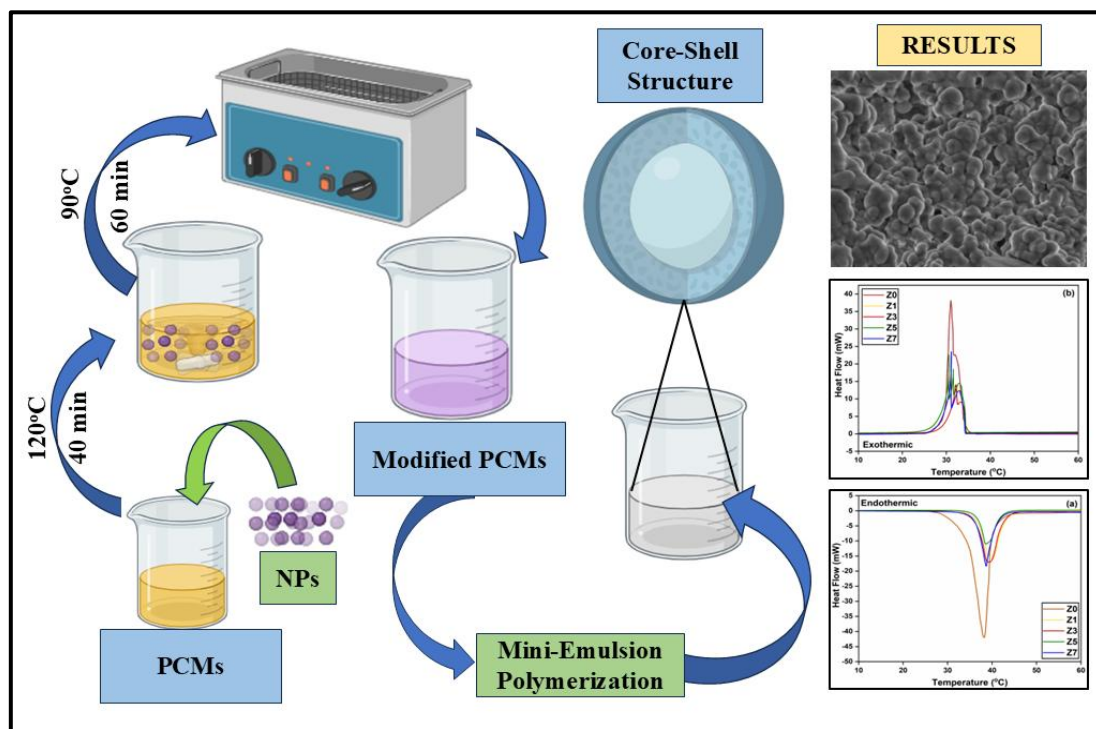
In the case of EPD5, excessive DVB crosslinking enhanced shell rigidity and encapsulation efficiency; however, increased capsule polydispersity, as confirmed by PSD analysis, contributed to comparatively non-uniform thermal distribution despite improved thermal resistance.

5.3. Significant Findings

The synthesis parameters for ESE microencapsulation were systematically investigated and optimized under Objective 3 by varying the DVB cross-linker concentration (0.5–5%) during the mini-emulsion polymerization of SM and BA. The optimized conditions yielded ESE-containing microcapsules with particle sizes of 0.16–0.22 μm , confirming the successful development of EPCM systems. The DSC study revealed that the thermograms of the produced microcapsules broadened with increasing cross-linker concentration, indicating a wider phase transition temperature range. Furthermore, EPD5's exothermic peak changed from a bimodal to a unimodal profile, indicating a move toward predominately heterogeneous nucleation behavior. The findings also showed that the developed microcapsules' latent heat enthalpy rose from 98.6 to 155.6 J.g^{-1} as the cross-linker content increased from 0.5% to 5%. Furthermore, EPD5 demonstrated a maximum encapsulation ratio of 71.1%. However, increasing the cross-linker concentration above 5% led to a significant drop in enthalpy. The TGA study showed that all synthesized MPCMs showed a clear two-step deterioration pattern, indicating the successful formation of a core-shell structure and improved thermal stability, while pure PCM exhibited a single-step thermal degradation. The first stage involves the decomposition of the encapsulated PCM, whereas the second involves the degradation of the polymer shell. Notably, EPD5 had the greatest initial mass loss, which can be attributed to its higher encapsulation ratio, as it contains more PCM within the polymer shell. Additionally, the addition of DVB as a cross-linking agent enhances the microcapsules' thermal resilience and structural integrity at high temperatures. The FE-SEM photographs indicated that the polymer network is more tightly bound and less prone to deformation, the increasing crosslinking produces a smoother and more compact surface morphology. After 50 cycles of charging and discharging, the EPD5 MPCMs' latent heat slightly decreased from 170.5 J.g^{-1} to 169.1 J.g^{-1} . With the optimum PCM loading and consistent thermal behavior, EPD5 is ideal for thermal regulation in buildings and solar energy storage systems.

CHAPTER 6

FABRICATION OF ZnATH-(O) NPs - INTEGRATED MICROENCAPSULATED PHASE CHANGE MATERIALS



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CHAPTER 6

FABRICATION OF ZnATH-(O) NPs -INTEGRATED MICROENCAPSULATED PHASE CHANGE MATERIALS

6.1. Introduction

A novel MPCM was synthesized via mini-emulsion polymerization technique by introducing anthocyanin-mediated Zn-ATH(O) NPs into the PCM matrix, and encapsulated within the polymer shell of Poly(St-co-BA) crosslinked with DVB.

In the preceding study, it was found that by introducing 0.5 wt% cross-linker with respect to the monomer increased the microcapsules' thermal stability, but it also led to decrease in the total thermal storage properties. To address this constraint and achieve balanced performance, anthocyanin-mediated ZnO nanoparticles [Zn-ATH(O) NPs] were ultrasonically integrated into the PCM matrix followed by the polymerization. The phytochemicals found in ATH serve as natural capping agents, enhancing the functionality and durability of the ZnO NPs' surface while regulating their controlled growth. This distinct surface chemistry ensures homogeneous dispersion of the NPs inside the PCM matrix, considerably increasing the thermal conductivity while successfully suppressing leakage. As a result, during repeated melting and solidification, the MPCMs demonstrated excellent cycle stability, increased heat transfer efficiency, and better LHS. While providing a sustainable, ecologically safe synthesis technique, ATH-derived ZnO NPs show greater compatibility with the organic PCM environment than chemically synthesized ZnO NPs, which frequently suffer from toxicity, surface imperfections, and poor dispersion. This method not only tackles the drawbacks of cross-linker-based stabilization, but it also paves the way for the development of high-performance MPCMs. FE-SEM with EDX analysis were used to characterise the morphology and elemental analysis of MPCMs, while FTIR was used to investigate the chemical interactions between the shell and core. DSC and TGA were used to assess the phase change behavior and thermal stability.

6.2. Results and Discussion

6.2.1. Thermal Performance of the Modified MPCMs

The phase change behavior and TES performance of the modified MPCMs with different concentrations of ZnATH-(O) NPs (1, 3, 5, 7, and 9 wt. %) were assessed by DSC technique

[**Figure 6.1 (a & b)**]. DSC measurements were carried out at a heating and cooling rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ in a N_2 atmosphere at temperature ranging from 10 to $70\text{ }^{\circ}\text{C}$.

The pure PCM, ESE exhibited a melting temperature of $38.9\text{ }^{\circ}\text{C}$ and a crystallization temperature of $30.5\text{ }^{\circ}\text{C}$, with a melting enthalpy of $239.9\text{ J}\cdot\text{g}^{-1}$ and crystallization enthalpy of $237.7\text{ J}\cdot\text{g}^{-1}$, as determined by DSC. Conversely, the blank MPCM sample (without ZnATH-(O) NPs filler) displayed melting temperature of $38.2\text{ }^{\circ}\text{C}$ and a latent heat of fusion of $104.4\text{ J}\cdot\text{g}^{-1}$, with a corresponding crystallization temperature of $31\text{ }^{\circ}\text{C}$ and crystallization enthalpy of $98.6\text{ J}\cdot\text{g}^{-1}$. The confinement of ESE within the polymeric shell restricts molecular mobility and alters the crystallization environment, which may contribute to the observed shifts in the melting and crystallization temperatures relative to the pure PCM.

The addition of ZnATH-(O) NPs gradually raised the enthalpies of the modified MPCMs as illustrated in **Figure 6.1 (c)**. The addition of $1\text{ wt.}\%$ NPs resulted in a small increase in latent heat of melting to $115.4\text{ J}\cdot\text{g}^{-1}$, suggesting improved TES behaviour. With further loading, the enhancement became more pronounced — $122.8\text{ J}\cdot\text{g}^{-1}$ at $3\text{ wt.}\%$, $136.2\text{ J}\cdot\text{g}^{-1}$ at $5\text{ wt.}\%$, and reaching a maximum of $186.8\text{ J}\cdot\text{g}^{-1}$ at $7\text{ wt.}\%$ ZnATH-(O) NPs. An analogous pattern was noted in the latent heat of crystallization. This steady improvement may be associated with the incorporation of ZnATH-(O) NPs, which may influence the thermal behavior of the encapsulated PCM during the phase transition. Furthermore, NPs might function as a heterogeneous nucleation agent, promoting faster and more consistent PCM crystallization within the microcapsules.

However, the latent heat of the resulting sample only reached $69.9\text{ J}\cdot\text{g}^{-1}$ when the loading amount of ZnATH-(O) NPs grew up to $9\text{ wt.}\%$, which is lower than that of the microcapsules without NPs. A combination of structural and compositional reasons can explain the decrease in heat storage capacity with larger ZnATH-(O) NP loadings (especially at $9\text{ wt.}\%$). Excessive filler content disrupts the polymerization of the shell-forming monomers, resulting in a coarse and mechanically fragile shell that is susceptible to rupture under mechanical or thermal stress. This results in PCM leakage or reduced confinement since it undermines the integrity of the core-shell structure. High ZnATH-(O) NP loading further raises the possibility of NPs agglomeration inside the PCM core, which obstructs effective phase transition and interferes with crystallization pathways. Furthermore, inorganic filler occupies a larger percentage of the

microcapsule mass than latent heat-storing material, which lowers the effective PCM content per gram of capsule.

Table 6.1: Phase change properties of the modified MPCMs

Sample No.	NPs (%)	Melting Process				Crystallization Process				E _R (%)	E _{ES} (%)
		T _{om} (°C)	T _{pm} (°C)	T _{em} (°C)	ΔH _m (J.g ⁻¹)	T _{oc} (°C)	T _{pc} (°C)	T _{ec} (°C)	ΔH _c (J.g ⁻¹)		
Z0	0	35.0	38.2	39.8	104.4	32.5	31	29.5	98.6	43.5	42.5
Z1	1	28.9	40.0	50.0	115.4	34.3	31.1	19.3	108.2	48.1	46.8
Z3	3	28.5	39.3	48.3	122.8	34.6	32.1	17.5	133.7	51.2	53.7
Z5	5	31.0	38.6	47.1	136.2	34.6	30.5	17.4	182.8	56.8	66.8
Z7	7	26.4	38.7	46.5	186.8	34.3	31.1	20.8	185.0	77.9	77.8

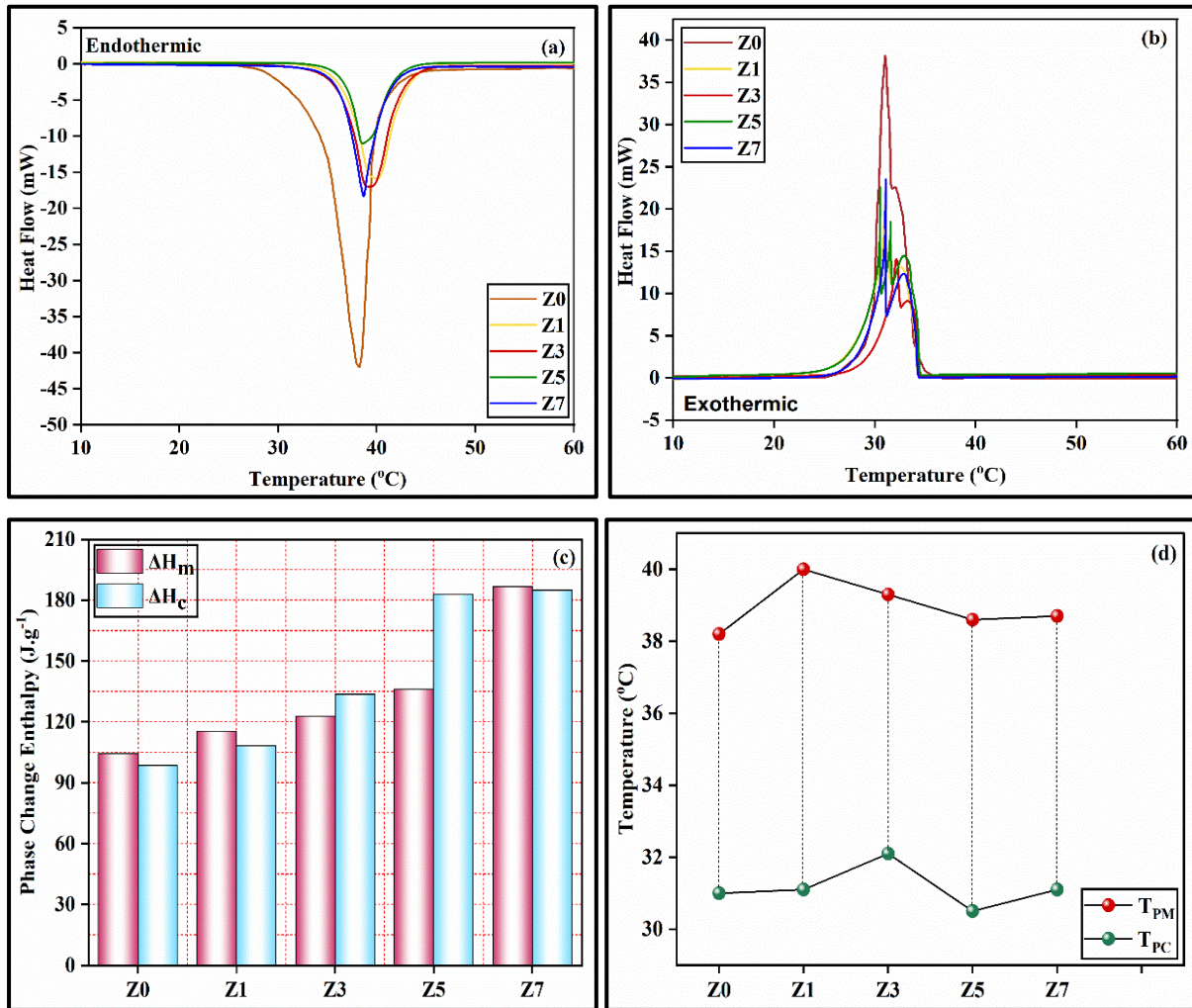


Figure 6.1: (a,b) DSC thermograms, (c) Phase change enthalpies and (d) Supercooling phenomenon of the modified MPCMs with varying amounts of ZnATH-(O) NPs

The observed decrease in enthalpy and energy storage performance at high filler concentrations is caused by the combined impact of poor shell quality, reduced core volume, and impaired crystallization. As a result, 7 wt.% NPs was found as the most optimal loading, facilitating the production of structurally reliable microcapsules with enhanced thermal behaviour [237].

6.2.1.1. Phase Change Performance of the Modified MPCMs

Encapsulation ratio and encapsulation efficiency for each filler concentration were determined using the equations 2.1 and 2.2. **Table 6.1** provides an overview of the findings, highlighting the trends from 0 to 7 wt.% ZnATH-(O) NP loading. The findings unequivocally show that both parameters gradually rise from 0 to 7 wt.% ZnATH-(O) NPs. This trend indicates that the moderate incorporation of ZnATH-(O) NPs favourably influences the thermal response of the microencapsulated PCM, resulting in improved phase transition characteristics. The optimum performance was obtained at 7 wt.% NPs, where the maximum values of both encapsulation ratio and encapsulation efficiency were recorded, demonstrating that this concentration allows for both efficient energy storage and microstructural integrity.

6.2.1.2. Supercooling of the Modified MPCMs

One of the disadvantages of PCMs in TES applications with regard to energy efficiency is supercooling. The impact of ZnATH-(O) NPs loading on the crystallization kinetics of the MPCMs was examined by evaluating supercooling (ΔT_{SC}), which is the difference between the melting and crystallization peak temperatures. **Figure 6.1 (d)** depicts the associated supercooling trend with different NPs loading. At 1 wt.% and 5 wt.% ZnATH-(O) NPs, a discernible rise in supercooling was noted. The aggregation of ZnATH-(O) NPs or their restricted nucleating capacity may be the cause of this behaviour, which interferes with the normal packing of ESE molecules and prevents effective heat release during solidification. This results in a decrease in crystallization kinetics, as the PCM needs to cool down more deeply to start crystallizing [238].

In contrast, MPCMs containing 0, 3, and 7 wt.% ZnATH-(O) NPs showed comparatively less supercooling, indicating that the NPs were either evenly distributed or effectively functioned as heterogeneous nucleation sites at these concentrations, facilitating a more consistent and prompt phase transition [239]. The favourable interaction between filler and core material at

this composition is highlighted, in particular, by the unaltered supercooling value at 3 wt.% ZnATH-(O) NPs when compared to the blank MPCM sample (without ZnATH-(O) filler).

6.2.2. Thermal Stability of the Modified MPCMs

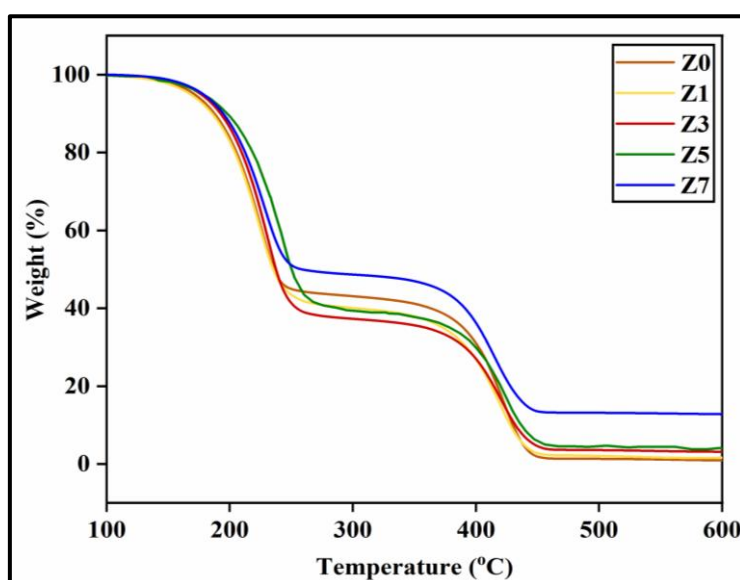
Thermal stability is inextricably linked to the long-term reliability and operational safety of phase PCMs in TES systems. In order to evaluate this, TGA was carried out on MPCMs having varying loadings (0, 1, 3, 5, and 7 wt.%) of ZnATH-(O) NPs in a N₂ atmosphere. As shown in **Figure 6.2**, all samples demonstrated a distinctive two-step degradation pattern between 50 °C and 850 °C. The first degradation stage, which occurs between 142.2 °C and 143.8 °C, involves the evaporation and disintegration of the encapsulated ESE. The second stage shows the thermal breakdown of the polymer shell material, with temperatures ranging from 301.8 °C to 335.5 °C. **Table 6.2** summarises the detailed degradation points and residual weights of the prepared MPCMs.

The first-step degradation temperature increased slightly with filler addition, showing that the presence of ZnATH-(O) NPs delayed the commencement of PCM volatilization. This improvement is due to the thermal barrier effect of ZnATH-(O) NPs, which inhibits heat transfer within the core and prevents premature decomposition. The Z7 sample had the highest first-step deterioration temperature beginning at 143.8 °C, indicating optimal PCM retention under heating.

The second-stage degradation temperature, which affects shell stability, dramatically increased with ZnATH-(O) concentration, from 301.8 °C in pristine MPCM to 335.5 °C for the 7 wt.% ZnATH-(O) loaded sample. This upward shift shows that ZnATH-(O) NPs contribute to stabilise the shell structure by increasing heat resistance and inhibiting thermal degradation. The uniform dispersion of NPs within the PCM core may help reinforce the interface between the core and shell, enhancing structural integrity during thermal stress. The stability of the system is further revealed by the residual weight (~460°C). Among all formulations, the sample with 7 wt.% ZnATH-(O) NPs retained the largest residue, 13.1%, whilst the blank MPCM showed only 2.0%. This substantial residue indicates the presence of undecomposed NPs and perhaps carbonized shell material, implying that a major amount of the NPs retained thermally stable during the degradation process.

Table 6.2: Thermal degradation profile of different MPCMs

MEPCM	1 st Degradation Temperature (°C)	2 nd Degradation Temperature (°C)	Residual Mass (%) with Temperature (°C)
Z0	142.2	301.8	2% (449.2)
Z1	142.5	311.3	2.1% (455.9)
Z3	142.8	321.0	3.5% (461.7)
Z5	142.8	332.4	4.3% (462.6)
Z7	143.8	335.5	13.1% (464.7)

**Figure 6.2: TGA thermograms of modified MPCMs with different amounts of ZnATH-(O) NPs**

The results obtained demonstrate the addition of ZnATH-(O) NPs improves both the core and shell thermal endurance of MPCMs. The microcapsules containing 7 wt.% ZnATH-(O) NPs perform the best out of all the formulations, combining the greatest degradation temperatures with superior thermal residue retention. This behaviour is consistent with the previously observed enhancements in LHS, phase change behaviour and encapsulation efficiency, indicating that 7 wt.% NPs is the optimal filler concentration for optimising the thermal reliability and energy storage potential of ESE-based MPCMs.

6.2.3. FTIR Analysis of the Modified MPCMs

FTIR spectroscopy was employed to confirm the successful microencapsulation of ZnATH-(O) NPs- doped ESE within the Poly(St-co-BA) shell. The FTIR spectrum of the microcapsules (**Figure 6.3**) indicates important vibrational functional group peaks associated with the polymer matrix, PCM core, and incorporated ZnATH-(O) NPs as fillers. All the synthesised microcapsules show three intense absorption peaks at 2956 cm^{-1} , 2913 cm^{-1} , and 2843 cm^{-1} , which correspond to symmetric and asymmetric stretching vibration peaks of methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2$) groups of ESE [173]. The strong absorption band at 1470 cm^{-1} and 714 cm^{-1} , corresponding to C-H bending vibrations and the asymmetric deformation vibration of $-\text{CH}_3$, thereby confirming the presence of the core PCMs, respectively [240]. The peak at 1726 cm^{-1} is associated with the C=O stretching vibration of the ester group in PBA, indicating the successful incorporation of the co-monomer in the shell [206]. The C=C stretching vibration of aromatic rings is observed around 1601 cm^{-1} , mainly due to contributions from styrene and the DVB cross-linker [241].

In addition, the organic moieties present in the ATH extract contributed characteristic C–H, C=O, and C–O stretching vibrations; however, these peaks extensively overlapped with the characteristic absorption bands of the polymer shell components, making their individual spectral contributions less distinguishable [242]. Furthermore, the characteristic Zn–O stretching vibration observed in the lower wavenumber region $\sim 419\text{ cm}^{-1}$ confirmed the presence of ZnATH-(O) NPs within the microcapsules. The absence of a broad O–H stretching band in the $3200\text{--}3500\text{ cm}^{-1}$ region suggested strong interactions between ATH hydroxyl groups and ZnO surfaces or their involvement in coordination interactions within the polymer matrix. These results validate the effective encapsulation of ZnATH-(O) NPs-doped paraffin within a crosslinked Poly(St-co-BA) shell structure, with all essential components preserving their distinctive spectrum characteristics without evidence of chemical degradation.

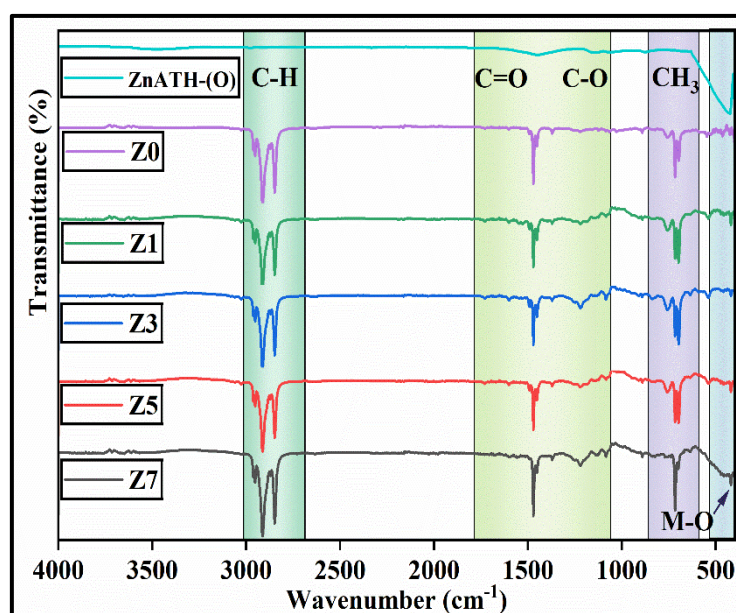


Figure 6.3: FTIR spectra of ZnATH-(O) NP, Z0, Z1, Z3, Z5 and Z7 MPCMs

6.2.4. PXRD Analysis of the Modified MPCMs

The crystallinity of modified MPCMs was evaluated using PXRD, and the corresponding diffraction patterns are presented in **Figure 6.4**. It was observed that all the samples exhibit three prominent diffraction peaks at $2\theta = 19.27^\circ$, 23.46° , and 24.82° , which are characteristic of ESE and can be indexed to (010), (105), and (-101) crystallographic planes, respectively (JCPDS card No. 45-1543). These reflections are characteristic of the triclinic crystalline phase of ESE [206].

The parental ESE was enclosed within a polymer shell composed of PB-co-PBA crosslinked with DVB. Being amorphous, these polymer shells exhibit a broad peak between 15° and 25° [243]. The PXRD patterns of Z0, Z1, Z3, Z5, and Z7 microcapsules reveal all the crystalline peaks of ESE with a reduction in relative intensity along with a broad amorphous peak corresponding to the Poly(St-co-BA) polymer shell crosslinked with DVB. Besides these, the MPCMs with ZnATH-(O) NPs (Z1, Z3, Z5, and Z7) also showed three distinct diffraction peaks at $2\theta = 31.72^\circ$, 34.36° , and 36.2° , corresponding to the (100), (002), and (101) reflections of the hexagonal wurtzite phase of ZnO (JCPDS card No. 01-089-0511) [244]. The presence of these peaks confirms the successful incorporation of crystalline ZnATH-(O) NPs into the MPCM's matrix. As the loading of ZnATH-(O) NPs was increased from 0% to 7%, a gradual

reduction in amorphous nature was observed with overall increase in the crystallinity, which is consistent with EDX data. This can be attributed to strong interfacial interactions among the ESE core, Poly(St-co-BA) shell and incorporated ZnATH-(O) NPs nanofillers, thereby promoting a more ordered structural configuration within the MPCMs [245].

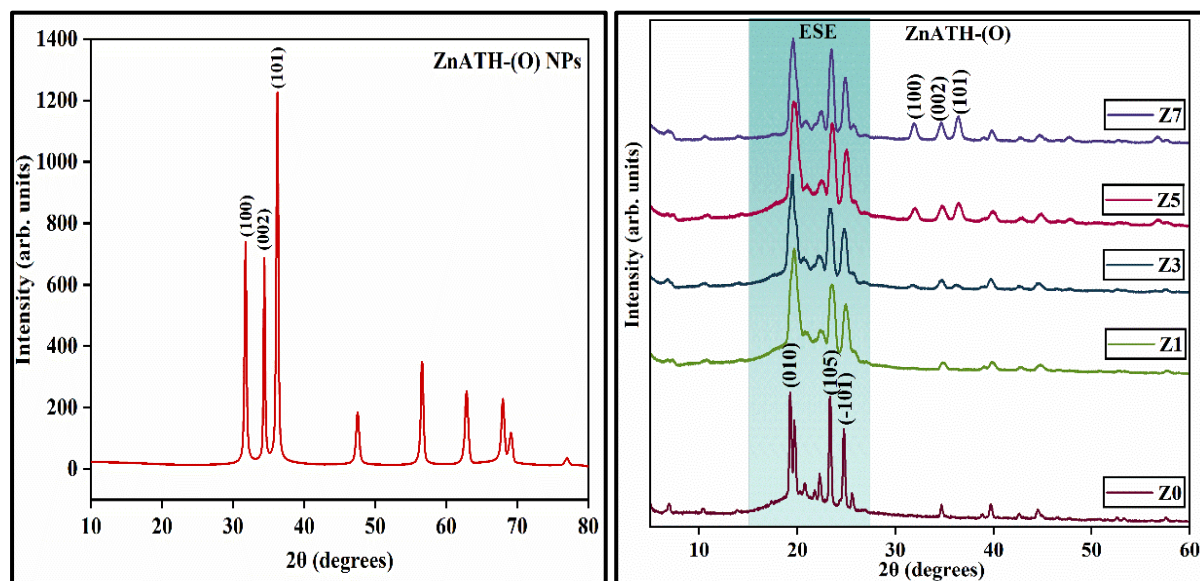
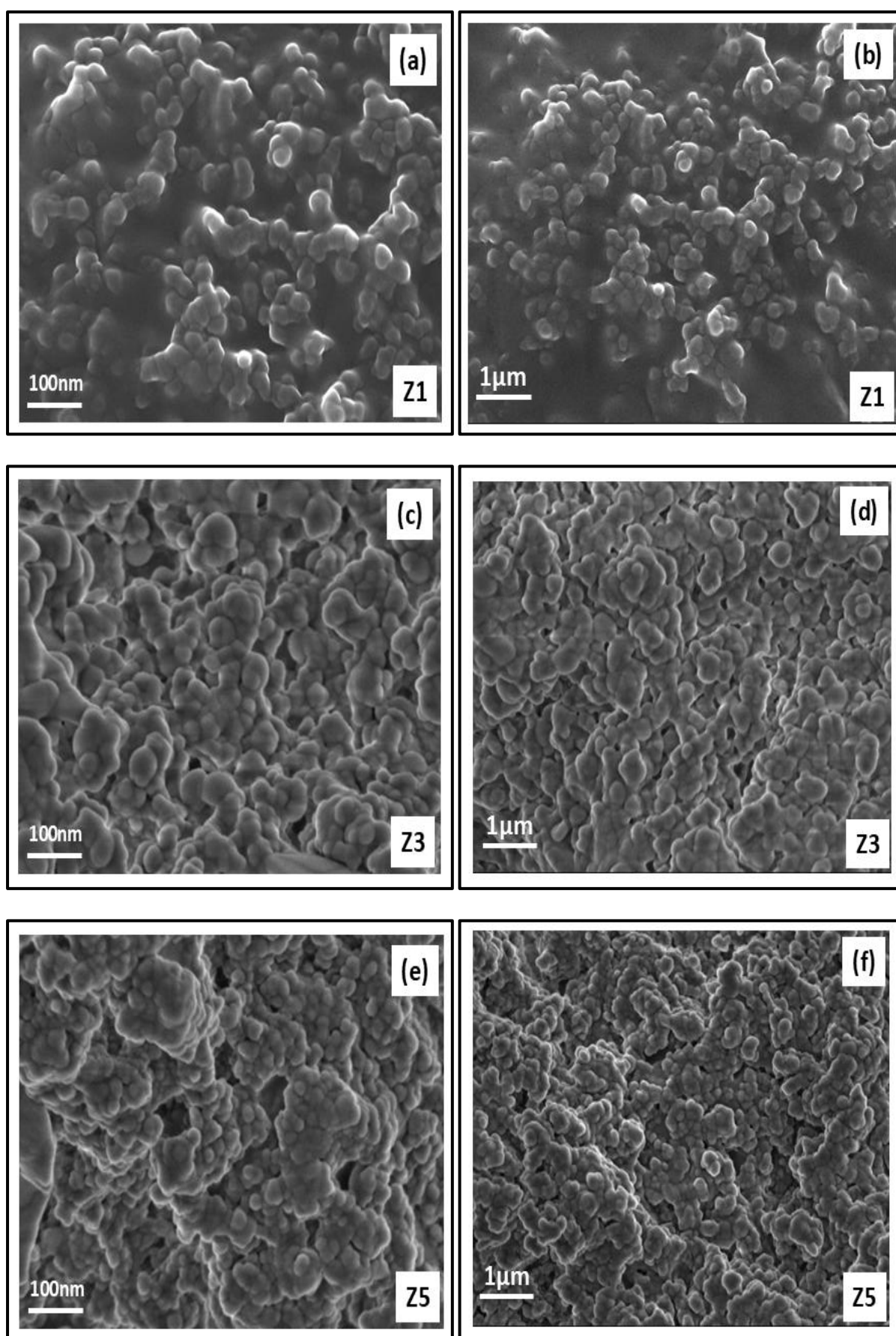


Figure 6.4: PXRD pattern of ZnATH-(O) NP, Z0, Z1, Z3, Z5 and Z7 MPCMs

6.2.5. Morphology of the Modified MPCMs

The morphology and microstructure of microcapsules with different amounts of ZnATH-(O) NPs were observed by FE-SEM. Typical SEM images of the synthesized MPCMs are shown in **Figure 6.5**. Clearly, all the microcapsules exhibited compact smooth surfaces and regular spherical shapes. The compact shell structure to encapsulate ESE can prevent the inner PCM from leaking during the phase-change procedure. These results demonstrate that the ZnATH-(O) NPs were uniformly bonded with the PCMs, instead of being placed on the surface of the microcapsules. The dispersion of these particles appears to be good. The agglomeration of the microcapsules increased with a higher ZnATH-(O) NPs content. When the content of ZnATH-(O) was 7 wt%, the microcapsules exhibited a more pronounced agglomeration phenomenon. This could be caused by the substantial addition of ZnATH-(O) NPs and their strong surface activity, which can readily lead to bunch of agglomeration [237].



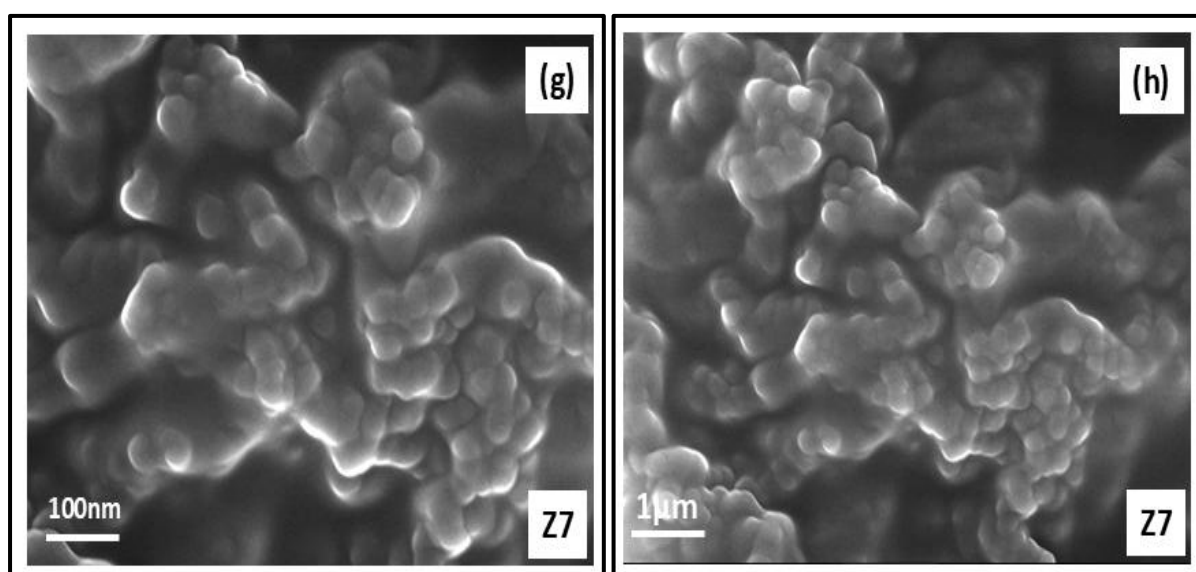


Figure 6.5: FE-SEM images of the modified MPCMs at different magnifications (100nm and 1μm)

The EDX spectrum in **Figure 6.6** shows the elemental composition of each sample. The surface of the microcapsules can be scanned for C, H, O, and Zn elements [245]. At lower ZnATH-(O) loadings (1%, 3%, and 5%), the elemental zinc content detected on the surface of the microcapsules was minimal, measuring approximately 0.2 wt%. This suggests that only a negligible amount of NPs interacted with or migrated to the outer polymer shell during synthesis. The majority of the NPs in these samples remained well-embedded within the paraffin core, indicating limited surface exposure and good encapsulation stability.

In contrast, a significant increase in surface ZnATH-(O) content was observed at 7 wt% loading, where the EDX spectrum revealed approximately 21.2 wt% zinc on the surface of the microcapsules. This substantial increase implies that excessive ZnATH-(O) NPs content promotes migration or entrapment at the polymer interface during the encapsulation process. The high surface concentration of ZnATH-(O) at this level confirms strong interactions between the NPs and the shell-forming polymer matrix, likely due to saturation of the paraffin core and limited encapsulation capacity.

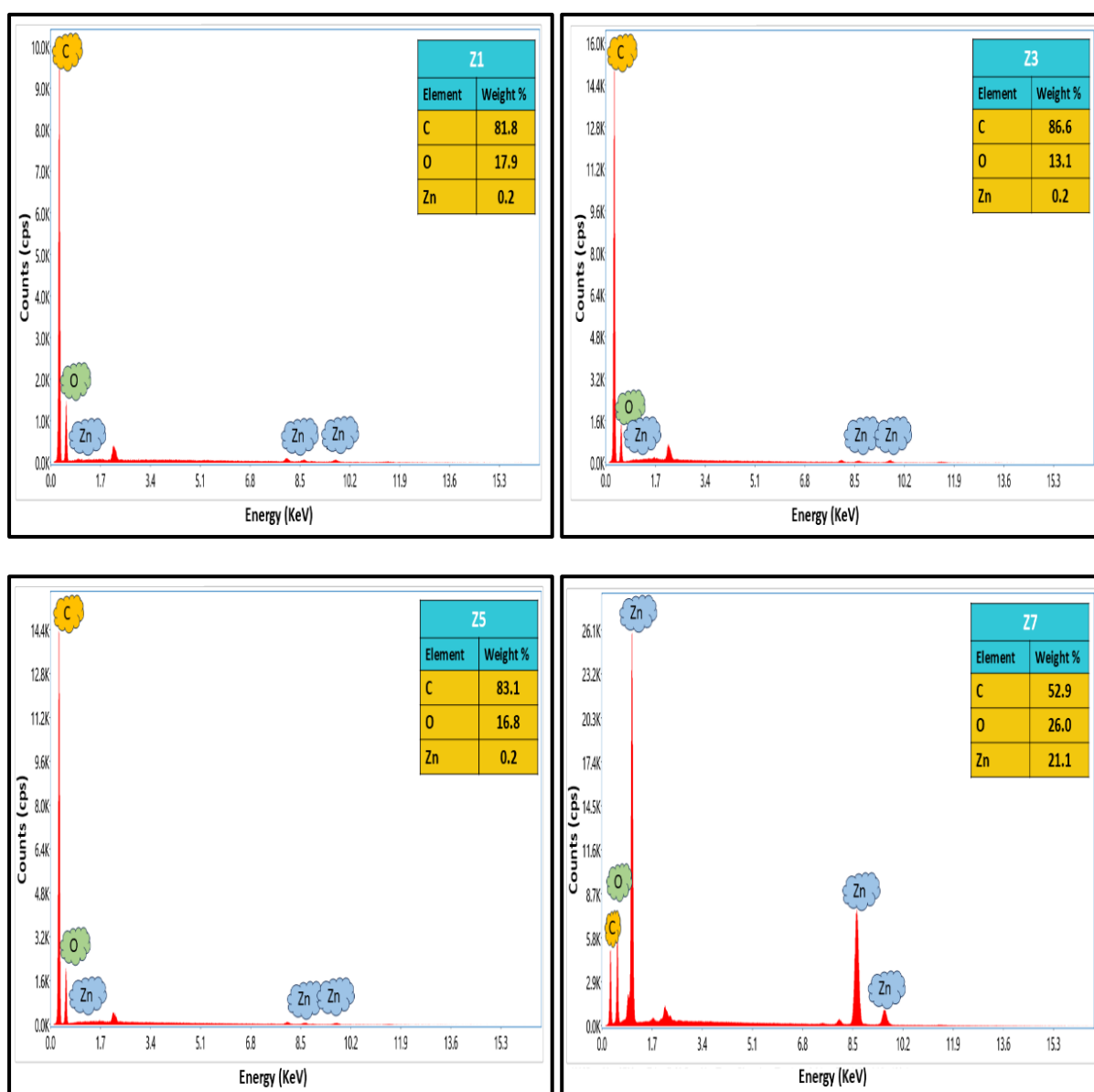


Figure 6.6: Surface elemental analysis of the modified MPCMs

6.2.6. Exudation Stability Test of the Modified MPCMs

The leakage resistance of the modified MPCMs was assessed using ESE as a reference material. Microcapsule samples with varied ZnATH-(O) ratios were mounted in the centre of a filter paper and exposed to thermal stimulation by placing the filter paper on a heating plate at 60 °C. To monitor heat distribution and leakage behaviour, infrared images were acquired at various time intervals. The corresponding thermograms are shown in **Figure 6.7**, with a colour

scale that proceeds from black and dark blue (coolest regions) to light blue and yellow to red (hottest regions) [246].

The pure ESE sample exhibited rapid heat transfer behaviour, as evidenced by the quick transformation of the sample surface into red and white regions with increasing heating time. At 5 min, the ESE sample showed nearly complete temperature saturation, indicating poor thermal resistance and direct heat diffusion due to the absence of an encapsulating shell structure. In contrast, all synthesized MPCM samples (Z0, Z1, Z3, Z5, and Z7) maintained distinct cooler blue/green regions even after prolonged heating, confirming the effectiveness of the polymer shell in controlling heat transfer and enhancing TES behaviour. The encapsulating polymer shell acts as a thermal barrier and delays heat penetration while the encapsulated ESE absorbs thermal energy through LHS during the phase transition process.

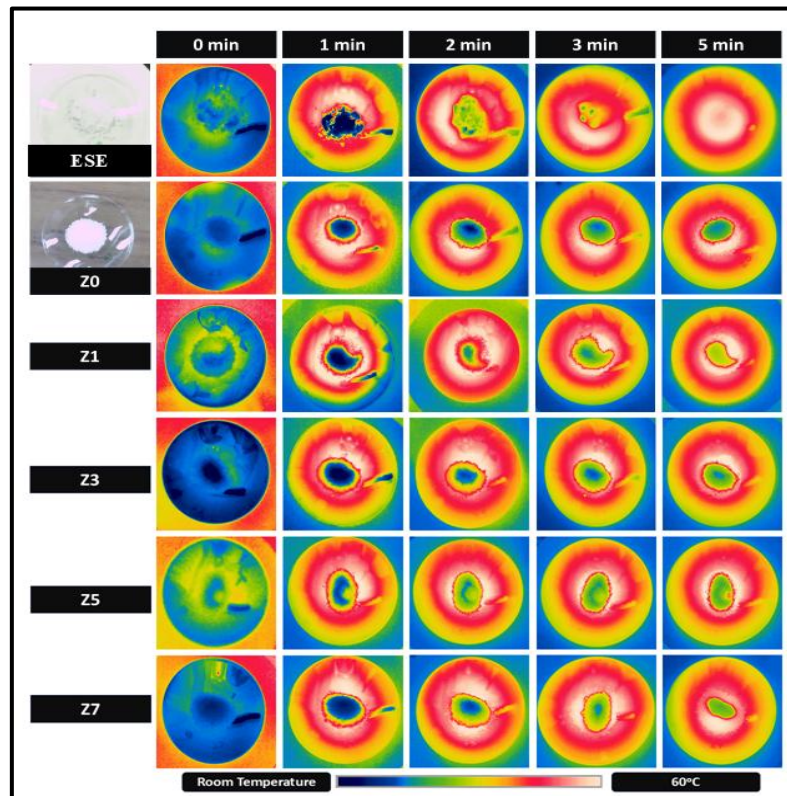


Figure 6.7: Infrared thermographic images of the different MPCMs

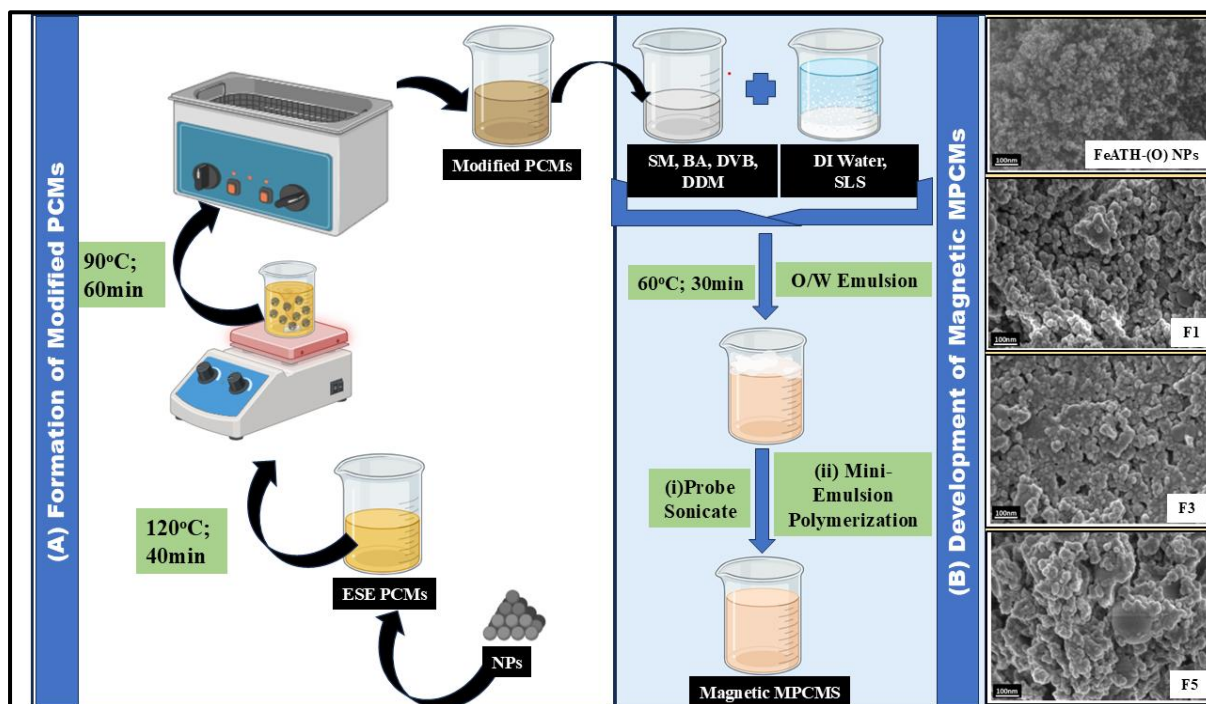
Among the encapsulated samples, Z1 and Z5 exhibited relatively faster reduction of the cooler regions during heating. This behaviour may be correlated with their comparatively higher supercooling values, which suggest less efficient crystallization behaviour. In the Z1 sample, the lower NP concentration may have been insufficient to provide effective heterogeneous nucleation sites, whereas in Z5, partial NP agglomeration and disturbance of the internal shell microstructure may have hindered ordered crystal growth and reduced thermal buffering efficiency. Conversely, Z0, Z3, and Z7 displayed more stable and persistent cooler regions throughout the heating period, indicating improved thermal regulation and delayed heat propagation. The comparatively lower supercooling behaviour of these samples suggests more effective heterogeneous nucleation facilitated by the combined contribution of the ZnATH-(O) NPs and the internal morphology of the polymer shell. Particularly, Z3 and Z7 exhibited more homogeneous temperature distribution and enhanced thermal stability, demonstrating improved latent heat absorption and controlled thermal diffusion behaviour. These findings clearly show that the synthesised microcapsules have efficient encapsulation and thermoregulatory properties, indicating their viability for TES applications [240].

6.3. Significant Findings

The incorporation of ZnATH-(O) as a functional filler, in accordance with Objective 4, was investigated to improve the functional performance of MPCMs. A series of MPCMs were prepared via mini-emulsion polymerization using Poly(St-co-BA) as the shell material, ESE as the core material, and ZnATH-(O) as the filler. The results of ZnATH-(O) NPs addition, core to shell mass ratio and the reaction stirring rate on the attributes of microcapsules were investigated. The DSC results showed that the highest encapsulation ratio and encapsulation efficiency of 77.9 and 77.8% were achieved when the 7 wt% ZnATH-(O) NPs were added, the core to shell mass ratio was 1:1 and the stirring rate was 5000 rpm, respectively. TGA analysis demonstrated that the Poly(St-co-BA) shell effectively retards and blocks the decomposition of the ESE core PCM at elevated temperatures and maintains good thermal reliability. FTIR and PXRD manifested that the MPCMs functionalized by ZnATH-(O) were successfully synthesized and ZnATH-(O) NPs were uniformly dispersed in the PCMs matrix. FE-SEM confirmed that all the microcapsules exhibited compact smooth surfaces and regular spherical shapes. Moreover, agglomeration of the MPCMs increased with a higher ZnATH-(O) NPs.

CHAPTER 7

FABRICATION OF FeATH-(O) NPs - INTEGRATED MICROENCAPSULATED PHASE CHANGE MATERIALS



Publication from this chapter: Gunjan Varshney, Sarla Yadav, Raminder Kaur, Mohammad Zulfeqar, “Synergistic Effects of FeACY-(O) NPs on the Thermal Performance of Microencapsulated Phase Change Materials (MEPCMs)”, *Fuels* (**1.F.=7.5**) (SCIE indexed) (Elsevier) (under review)

CHAPTER 7

FABRICATION OF FeATH-(O) NPs -INTEGRATED MICROENCAPSULATED PHASE CHANGE MATERIALS

7.1. Introduction

FeATH-(O) NPs-integrated MPCMs were fabricated through the mini-emulsion polymerization technique, with a DVB-crosslinked Poly(St-co-BA) hybrid polymer shell. Although these microcapsules exhibit good thermal stability, but their total thermal performance is lower. To mitigate this trade-off, Fe-ATH(O) NPs were ultrasonically integrated into the PCM matrix prior to polymerization.

FeO NPs have garnered significant attention among the different thermally conductive fillers investigated so far, owing to their special combination of high thermal conductivity, magnetic behaviour, chemical stability, and environmental compatibility [247]. The high surface area-to-volume ratio of FeO NPs promotes effective phonon transport and expedite up the process of heat conduction in composite systems. Their magnetic property also makes them adequate for integration into magnetically powered heat management and energy storage devices [248]. Therefore, incorporating FeO NPs into polymer-based microcapsules is a potential approach to produce next-generation energy storage materials with enhanced thermal reliability and heat transfer efficiency. Compared to traditional chemically synthesized FeO NPs, ATH-derived FeO NPs have been used in this study. Fe-ATH(O) NPs demonstrate superior compatibility with the organic PCM, providing a sustainable and environmentally friendly substitute. ATH phytochemicals operate as natural capping agents, boosting the surface characteristics of FeO NPs and facilitating a uniform dispersion in the ESE. This improves thermal conductivity, and assures consistent performance over numerous phase transition cycles. Thus, this strategy promotes the development of high-performance magnetic MPCMs while minimizing the adverse effects associated with cross-linker incorporation. The phase change performance and thermal stability were evaluated using DSC and TGA. The chemical interactions between the core and the shell were examined using FTIR. The morphology and elemental analysis of MPCMs were assessed via FE-SEM with EDX.

7.2. Results and Discussion

7.2.1. Thermal Performance of the Magnetic MPCMs

The DSC demonstrates the amount of thermal energy absorbed or released by the magnetic MPCMs in comparison to a conventional ESE. The heat flow is plotted against temperature on the DSC thermograms. DSC measurement is used to obtain the heating and cooling curves of microcapsules, from which the thermal parameters of the capsules are derived. For data collection, all samples were heated to 100 °C, and subsequently cool to 0 °C. The average value obtained from three DSC experiments is reported. The DSC (**Figure 7.1**) curves show that the pure ESE, F0 MPCM, and microcapsules with varying wt% of NPs have nearly identical phase change behaviour with single melting and double crystallization peaks, indicating that both ESE and NPs have been encapsulated inside the shell and that there is no reaction between the shell and the core material. Conversely, the addition of NPs causes the endothermic DSC peaks to broaden and the phase transition temperature to rise, indicating improved thermal stability and modified crystallization kinetics in the doped PCM matrix. The DSC data includes the microcapsule's associated enthalpy and melting and crystallization points, are listed in **Table 7.1**.

The DSC thermogram of pure ESE displays a single endothermic peak during melting and two distinct exothermic peaks during crystallization. The double exothermic transitions are characteristic of paraffin, arising from its rotator phase behavior, where crystallization proceeds in two steps: an initial transformation from the nucleated liquid into a metastable rotator phase, followed by conversion into the stable triclinic crystalline structure. The melting temperature was recorded at approximately 38.9 °C with a heat of fusion of 239.9 J.g⁻¹, while crystallization commenced at around 30.5 °C with a heat of solidification of 237.7 J.g⁻¹ [206]. These sharp and well-defined transitions highlight the excellent phase change characteristics of PCM, establishing it as a reliable benchmark material for evaluating the thermal performance of the modified microcapsules.

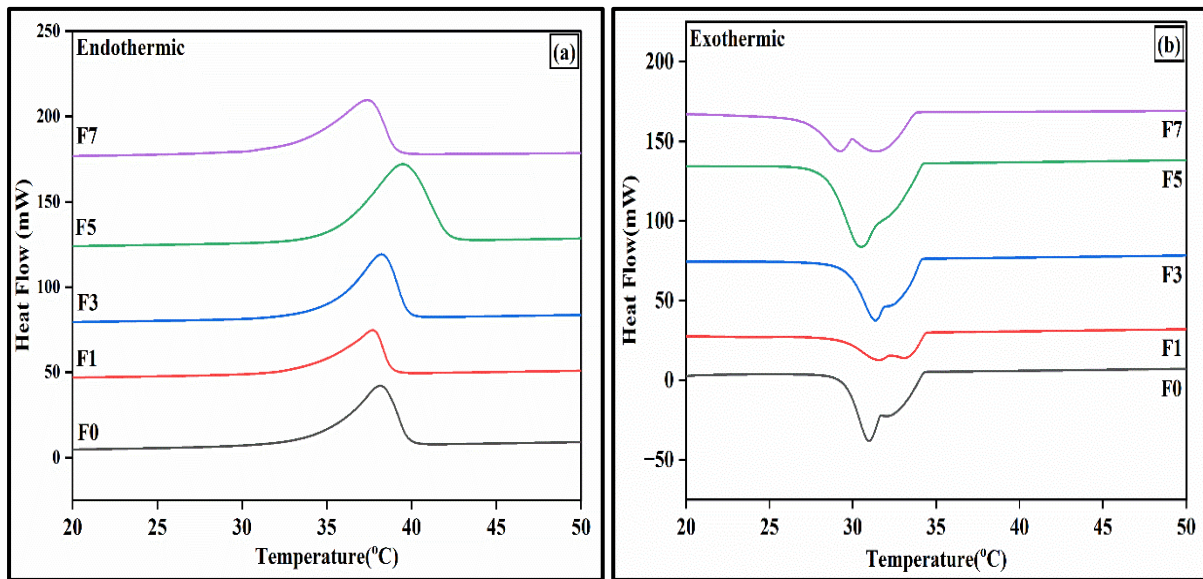


Figure 7.1: Endothermic and exothermic DSC thermograms of different MPCMs prepared with or without FeATH-(O) NPs

Table 7.1: Phase change characteristic data and encapsulation parameters of the synthesized magnetic microcapsule samples

Sample No.	NPs (%)	Melting Process				Cooling Process				E _R (%)	E _{ES} (%)
		T _{om} (°C)	T _{pm} (°C)	T _{em} (°C)	ΔH _m (J.g ⁻¹)	T _{oc} (°C)	T _{pc} (°C)	T _{ec} (°C)	ΔH _c (J.g ⁻¹)		
F0	0	35.0	38.2	39.8	104.4	32.5	31	29.5	98.6	43.5	42.5
F1	1	34.6	37.7	38.8	117.6	34.3	31.6	29.1	105.7	49.0	46.7
F3	3	35.1	38.2	39.8	142.6	34.1	31.4	29.6	132.0	59.4	57.5
F5	5	35.5	39.5	42.1	226.2	33.1	30.5	28.4	212.4	94.3	91.8
F7	7	33.3	31.5	39.0	122.3	33.7	31.4	30.9	120.5	51.0	50.8

The encapsulated F0 MPCMs exhibited melting and crystallization temperature of 38.2 °C and 31 °C, with corresponding latent heat of 104.4 J.g⁻¹ and 98.6 J.g⁻¹, respectively. The decrease in latent heat compared to pure ESE arises from the presence of the Poly(St-co-BA) polymer shell, which was crosslinked with DVB crosslinker. Crosslinker strengthens the shell structure and enhances the thermal stability of the microcapsules, which was validated through TGA. To

enhance the thermal performance of the F0 MPCM, FeATH-(O) NPs were incorporated into the PCM matrix at varying weight fractions of 1, 3 and 5%. The obtained results suggest that the inclusion of FeATH-(O) NPs significantly improves the heat transfer rate, and this effect becomes more pronounced with higher NPs loading [249]. As shown in Table 7.1, the rise in the latent heat enthalpies of the MPCMs was observed in contrast to the steady rise in the NP concentration in the PCM matrix. The observed onset melting and crystallization temperatures for a maximum FeATH-(O) loading of 5% are 35.5 °C and 33.1 °C, respectively. The peak crystallization and melting temperatures have been recorded at 30.5 °C and 39.5 °C, along with analogous enthalpies of 212.4 J.g⁻¹ and 226.2 J.g⁻¹, respectively.

On the contrary, by the addition of 7% NPs, the decline in the latent heat enthalpy was observed i.e. 122.3 J.g⁻¹. This can be ascribed by the excessive amount of NPs loading, which causes agglomeration and uneven dispersion in the PCM matrix. These agglomerates reduce the effective contact between the PCM and polymer shell by disrupting the microcapsule's structural integrity and impeding the appropriate development of the PCM core-shell interface. Moreover, the relative quantity of PCM accessible for phase transition is reduced by the increased concentration of NPs. The dense network of NPs also limits the PCM's molecular mobility and crystallization, which reduces its capacity to effectively absorb and release latent heat [237], [250].

Based on the above latent enthalpy values, the encapsulation ratio and encapsulation efficiency of ESE in these MPCMs can be calculated according to the equations 2.1 and 2.2. The outcomes of encapsulation ratio and encapsulation efficiency are also presented in Table 7.1, reflecting the different phase transition properties of MPCMs. The encapsulation efficiency of samples is 42.5%, 46.7%, 57.5%, and 91.8%, corresponding to the sample without NPs and the MPCMs with 1 wt%, 3 wt%, and 5 wt% FeATH-(O) respectively. The encapsulation efficiency is directly proportional to the latent heat of the microcapsules. Evidently, the encapsulation efficiency also increases with the addition amount of FeATH-(O), and the sample with 5 wt% FeATH-(O) exhibits the largest encapsulation efficiency, which ensures excellent TES capacity for the MPCMs [251]. This result also confirms that the addition of FeATH-(O) enhances the encapsulation of ESE resulting in the latent heat improvement of the MPCM.

7.2.2. Thermal Stability of the Magnetic MPCMs

TGA was performed to examine the thermal degradation behaviour of the pure ESE, blank MPCM, and FeATH-(O) NPs-modified MPCMs, as illustrated in **Table 7.2** and **Figure 7.2**. The pure ESE showed a one-step decomposition process that started at about 75 °C and terminated at 265 °C. This single-stage mass loss corresponds to the volatilization and disintegration of ESE, which has a low molecular weight and no protective shell [252].

Table 7.2: Thermal degradation profile of different magnetic MPCMs

MPCMs	I st Thermal Degradation Temperature (°C)	II nd Thermal Degradation Temperature (°C)	Residual Mass (%) with Temperature (°C)
F0	142.2	301.8	2 (449.2)
F1	125.5	281.3	2.8 (461.1)
F3	116.2	259.2	2.8 (462.6)
F5	127.1	291.1	7.9 (466.6)

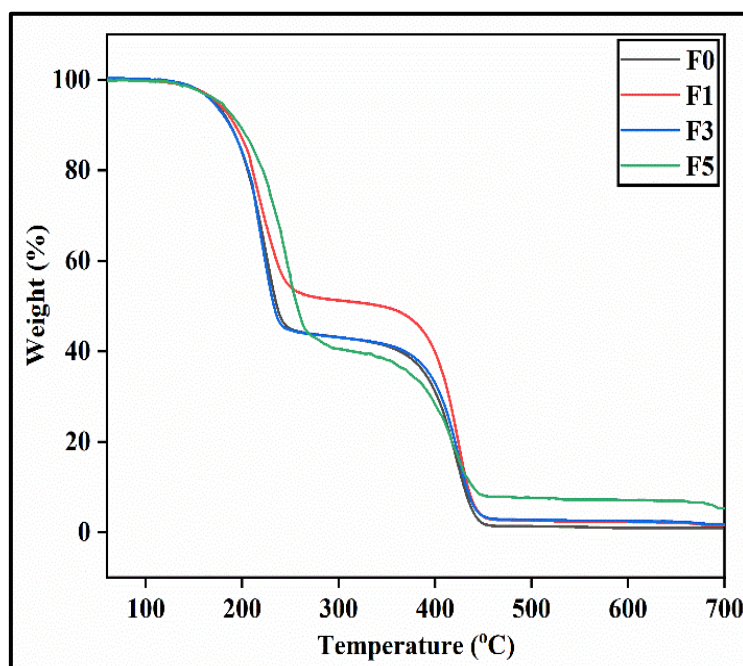


Figure 7.2: TGA thermograms of magnetic MPCMs synthesized by varying FeATH-(O) NPs

In contrast, all MPCMs revealed a two-step degradation pattern, indicating that PCM was successfully microencapsulated within the polymer shell of Poly(St-co-BA). The encapsulated ESE evaporates and disintegrates in the first step, while the Poly(St-co-BA) shell decomposes thermally in the second stage. For the blank F0 MPCM, the initial disintegration occurred at 142.2 °C, followed by the second at 301.8 °C, leaving a 2 % remnant at 449.2 °C. The two-stage weight loss and elevated deformation temperatures compared to the pure PCM highlight the thermal protection provided by the polymer shell and the cross-linker, which functions as a physical barrier to thermal exposure.

The degradation temperatures showed discernible changes once FeATH-(O) NPs were introduced. At 1 and 3 wt% FeATH-(O) NPs loading, the first and second deterioration temperatures dropped marginally to 125.5-116.2 °C and 281.3-259.2 °C, respectively. The reduction in degradation onset is due to the catalytic effect of FeATH-(O) NPs, which have active surface sites that promote polymer chain scission and expedite the decomposition process. These surface-active metal oxide sites diminish the activation energy of the polymer breakdown, triggering degradation at relatively lower temperatures [253]–[256].

The thermal degradation temperatures increased once again when the NPs loadings were increased to 5 wt%. The first and second phases of the degradation took place at 127.1 °C and 291.1 °C, respectively, while the highest temperature of disintegration reached 466.6 °C, leaving a noticeably greater residue of 7.9%. The barrier and char-forming properties of the FeATH-(O) NPs are responsible for the increased heat resistance at this greater loading [256]. The distributed NPs operate as thermal barriers, preventing the diffusion of volatile degradation products and stimulating the formation of a dense, thermally stable char layer to protect the underlying matrix. The elevated char yield and structural compactness are confirmed by the gradual rise in residual mass with higher FeATH-(O) content. The NPs improve the material's overall thermal endurance by strengthening the interfacial bond between the PCM core and polymer shell, which limits polymer mobility.

This indicates that FeATH-(O) NPs serve as both a catalyst at low concentrations and a thermal stabiliser at larger loadings, thereby, improving MPCM's overall thermal reliability for long-term TES applications.

7.2.3. FTIR Analysis of the Magnetic MPCMs

FTIR analysis was carried out to identify the chemical structure and compositions of FeATH-(O) NPs and MPCMs (F0, F1, F3, and F5) within the range of 500- 4000 cm^{-1} , as demonstrated in **Figure 7.3**. The FTIR spectrum of FeATH-(O) NPs exhibited characteristic peaks associated with the organic moieties of the ATH extract. The broad peak at 2088 cm^{-1} was attributed to –OH functional groups, indicating hydrogen bonding and carboxylic acid functionalities. The peak at 1644 cm^{-1} corresponded to aromatic C=C stretching vibrations, while the peak at 1533 cm^{-1} was assigned to the asymmetric stretching vibration of carboxylate groups. Furthermore, the characteristic peaks at 516 cm^{-1} and 428 cm^{-1} confirmed the Fe–O stretching and vibrational modes, indicating the successful formation of anthocyanin-mediated FeATH-(O) NPs. There is a shift in the peak position of M-O as compared to the FTIR spectrum of FeO, as reported in the literature, which is due to the addition of ATH extract, which acts as a reducing, capping and stabilizing agent in the synthesis of NPs [257]–[259]

However, the FTIR spectra of the magnetic MPCMs (F0, F1, F3, and F5) shows significant vibrational peaks linked to the ESE core, Poly(St-co-BA) shell and the filler FeATH-(O). The symmetric and asymmetric stretching vibrations of the methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2$) groups of ESE are represented by three strong absorption peaks in the produced MPCMs at 2952, 2913, and 2848 cm^{-1} . The presence of ESE core is confirmed by the absorption bands at 1471 and 715 cm^{-1} , which are linked to the vibrations of C-H bending and $-\text{CH}_3$ asymmetric deformation vibration. The C=O stretching vibration of the ester group in PBA is represented by the peak at 1733 cm^{-1} , which indicates that the co-monomer has been successfully incorporated into the shell [260]. The C=C stretching vibration of aromatic rings occurs at approximately 1598 cm^{-1} , which is due to styrene and the DVB cross-linker [206]. The synthesized MPCMs exhibit a distinct Fe-O stretching vibration at 538 and 418 cm^{-1} , indicating the existence of FeATH-(O) in the ESE core. However, the absence of a substantial O-H stretching band in the 3200-3500 cm^{-1} region suggests that ATH hydroxyl groups have strong interactions with FeO surfaces, or perhaps they are partially involved in coordination or encapsulation inside the polymer matrix. The findings demonstrate that FeATH-(O) NPs-fabricated ESE was successfully encapsulated within a crosslinked Poly(St-co-BA) shell structure, with all essential components retaining their distinct spectrum properties and exhibiting no indications of chemical deterioration.

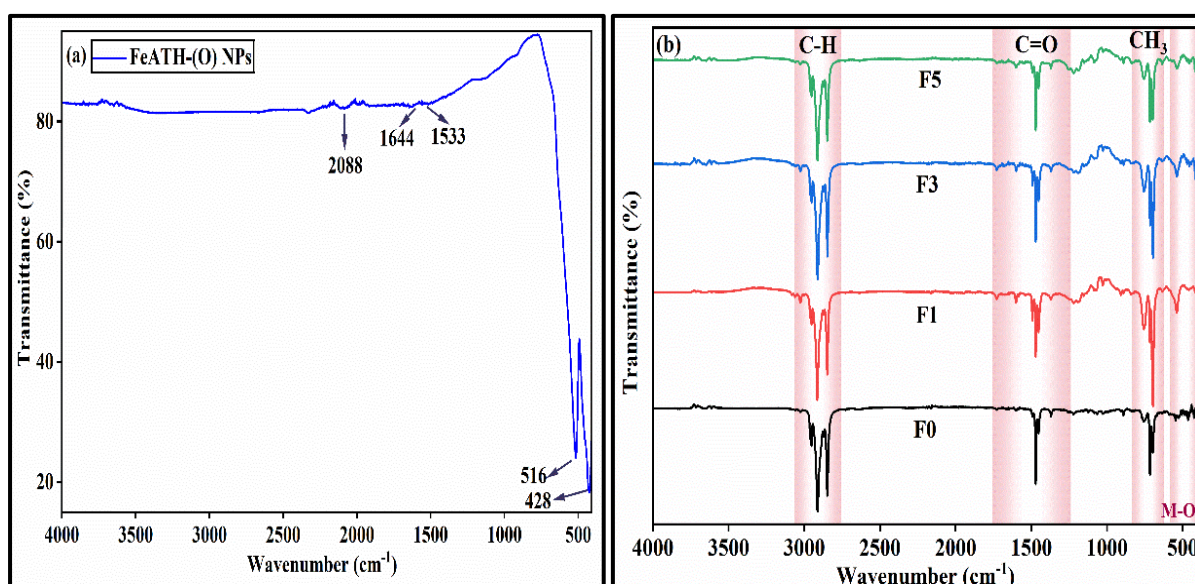


Figure 7.3: FTIR spectra of FeATH-(O) NPs and all synthesized MPCMs (F0, F1, F3, and F5)

7.2.4. PXRD Analysis of the Magnetic MPCMs

The crystallinity of FeATH-(O) NPs and MPCMs was assessed through PXRD, with the resulting diffraction patterns illustrated in Figure 7.4. The PXRD pattern of FeATH-(O) NPs exhibits a structure analogous to that of FeO NPs, with a slight shift in the peak positions, attributable to the integration of ATH extract into the Fe-(O) matrix, thereby affirming the dual role of ATH extract as both a reducing and capping agent. The PXRD pattern of FeATH-(O) NPs shows prominent peaks at 2θ value of 24.18° , 33.19° , 35.68° , 43.57° , 49.52° , 54.13° , 57.88° , 64.10° , 66.12° , 72.37° , 75.57° corresponding to (012), (104), (110), (202), (024), (116), (018), (300), (125), (119), and (220) crystal planes, signifying rhombohedral structure of FeO [Figure 7.4 (a)]. However, these values were consistent with those reported in literature and compared with the JCPDS file (JCPDS No. 01-079-0007) for FeO [257]–[259].

All the synthesized MPCMs (F0, F1, F3, and F5) displays distinct diffraction peaks of Poly(St-co-BA), ESE core and FeATH-(O) NPs. Varshney et al., found that the PXRD analysis of the parental ESE exhibits strong diffraction peaks with different 2θ values, which are consistent with the standard JCPDS card No 45-1543. This proves that the pure ESE has a unique triclinic crystal structure [206], [260]. A polymer shell composed of PB-co-PBA crosslinked with DVB

encased the parental ESE. The amorphous polymer shell exhibits a broad hump between 15° and 25° . All of the crystalline peaks of ESE are visible in the PXRD patterns of the F0-F5 microcapsules [Figure 7.4 (b)], along with a broad amorphous hump connected to the Poly(St-co-BA) polymer shell which was crosslinked with DVB [206]. Furthermore, three unique diffraction peaks at $2\theta = 24.84^\circ$, 33.14° , and 35.68° were seen in the MPCMs containing FeATH-(O) NPs (F1, F3, and F5). The obtained peaks show that the crystalline FeATH-(O) NPs were successfully integrated into the MPCM matrix. The increase in FeATH-(O) NP loading from 0% to 5% resulted in a steady decrease in amorphous characteristics and a corresponding rise in crystallinity, aligning with the EDX data. This is owing to the strong interfacial relations between the core PCM, Poly(St-co-BA) polymer shell, and FeATH-(O) NP nanofillers, which improve structural ordering inside the MPCMs.

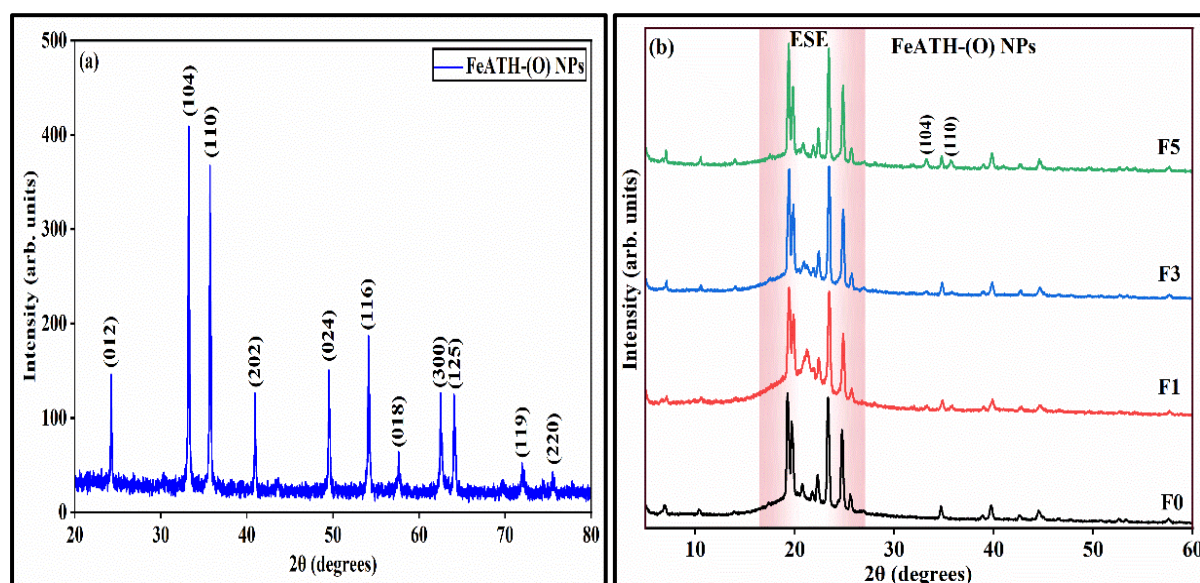
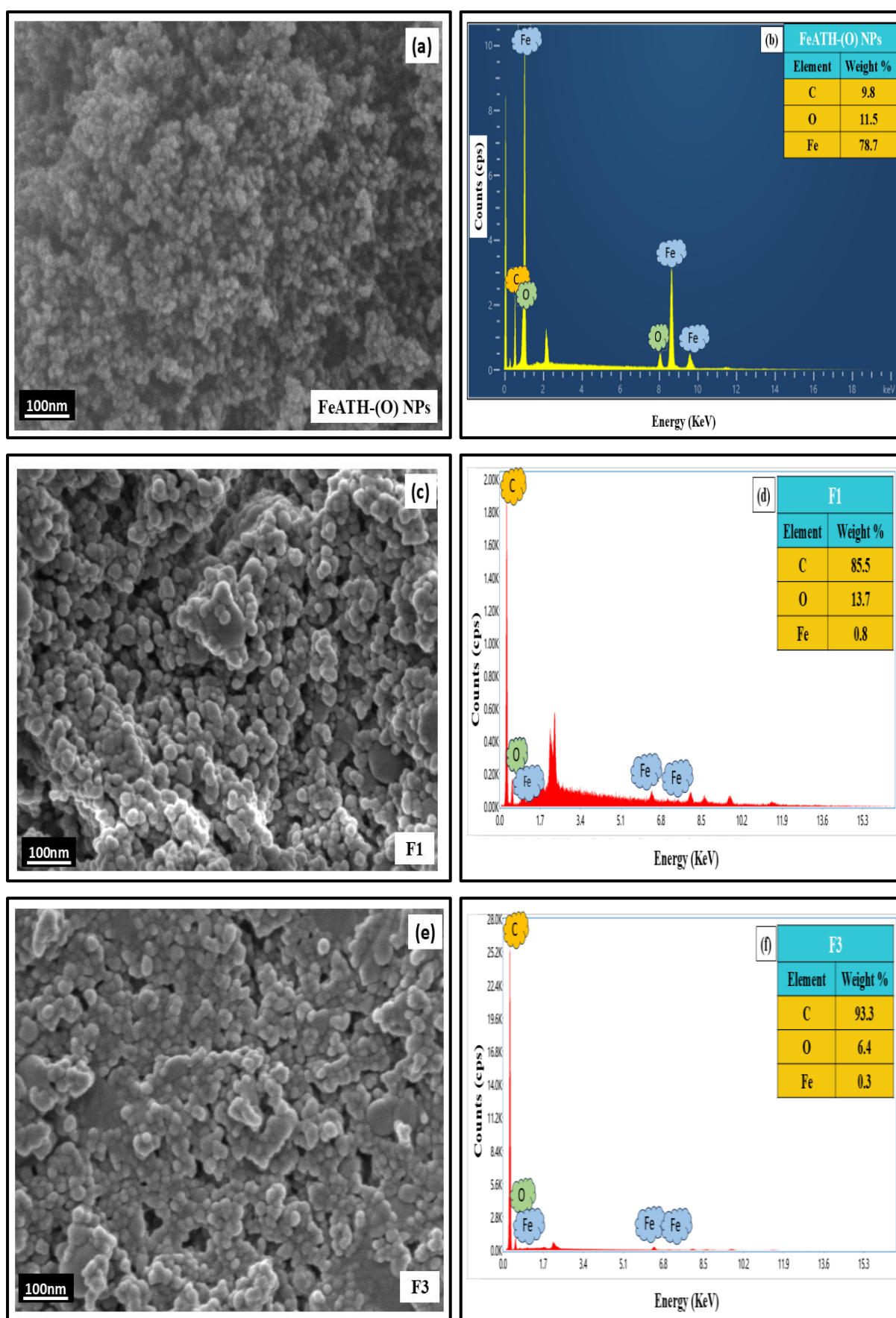


Figure 7.4: PXRD pattern of (a) FeATH-(O) NPs, and (b) MPCMs (F0, F1, F3, and F5)

7.2.5. Morphology of the Magnetic MPCMs

The morphology, microstructure and elemental analysis of FeATH-(O) NPs and MPCMs containing varying quantities of 1%, 3%, and 5% of FeATH-(O) NPs were examined using FE-SEM with EDX analysis (Figure 7.5). The FE-SEM micrograph of green synthesized FeATH-(O) NPs [Figure 7.5 (a) and (b)] shows agglomerated spherical particles with uniform

distribution of Fe, O and C [257]–[259]. Although all the MPCMs had compact, smooth surfaces and uniform spherical geometry [Figure 7.5 (c) – (h)]. The compact shell structure, which encloses the ESE, can prevent PCM from seepage throughout the phase transition process. The outcomes indicate that the FeATH-(O) NPs were uniformly integrated within the PCMs rather than only adhering to the surface of the MPCMs. Additionally, it was observed that the aggregation of the MPCMs intensified with an increased concentration of FeATH-(O) NPs. At a FeATH-(O) level of 5 wt%, the MPCMs demonstrated a more significant agglomeration behaviour. This may result from the significant introduction of FeATH-(O) NPs and their pronounced surface activity, which can easily induce extensive agglomeration [261]. The elemental Fe content on the surface of the MPCMs was 0.8%, 0.3%, and 0.1% for FeATH-(O) loadings of 1%, 3%, and 5%. This suggests that very few NPs interacted with or passed through the outer polymer shell during synthesis. The majority of the NPs in these samples stayed firmly embedded in the ESE core, indicating limited surface exposure and strong encapsulation stability.



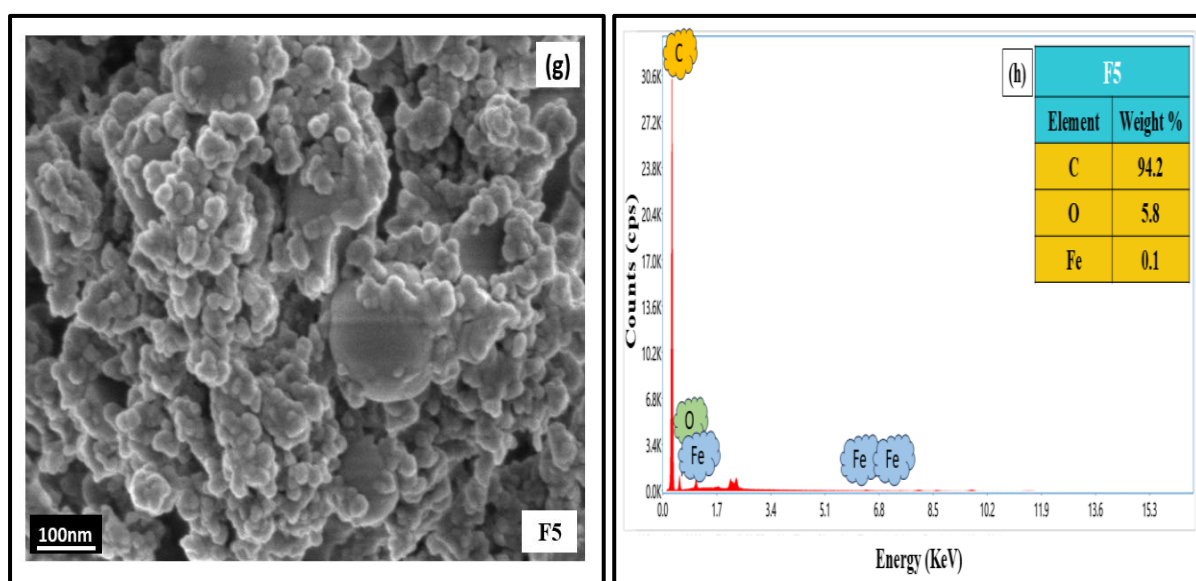


Figure 7.5: FE-SEM micrograph with EDX spectra of (a,b) FeATH-(O) NPs, and (c-h) MPCMs (F1, F3, F5)

7.2.6. Exudation Stability Test of the Magnetic MPCMs

The produced magnetic MPCM's leakage inhibition was evaluated using pure ESE and F0 as a benchmark. Microcapsule samples containing different FeATH-(O) NP ratios were placed in the centre of a filter paper and heated on a heating plate set to 60 °C. IFT images were obtained at regular intervals to evaluate the heat distribution and probable leaking behaviour. **Figure 7.6** depicts the comparable thermograms, with a colour gradient ranging from black and dark blue (illustrating the cooler zones) to light blue, yellow, and red (showing warmer zones). The thermographic photographs showed that the ESE appeared to go through a solid-liquid phase transition after 2 min of heating. The phase change terminated after around 5 min, and no solid residue could be seen, indicating perfect melting and apparent leakage.

On the contrary, the F0 sample, consisting of encapsulated ESE without NPs, already exhibited improved thermal resistance compared to pure ESE due to the insulating effect of the polymer shell. Upon incorporation of FeATH-(O) NPs (F1–F5), a further enhancement in thermal regulation behaviour was observed, particularly for F3 and F5, which retained more stable and persistent cooler regions during heating. The improved thermal response may be attributed to the effective distribution of NPs within the encapsulated PCM system, which enhanced

interfacial interactions, shell compactness, and resistance to heat penetration. In addition, the NPs promoted more controlled thermal diffusion and improved latent heat utilization by restricting direct heat transfer to the encapsulated ESE core.

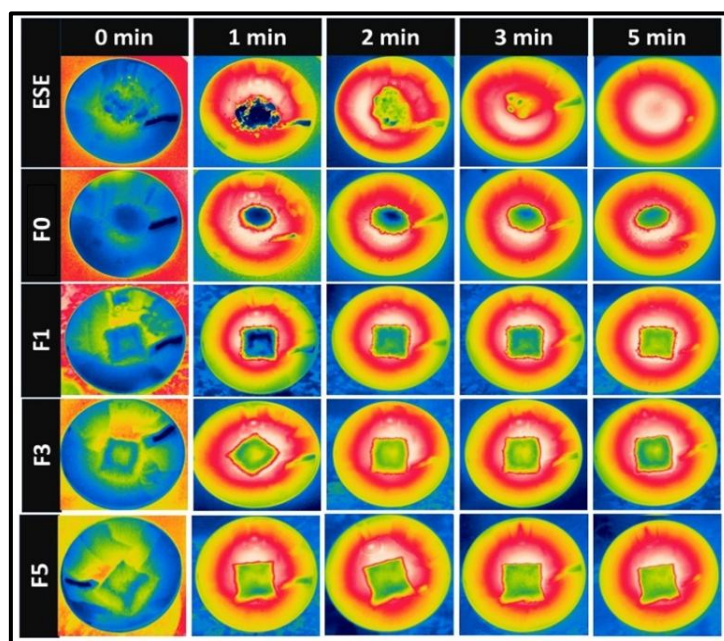


Figure 7.6: IFT imaging of the magnetic MPCMs with different weight ratio of NPs

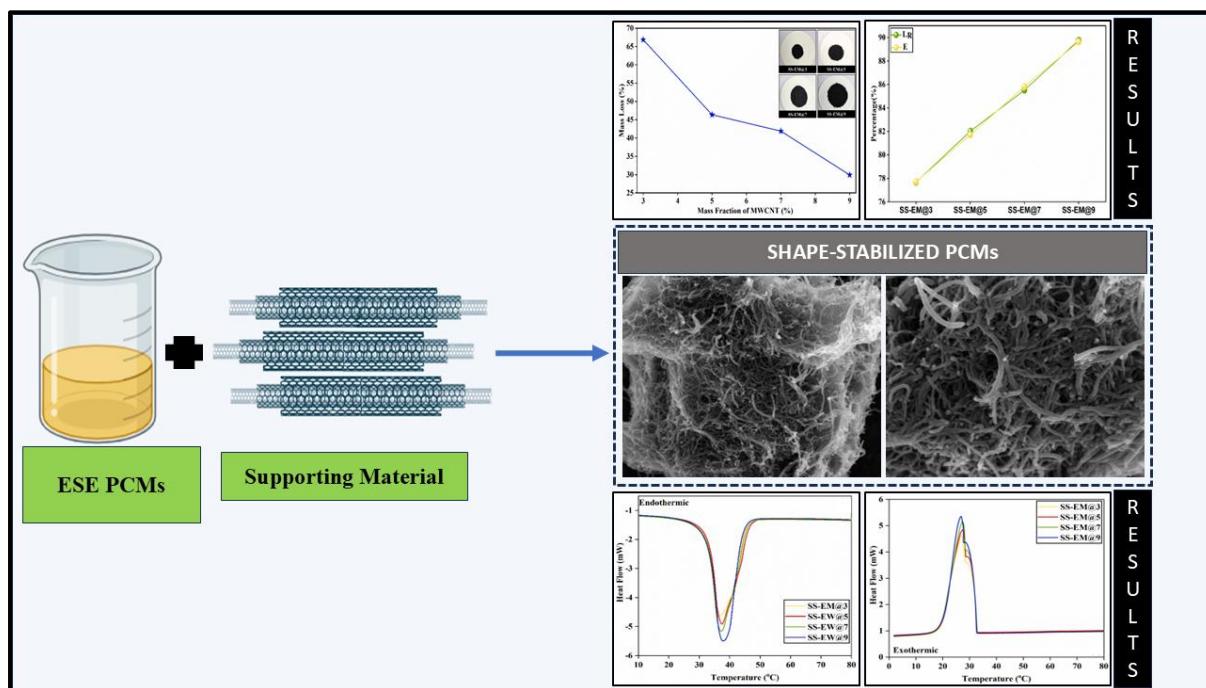
7.3. Significant Findings

The scope of Objective 4 was extended through the incorporation of FeATH-(O) NPs into ESE/Poly(St-co-BA) MPCM systems. Using mini-emulsion polymerization, MPCMs comprising ESE as the core and Poly(St-co-BA) as the hybrid shell were successfully synthesized in the presence of FeATH-(O) NPs. The microcapsules prepared without NPs decreases the latent heat compared to the pure PCM. The MPCMs exhibited melting and crystallization temperature of 38.2 °C and 31 °C, with corresponding latent heat of 104.4 J.g⁻¹ and 98.6 J.g⁻¹, respectively. The MPCMs with 5 wt % FeATH-(O) NPs reflects the highest rise in the latent heat enthalpies i.e. 226.2 (ΔH_c) and 212.4 J.g⁻¹ (ΔH_c). DSC results showed excellent encapsulation ratio and encapsulation efficiency of 94.3 and 91.8%, respectively. Thereby, the inclusion of FeATH-(O) NPs significantly improves the heat transfer rate of the microcapsules. IFT and TGA investigations indicated that the Poly(St-co-BA) shell efficiently

suppresses the deterioration of the ESE core at high temperature of 467 °C and left 7.9 wt% residue, resulting in a remarkable thermal stability and reliability. PXRD analysis revealed a steady decrease in the amorphous polymer shell characteristics and an increase in crystallinity with the addition of NPs. All microcapsules had regular spherical shapes and compact, smooth surfaces, as verified by FE-SEM. Furthermore, MPCM agglomeration rose when FeATH-(O) NPs increased. The characterization investigations of the produced microcapsules proved their application in TES systems. These microcapsules can be used in solar energy storage, waste heat recovery, electronics cooling, and building temperature regulation—all of which require efficient heat storage and release for enhanced energy efficiency.

CHAPTER 8

PREPARATION OF MULTI-WALLED CARBON NANOTUBES-MEDIATED SHAPE-STABILIZED PHASE CHANGE MATERIALS



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CHAPTER 8

PREPARATION OF MULTI-WALLED CARBON NANOTUBES-MEDIATED SHAPE- STABILIZED PHASE CHANGE MATERIALS

8.1. Introduction

A series of SSPCMs were fabricated using different mass percentages of ESE and MWCNTs. The vacuum impregnation method was used to infiltrate ESE into the hollow structure of MWCNTs. The thermal conductivity of organic PCM ESE was enhanced with the incorporation of highly conductive MWCNTs. The mixture rule is used to estimate the effective thermophysical properties of the prepared composites from their constituents. FE-SEM, FTIR analysis, PXRD techniques were used to investigate the microstructure of SSPCMs. The thermal properties of were evaluated using DSC and TGA. The leakage percentage of ESE/MWCNT composites was calculated to identify the holding capacity of the supporting material.

8.2. Results and Discussion

8.2.1. Leakage Test of ESE/MWCNT Composites

The change in weights of four shape-stabilized samples with respectively 3, 5, and 7% loading of MWCNTs to the ESE by mass fraction, both before and after drying is determined by equation 2.10 and illustrated in **Table 8.1**. A polyline diagram, **Figure 8.1**, is drawn in order to observe them more intuitively. The weight difference before and after the ESE/MWCNT drying process is 5.8, 3.9, and 3.6 g, respectively, when the corresponding mass fraction of MWCNTs added to the ESE is 3, 5, and 7%. The corresponding leakage percentages are 66.8, 46.4, and 41.9%. These instances can be explained by the fact that ESE remains in the system even after the MWCNTs have fully absorbed it when less supporting material is introduced. The unabsorbed ESE either evaporates or is absorbed by the filter paper after vacuum drying. When the mass fraction of MWCNTs reaches about 9%, the weight difference is 2.5 g, and the weight loss percentage stays steady at 29.9%. However, a small amount of leakage was observed on the filter paper, which, according to the criteria listed in Table 2.3, corresponds to slight leakage ($10 < L\% \leq 30$) while the composites remain structurally stable. Consequently, it may be inferred that 91:9 is the ideal ESE to MWCNTs ratio.

Table 8.1: Leakage test of the different composites produced by varying the MWCNTs ratio

Sample Code	Initial Mass (g)	Final Mass (g)	Mass Loss (g)	Leakage Percentage
SS-EM@3	8.63	2.86	5.77	66.85
SS-EM@5	8.52	4.57	3.95	46.36
SS-EM@7	8.69	5.05	3.64	41.88
SS-EM@9	8.49	5.95	2.54	29.91

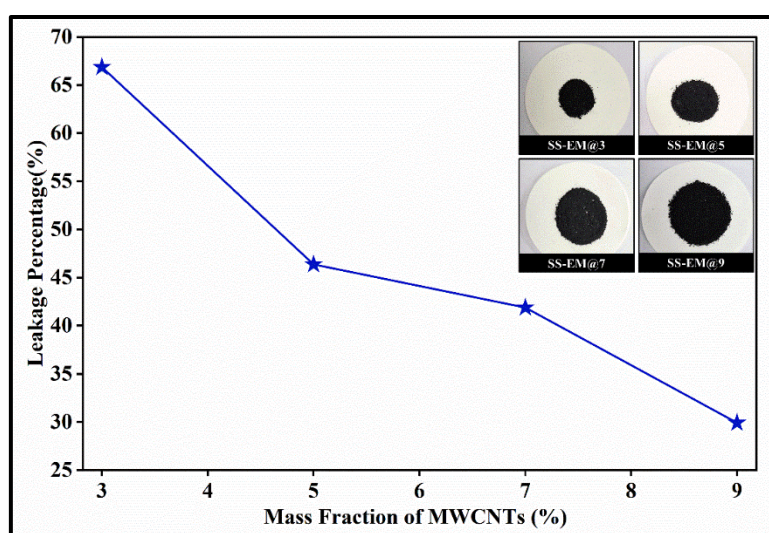


Figure 8.1: Leakage percentage of the prepared ESE/MWCNT composites

8.2.2. Thermal Behavior of the ESE/MWCNT Composites

DSC tests were performed to determine the impact of the MWCNTs ratio on the melting/freezing temperatures and the corresponding enthalpies of the synthesized SSPCM composites. **Figure 8.2 (a) and (b)** show the DSC curves of the as-prepared ESE/MWCNT composites. The DSC thermogram of the parental ESE demonstrated a single endothermic melting peak, whereas its crystallization curve exhibited two exothermic peaks, implying bimodal phase transition behavior. A liquid–solid transition from the nucleated liquid phase to the rotator phase and a solid–solid transformation from the rotator phase to a stable triclinic structure are the two subsequent transitions that give rise to this behavior.

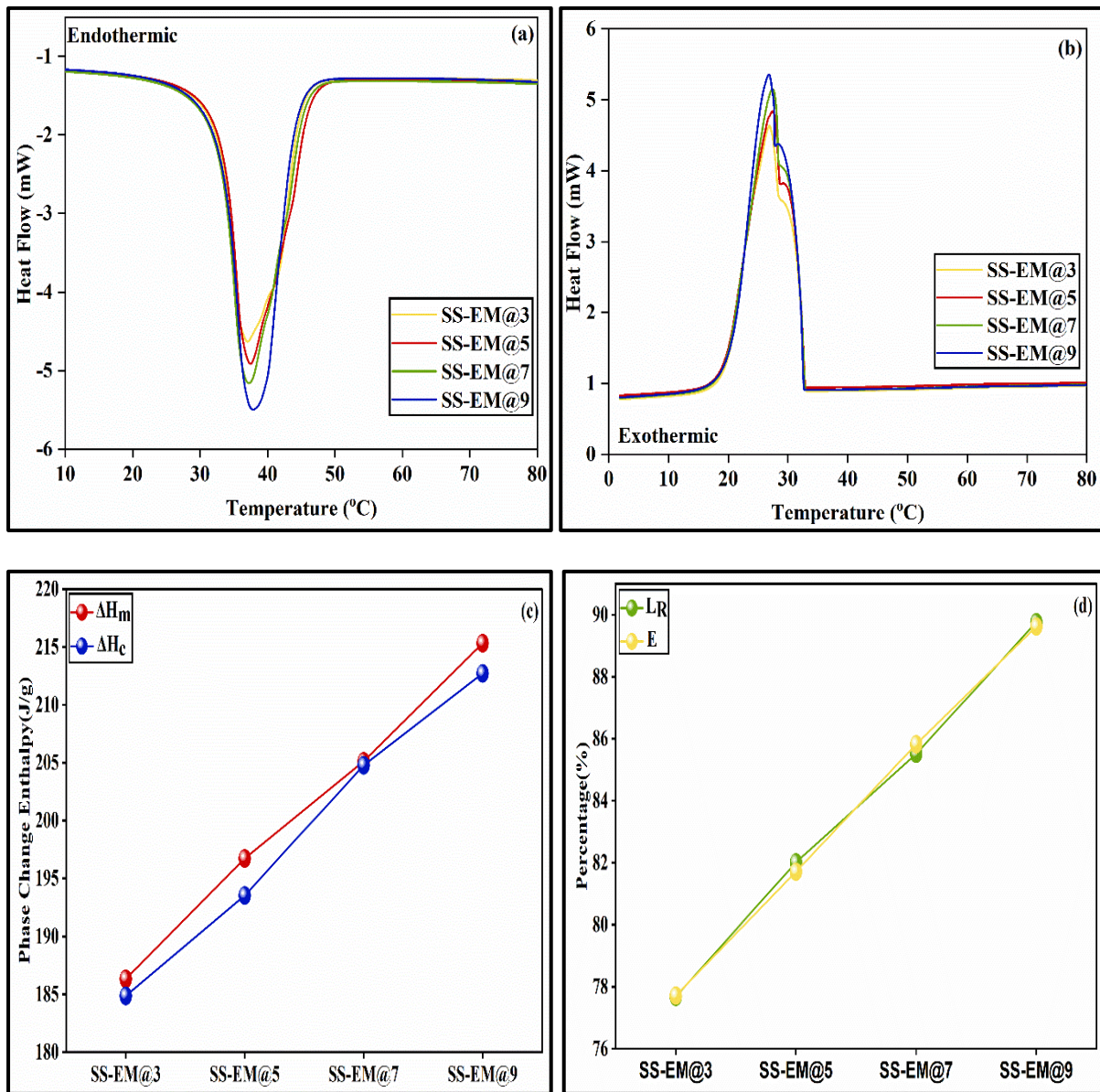


Figure 8.2: (a) Endothermic, (b) Exothermic DSC thermograms, (c) Phase change enthalpies and (d) Loading ratio and efficiency of the ESE/MWCNT composites prepared with different mass fraction of MWCNTs

The prepared composites showed a similar pattern, indicating that no chemical reaction took place during their synthesis [206]. The melting and crystallization temperatures of ESE were recorded as 38.9 °C and 30.5 °C, respectively [206]. The addition of MWCNTs as supporting materials caused the phase transition temperatures in the composites to slightly move toward lower values. The MWCNTs framework reduces the phase change temperature by boosting the

dispersion of ESE and offering additional nucleation sites. As the MWCNTs mass fraction increased, this shift became more apparent [262].

Table 8.2 summarizes the thermal properties of ESE/MWCNT composites at various MWCNT loadings. The latent heat rose proportionally with MWCNTs concentration, showing higher TES efficiency. The high adsorption and capillary effects of MWCNTs, which successfully sustain and retain the ESE within the composite, are responsible for this improvement. SS-EM@9 showed the largest percentage rise in latent heat of all the samples.

Table 8.2: Thermal properties of the synthesized ESE/MWCNT composites

Sample Code	T_m (°C)	$\Delta H_{Exp,m}$ (J.g ⁻¹)	$\Delta H_{Theo,m}$ (J.g ⁻¹)	T_c (°C)	$\Delta H_{Exp,c}$ (J.g ⁻¹)	$\Delta H_{Theo,c}$ (J.g ⁻¹)	L_R (%)	E (%)
SS-EM@3	37.0	186.3	223.1	26.9	184.8	230.6	77.7	77.7
SS-EM@5	37.5	196.7	227.9	27.4	193.5	225.8	82.0	81.7
SS-EM@7	37.2	205.1	223.1	27.4	204.8	221.1	85.5	85.8
SS-EM@9	37.9	215.3	218.3	26.8	212.7	216.3	89.8	89.6

T_m : Melting temperature; T_c : Crystallization temperature; $\Delta H_{Exp,m}$: Experimental melting enthalpy; $\Delta H_{Theo,m}$: Theoretical melting enthalpy; $\Delta H_{Exp,c}$: Experimental crystallization enthalpy; $\Delta H_{Theo,c}$: Theoretical crystallization enthalpy

8.2.2.1. Loading Ratio (L_R) and Heat Storage Efficiency (E)

The phase change performance of the produced nanocomposite PCMs was evaluated utilizing the loading ratio and heat storage efficiency determined by equations 2.1 and 2.2 respectively. As illustrated in **Figure 8.2 (d)**, the loading ratio and the heat storage efficiency are nearly identical as the composite's MWCNT loading percentage is varied. The loading rate and encapsulation efficiency both rise when ESE content is added to MWCNTs up to a maximum mass fraction of 9%. This enhancement is ascribed to the MWCNT's effective absorption capacity, which minimizes leakage by successfully retaining the ESE within the supporting matrix.

Table 8.3 provides a comparative assessment of previously reported PCM/MWCNT composites to help comprehend the current research context. While a number of research have

examined MWCNT-supported PCM composites with various PCMs and MWCNT contents, the current study offers a unique PCM and supporting material composition combination with enhanced TES properties. The comparison emphasizes the effect of PCM types and MWCNT loadings on thermal performance, demonstrating the novelty and significance of the current composite system.

Table 8.3: Comparative analysis of MWCNT-supported PCM composites reported in the literature with different PCM compositions and MWCNT loadings

S.No.	SSPCMs	PCM wt. %	ΔH_m , SSPCMs (J.g ⁻¹)	ΔH_m , PCM (J.g ⁻¹)	L _R (%)	Ref.
1.	Steric Acid/MWCNT	47	91.9	196.7	46.7	[263]
2.	PW-5%-CNT	95	128.2	151.8	84.4	[264]
3.	Fatty acid/CNTs	80	101.6	140.5	72.3	[265]
4.	Paraffin/diatomite/MWCNT	47.25	89.4	201.5	44.4	[266]
5.	Lauric acid/MWCNT	96.5	137.3	151.6	90.6	[267]
6.	Paraffin/MWCNT	99.5	180.1	210	85.8	[268]
7.	Lauryl alcohol/MWCNT/Gum Arabic	93	195.3	217.8	89.7	[269]
8.	ExP/C20/CNT	60	157.4	275.9	57.0	[270]
9.	Palmetic acid- Stearic acid/CNTs	92	163.0	177.7	91.7	[271]
10.	Paraffin/A-CNT	88	172.14	193.2	89.1	[272]
11.	MWCNT-COOH@PEG	47.6	146.7	170.3	86.1	[273]
12.	SS-EM@9	91	215.3	239.9	89.8	This work

8.2.2.2. Mixture Rule

Table 8.2 shows the latent heat data from the DSC investigation of the various ESE/MWCNT composites. The composites have a lower enthalpy than pure ESE because MWCNTs does not participate in the phase transition process. The theoretical enthalpy of ESE/MWCNT can be computed using equation 2.9.

The progressive reduction in the discrepancy between the theoretical and experimental latent heat values with increasing MWCNTs content (from 3 to 9 wt%) can be ascribed to the higher mass fraction of MWCNTs, which enhances the absorption and confinement of ESE within the SSPCMs structure [**Figure 8.3 (a)**]. As the CNTs network becomes denser, it gives paraffin more absorption sites and interfacial area, which encourages the SSPCMs to participate in the

phase transition more successfully and reduces the difference between calculated and measured enthalpy. This interpretation is consistent with the leakage test results, which show that larger MWCNT loadings improve structural integrity and minimize ESE loss, further supporting the premise that increasing CNTs content strengthens PCM retention and usage during phase transition.

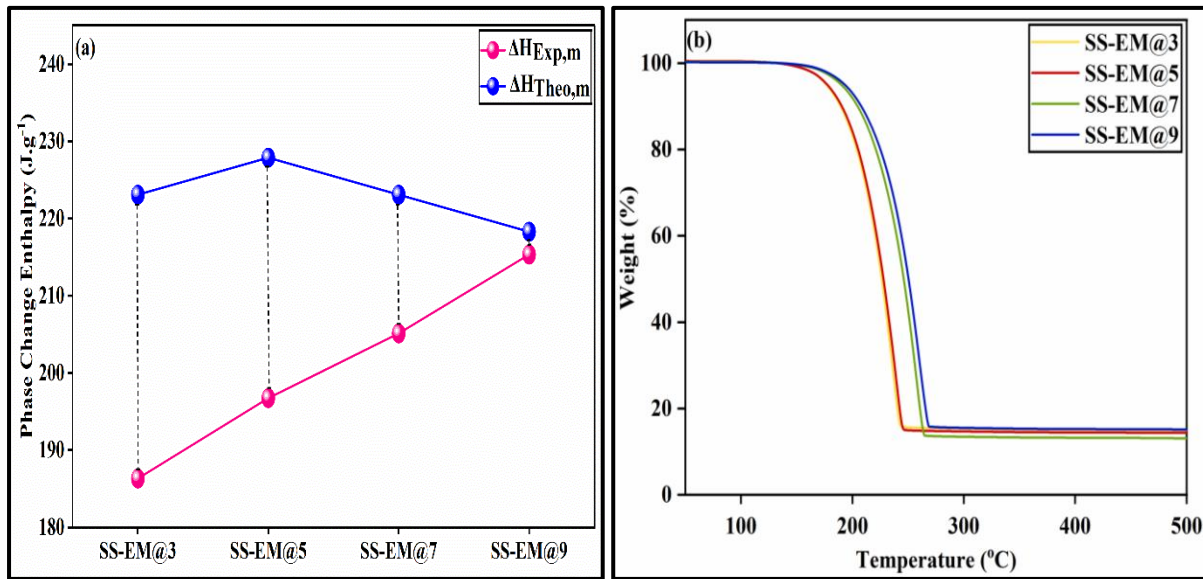


Figure 8.3: (a) Comparative analysis of the theoretical and experimental latent heat values; (b) TGA curves of ESE/MWCNT composites

8.2.3. Thermal Stability of the ESE/MWCNT Composites

Figure 8.3 (b) shows the TGA curves of the ESE/MWCNT shape-stabilized composites. The TGA curve of MWCNTs remained stable in N₂ at temperatures above 750 °C [274], [275]. This feature makes it an effective supporting material for solid-liquid PCMs. Compared to pure ESE, the weight loss onset temperatures for ESE/MWCNT composites are significantly higher [206]. The onset temperatures of the prepared composites increase from 153.11 °C for SS-EM@3 and SS-EM@5 to 166.76 °C SS-EM@7 and SS-EM@9, with increasing the loading content of MWCNTs [276]. In contrast, the onset temperatures of weight loss in several earlier findings were comparable to those of pure PCMs. This can be attributed by the linked pores of MWCNT's absorption ability on ESE, which includes intermolecular and capillary forces. The

findings showed that the as-prepared SSPCM composites had better thermal stability and could efficiently prevent seepage.

8.2.4. FTIR Analysis of the ESE/MWCNT Composites

The spectra of SS-EM@3, SS-EM@5, SS-EM@7 and SS-EM@9 showed five prominent peaks that indicated the existence of ESE [Figure 8.4 (a)]. The peaks found at 2957, 2912, and 2846 cm^{-1} are attributed to the C-H stretching vibration of methyl and methylene groups. The bending vibration of C-H is responsible for the peak at 1465 cm^{-1} . The 716 cm^{-1} absorption band corresponds to the ESE molecule's in-plane deformation rocking vibration [206]. The absorption peaks at 2976 cm^{-1} and 2897 cm^{-1} corresponded to the C-H stretching vibrations. Additionally, an absorption peak about 1613 cm^{-1} was observed in the MWCNT spectrum, which was attributed to the stretching vibration of C=C bonds. At around 1100-1200 cm^{-1} , the bonds corresponding to the C-C stretching of the MWCNT structure were observed [277]. The SS-EM@3, SS-EM@5, SS-EM@7, and SS-EM@9 only showed a combination of peaks analogous to the ESE and MWCNTs, and the addition of MWCNTs to the ESE did not produce any new peaks.

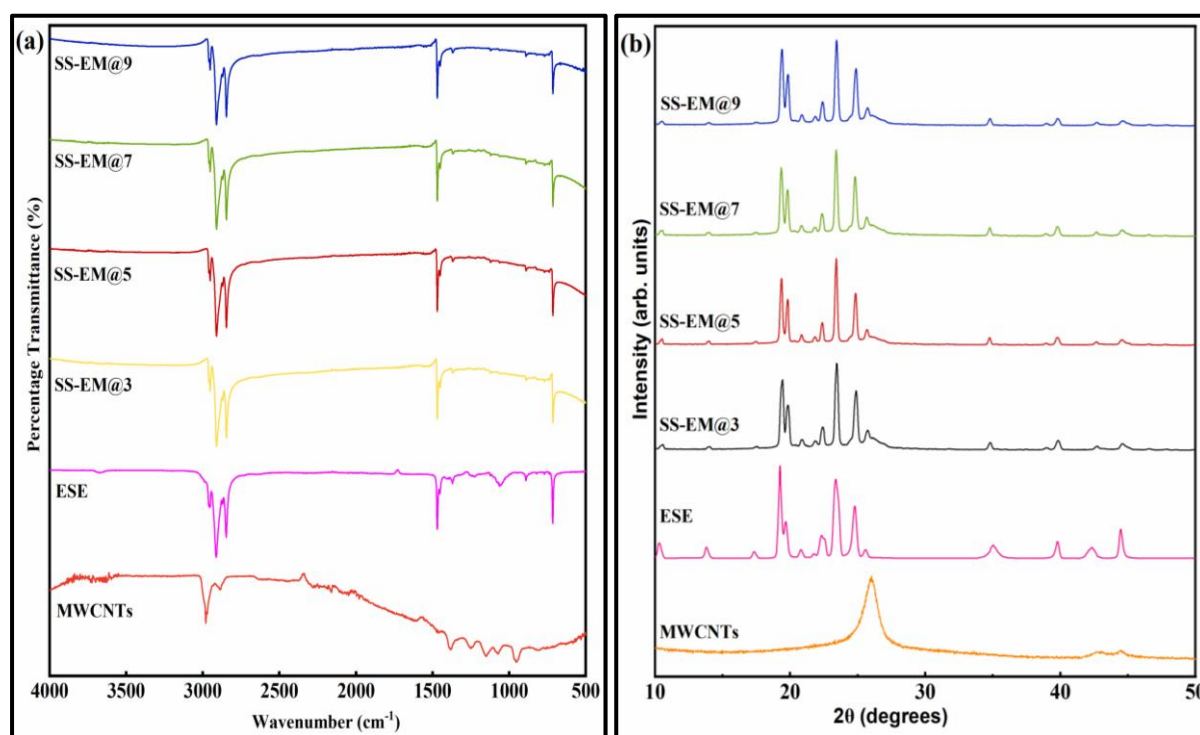


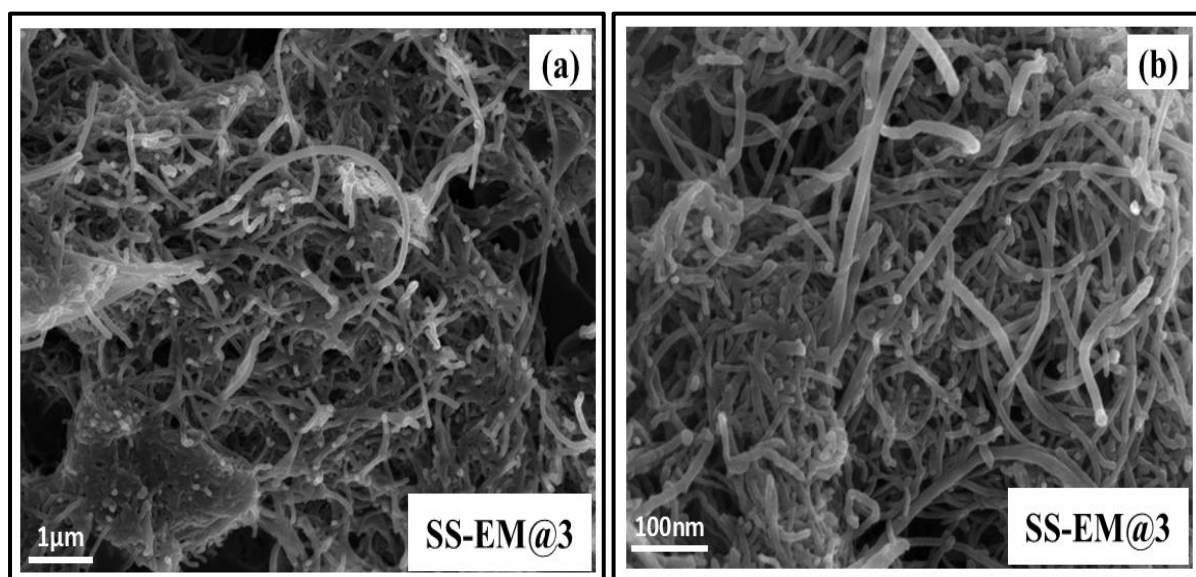
Figure 8.4: (a) FTIR spectra and (b) PXRD patterns of the ESE/MWCNT composites

8.2.5. PXRD Analysis of the ESE/MWCNT Composites

Figure 8.4 (b) shows the XRD patterns of MWCNTs, ESE, and ESE/MWCNT SSPCMs. The characteristic peak in MWCNTs is located at 26° , which corresponds to the graphitic structure's (002) diffraction [272]. Three notable distinctive peaks for pure ESE are found at 19.3° , 23.5° , and 24.8° [261]. Furthermore, the prepared SSPCMs displayed those unique ESE peaks. According to the XRD investigation, the diffraction peaks of MWCNTs and ESE overlap, demonstrating that both components contribute to the same diffraction regions.

8.2.6. Morphology of the Synthesized ESE/MWCNT Composites

Figure 8.5 shows the FE-SEM images of ESE/MWCNT shape-stabilized composites with 3, 5, 7, and 9 wt% MWCNTs, revealing a steady change in microstructure as the nanotube content increases. At 3 wt% of CNTs, the open gaps that were initially present in the entangled MWCNTs network are clearly reduced, and individual nanotubes and tiny bundles are consistently embedded within the smooth paraffin-rich regions.



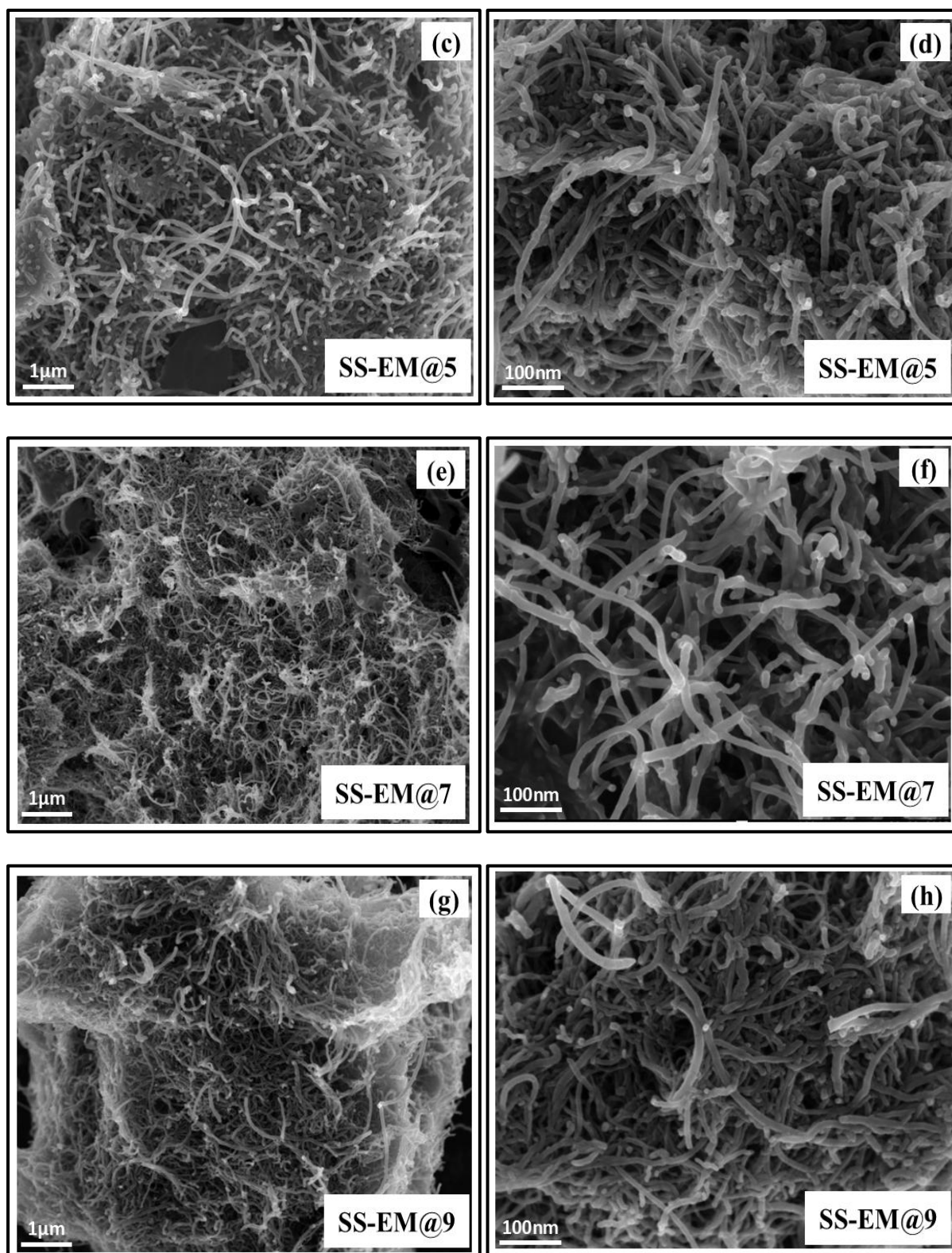


Figure 8.5: FE-SEM images of ESE/MWCNT composites at different magnifications produced by varying the mass fraction of MWCNTs

This suggests that ESE has effectively infiltrated into the interstitial voids. With 5 wt% MWCNTs, web-like CNTs framework and more interconnected network is formed, while the ESE phase more thoroughly occupies the spaces between the entangled nanotubes, resulting in a denser surface and increased structural strength. The morphology becomes CNT-dominated at 7 wt%, with a well-developed 3-D nanotube skeleton where ESE is primarily bound across small gaps and along the CNT surfaces. This efficiently suppresses leakage and minimizes free ESE domains. A highly entangled network with locally agglomerated CNT regions is seen when the MWCNTs content reaches 9 wt%. ESE is primarily present as a thin, continuous phase that fills micro-voids and coats CNT bundles, confirming its successful confinement within the carbon framework and contributing to the composite's exceptional shape stability [278], [279].

8.2.7. Thermal Reliability of the ESE/MWCNT Composite

It is critical that SSPCMs maintain their excellent thermal resilience even after repeated thermal cycling. Thermal cycling test on SS-EM@9 is performed to confirm the reliability of SSPCM due to its high loading ratio and efficiency. The temperature range for the thermal cycling test is 0 °C to 60 °C. The DSC thermogram of SS-EM@9 after 50 heating and crystallizing cycles are displayed in **Figure 8.6**, and **Table 8.4** provides comprehensive data. The latent heat slightly decreases from the initial 215.32 J.g⁻¹ to 214.52 J.g⁻¹ after 50 thermal cycles, whereas the SSPCM's melting and crystallization temperatures barely change. These findings demonstrate that SSPCMs impregnated into the MWCNTs supporting material are highly reliable, suggesting that they are appropriate for long-term recycling applications.

Table 8.4: DSC data of SS-EM@9 after 50 thermal cycles

No. of cycles	T _m (°C)	ΔH _m (J.g ⁻¹)	T _c (°C)	ΔH _c (J.g ⁻¹)
0	37.86	215.32	26.81	212.71
50	37.80	214.52	26.79	211.96

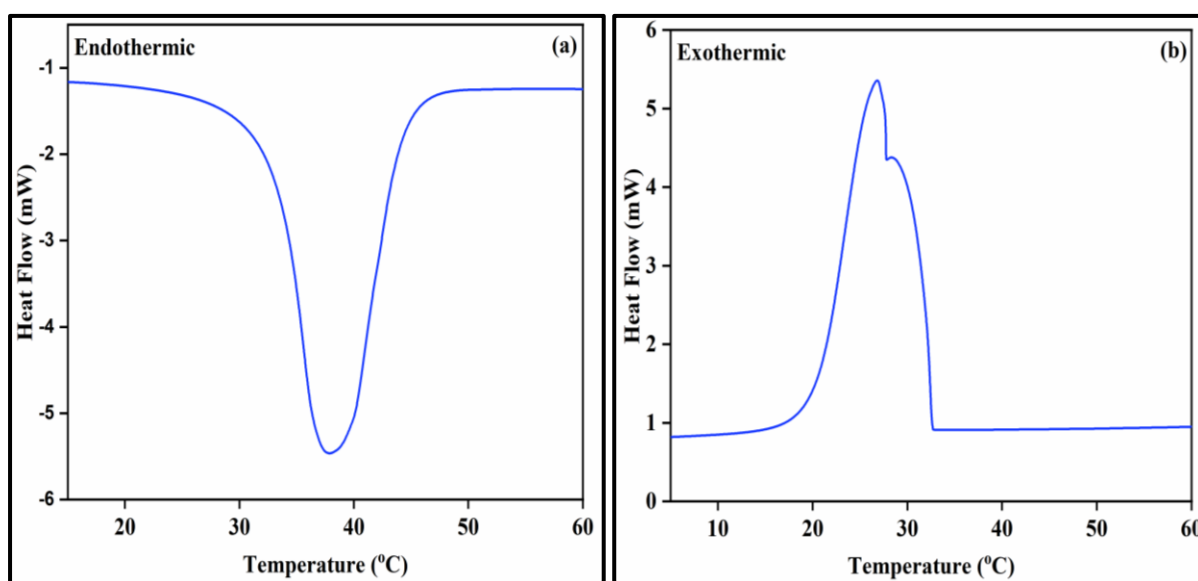


Figure 8.6: DSC thermogram of SS-EM@9 at 50th cycle of heating and cooling

8.3. Significant Findings

The development of SSPCMs, as outlined in Objective 5, was investigated using ESE/MWCNT composites with varying MWCNT mass fractions. The composites were prepared by the vacuum impregnation method. The thermal performance, thermal stability, morphology and chemical compatibility of the prepared shape-stabilized ESE/MWCNT composites were investigated in detail. The PCMs can be successfully absorbed by MWCNTs in a maximum fraction of 9 wt % with the leakage of 29.9%. DSC analysis was used to reveal that the melting and crystallization temperature along with their corresponding latent heat of ESE/MWCNT composites, which were increased with increasing the mass fraction of MWCNTs. The composite prepared with 3 wt% MWCNTs decreases the heat capacity compared to the pure PCM. The SS-EM@3 composite exhibited the melting and crystallization temperature of 37.0 °C and 26.9 °C, with corresponding latent heat of 186.3 J.g⁻¹ and 184.8 J.g⁻¹, respectively. On the contrary, the SSPCMs with 9 wt% reflects the highest rise in the enthalpies i.e. 215.3 (ΔH_m) and 212.7 J.g⁻¹ (ΔH_c). DSC results of SS-EM@9 showed excellent loading ratio and heat storage efficiency of 89.8 and 89.6%, respectively. Thereby, the inclusion of MWCNTs significantly improves the heat transfer rate of the ESE/MWCNT composites. TGA analysis elucidated that the addition of MWCNTs to ESE enhanced its thermal stability. The FTIR results showed that adding MWCNTs to ESE did not form any new peaks, and the

prepared composites only displayed a combination of peaks corresponding to the PCMs and the supporting material MWCNTs, such that a physical combination can be intuitively expected. The FE-SEM analysis confirmed that highly entangled network with locally agglomerated CNT regions is seen when the MWCNTs content reaches 9 wt%. After 50 thermal cycles, the latent heat of SS-EM@9 dropped marginally from 215.32 J.g⁻¹ to 214.52 J.g⁻¹. Therefore, ESE/MWCNT composites can be promising PCM candidate used in waste heat recovery, building temperature regulation, solar energy storage and electronics cooling due to their excellent thermal performance with high latent heat, good thermal stability and suitable chemical compatibility.

CHAPTER 9

CONCLUSIONS, FUTURE SCOPE AND SOCIAL IMPACT

CHAPTER 9

CONCLUSIONS, FUTURE SCOPE AND SOCIAL IMPACT

9.1. Conclusions

The escalating global energy demand, coupled with environmental concerns and the pressing need for efficient energy utilization, has driven the development of sustainable and efficient TES technologies. Among the available TES approaches, PCMs are particularly promising for LHS owing to their ability to store and release considerable amounts of thermal energy during phase transition. However, the practical utilization of paraffin-based PCMs is limited by several inherent drawbacks, including leakage during melting, poor structural integrity, relatively low thermal conductivity, and inadequate heat-transfer characteristics. In view of these limitations, the present research was undertaken to develop structurally stable and thermally reliable PCM systems through appropriate material design and modification strategies.

ESE was selected as the PCM owing to its suitable phase transition temperature, high LHS capacity, chemical stability, and cost effectiveness. To overcome the limitations associated with its direct utilization, different material-engineering strategies were investigated, including polymeric microencapsulation, nanoencapsulation, optimization of synthesis parameters, functional filler incorporation, and shape stabilization. These strategies were investigated with the objective of controlling the structural characteristics of ESE-based PCM systems while improving their thermal reliability and functional performance.

The first objective focused on the fabrication and evaluation of MPCMs for LHTES. ESE/Poly(St-co-BA) microcapsules were successfully synthesized through mini-emulsion polymerization, with ESE confined within a Poly(St-co-BA) polymeric shell. The incorporation of BA provided flexibility to the shell and contributed to improved structural integrity, while encapsulation effectively confined the PCM and reduced leakage during phase transition.

The second objective involved the design and performance evaluation of NPCMs. ESE/Poly(SMA-co-BA) nanocapsules were successfully developed using the mini-emulsion polymerization technique. The nanoscale encapsulation resulted in reduced particle dimensions and increased interfacial characteristics, demonstrating the potential of nanoencapsulation for developing PCM systems with improved dispersion and thermal responsiveness.

The third objective addressed the investigation and optimization of synthesis parameters for the development of EPCM systems. The effect of DVB cross-linker concentration on the characteristics and thermal behavior of ESE/Poly(St-co-BA) microcapsules was systematically examined. Optimization of the cross-linking conditions enabled control over the structural and thermal characteristics of the microcapsules and resulted in improved thermal reliability and cycling stability.

The fourth objective concerned the incorporation of suitable functional fillers into the developed PCM systems. ZnATH-(O) and FeATH-(O) NPs were incorporated into ESE-based MPCM systems to modify their functional and thermal characteristics. The results demonstrated that the nature and loading of the incorporated NPs influenced the overall performance of the resulting MPCMs.

The fifth objective focused on the development of SSPCMs with emphasis on structural stability and thermal performance. ESE/MWCNT composites containing different MWCNT mass fractions were prepared by the vacuum impregnation method. The MWCNT framework effectively restricted the mobility of molten ESE and provided structural stabilization to the composite PCM, demonstrating an alternative approach for addressing the leakage associated with conventional PCMs.

9.2. Comparative Assessment of the Developed PCM Systems

The developed PCM systems were subjected to a comparative assessment to evaluate the influence of different material-engineering strategies on their structural, encapsulation, and thermal characteristics. The key experimental parameters and corresponding numerical values obtained for the different PCM systems are compiled in **Table 9.1**.

Table 9.1: Comparative assessment of the developed ESE-based PCM systems

	ESE	ESE/Poly(S t-co-BA)	ESE/Poly(S MA-co-BA)	DVB- crosslinked MPCMs	Zn-ATH(O) NPs doped MPCM (Z7)	Fe-ATH(O) NPs doped MPCM (F5)	ESE/M WCNT SSPCM (SS- EM@9)
T_{0m} (°C)	35.5	35.7	32.6	35.0 (EPD0.5) 35.7 (EPD5)	26.4	35.5	-

T_{pm} (°C)	38.9	38.9	37.4	38.2 (EPD0.5) 39.4 (EPD5)	38.7	39.5	37.9
T_{em} (°C)	40.1	40.1	38.6	39.8 (EPD0.5) 42.6 (EPD5)	46.5	42.1	-
ΔH_m (J.g⁻¹)	239.9	220.5	224.6	104.4 (EPD0.5) 170.5 (EPD5)	186.8	226.2	215.3
T_{oc} (°C)	30.9	32.3	27.9	32.5 (EPD0.5) 34.4 (EPD5)	34.3	33.1	-
T_{pc} (°C)	30.5	31.1	25.1	30.9 (EPD0.5) 30.6 (EPD5)	31.1	30.5	26.8
T_{ec} (°C)	29.6	30.1	20.0	29.5 (EPD0.5) 27.4 (EPD5)	20.8	28.4	-
ΔH_c (J.g⁻¹)	237.7	218.6	191.7	98.6 (EPD0.5) 155.6 (EPD5)	185.0	212.4	212.7
E_R (%)	-	91.9	93.6	43.5 (EPD0.5) 62.4 (EPD5)	77.9	94.3	89.8
E_E (%)	-	91.6	87.2	42.5 (EPD0.5) 68.3 (EPD5)	77.8	91.8	89.6
C_{es} (%)	-	99.6	93.1	97.7 (EPD0.5) 96.1 (EPD5)	99.9	97.3	99.8
Thermal Stability (°C)	One step degradation (75)	Two step degradation (1 st : 151; 2 nd : 279)	Two step degradation (1 st : 165; 2 nd : 299)	Two step degradation	Two step degradation (1 st : 143; 2 nd : 335)	Two step degradation (1 st : 127; 2 nd : 291)	One step degradation on (153)

The investigations demonstrate that the performance of ESE-based PCM systems can be effectively tailored through control of material architecture, composition, synthesis conditions, and stabilization strategy. The five approaches investigated in this work—microencapsulation, nanoencapsulation, optimization of cross-linking conditions, functional filler incorporation, and shape stabilization—provided distinct routes for addressing the limitations associated with the direct utilization of ESE.

The present study therefore establishes a systematic materials-engineering framework for the development of EPCM and SSPCM systems for LHTES. The successful synthesis and evaluation of these materials demonstrate the importance of rational structural design in achieving improved PCM stability and performance. The findings obtained from the present investigation provide a scientific basis for the development of reliable and functionally enhanced PCM systems with potential applications in TES and thermal management.

9.3. Future Prospects

The synthesized EPCMs displayed remarkable TES efficiency and stability, indicating a high potential for the practical applications. These materials can be implemented effectively into a variety of application areas, where the temperature regulation is crucial. For instance, in the construction and building sector, these PCMs can be integrated into concrete composites, wall panels, insulation boards and plaster materials, in order to regulate the fluctuations of the indoor temperature and lower the energy required for heating and cooling. In the sector of renewable energy, they can be installed in solar thermal systems to store excess heat throughout the day and release it during non-sunlight hours, hence optimizing the total energy efficiency.

Additionally, these materials may also be employed in electronic device thermal management, where efficient heat dissipation is necessary to sustain steady operating temperatures and enhance device's lifespan. Temperature-controlled cold chain transportation and packaging are other intriguing applications, notably for medical supplies, pharmaceuticals and food products that require regulated thermal conditions during storage and transportation.

Emerging applications like wearable thermal regulation systems offer substantial prospects beyond these conventional domains. PCMs can be incorporated into wearable items or smart textiles to help and maintain appropriate body temperatures. They can also help in management of stress and anxiety-related illnesses, where controlled cooling or thermal comfort can offer physiological relief. These applications demonstrate PCM-based systems' adaptability in enhancing technological and human-centered solutions.

Future research can improve the performance and applicability of these materials through more extensive characterization and material design methodologies. It will be crucial to conduct long-term thermal cycling tests with numerous heating-cooling cycles in order to assess the reliability durability under feasible operating conditions. Furthermore, the fabrication of double-shell encapsulation systems may result in the increased both mechanical strength and thermal stability. Investigating eutectic blends of organic and inorganic PCMs is another crucial avenue for the future, especially in terms of extending thermal storage to higher temperature ranges while reducing typical drawbacks related to inorganic PCMs.

Currently, a significant amount of research in India is devoted to the synthesis and laboratory-scale development of sophisticated PCM materials. However, bridging the gap between the

material development and practical execution is frequently neglected. Many research institutions around the world emphasize on application-oriented studies, including system integration, prototype creation, and performance assessment in real-world scenarios. In order to effectively transfer the synthesized materials into practical technologies and large-scale energy solutions, future effort should concentrate on fortifying this link between material innovation and practical deployment.

9.4. Social Impact

The emergence of smart PCMs for TES has the potential to greatly enhance the quality of life and promote sustainable energy use. These materials can aid in the global shift toward cleaner and more sustainable energy systems by facilitating the effective storage and regulated release of thermal energy, hence reducing the reliance on traditional fossil fuels.

The produced MPCMs, NPCMs and SSPCMs shows immense potential for applications like wearable thermal regulation systems, renewable energy storage, electronic thermal management, energy-efficient buildings and temperature-controlled transportation. These applications can increase energy efficiency, lower energy consumption, and improve thermal comfort in everyday life.

From a broader perspective, the production and implementation of such materials actively promote a number of Sustainable Development Goals (SDGs), especially SDG 7 (Affordable and Clean Energy) through enhanced energy storage technologies, SDG 11 (Sustainable Cities and Communities) by encouraging energy-efficient infrastructure, and SDG 13 (Climate Action) by fostering lowered energy demand and carbon emissions. Therefore, developing PCM-based TES materials can be crucial to attaining sustainable technical and social advancement.

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LIST OF PUBLICATIONS, CONFERENCES, WORKSHOPS AND SEMINARS

Publications from the Thesis

1. **Gunjan Varshney**, Raminder Kaur and Mohammad Zulfequar (2024) “Fabrication and Evaluation of Eicosane/Poly(Styrene-co-Butylacrylate) Microencapsulated Phase Change Materials through Ultrasonicated Mini-Emulsion Technique”, *Chemical Engineering Journal*, 500,156994, DOI: <https://doi.org/10.1016/j.cej.2024.156994> (I.F.=13.3) (SCIE indexed) (Elsevier)
2. **Gunjan Varshney**, Pooja Singh, Sarla Yadav, Raminder Kaur (2024) “A Review on Unleashing the Potential Solution of Thermal Comfort: Exploring the Cutting-edge Progress of Advanced Engineering Application of Phase Change Materials Integrated Textiles”, *Sustainable Energy Technologies and Assessments*, 72, 104089, DOI: <https://doi.org/10.1016/j.seta.2024.104089> (I.F.=7.1) (SCI indexed) (Elsevier)
3. **Gunjan Varshney**, Raminder Kaur, Mohammad Zulfequar (2025), “Fabrication and assessment of n-eicosane/poly(stearylmethacrylate-co-butylacrylate) nanocapsules: impact of long alkyl polymer chains on thermal performance and stability”, *Nanoscale*, 17(46), 26923-26934, DOI: 10.1039/D5NR04183J (I.F.=5.1) (SCIE indexed) (RSC)
4. **Gunjan Varshney**, Sarla Yadav, Raminder Kaur, Mohammad Zulfequar (2026), “Fabrication of ZnATH-(O) NPs-Integrated Microencapsulated Phase Change Materials (MEPCMs) for Improved Heat Storage Capacity”, *Materials Research Bulletin*, 195, 113884, DOI: <https://doi.org/10.1016/j.materresbull.2025.113884> (I.F.=5.7) (SCIE indexed) (Elsevier)
5. **Gunjan Varshney**, Raminder Kaur, Mohammad Zulfequar (2026), “Tailoring Thermal Properties and Structural Integrity of n-Eicosane/Poly(Styrene-co-Butylacrylate) Microcapsules with Divinylbenzene Cross-Linker”, *Materials Chemistry and Physics*, 359, 132549, DOI: <https://doi.org/10.1016/j.matchemphys.2026.132549> (I.F.= 4.7) (SCIE indexed) (Elsevier)

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6. **Gunjan Varshney**, Sarla Yadav, Raminder Kaur, Mohammad Zulfequar, “Synergistic Effects of FeACy-(O) NPs on the Thermal Performance of Microencapsulated Phase Change Materials (MEPCMs)”, *Fuels* (I.F.=7.5) (SCIE) (Elsevier) (under review)
 7. **Gunjan Varshney**, Shikha Jain, Raminder Kaur, Mohammad Zulfequar, “Preparation and valuation of MWCNT-Mediated Shape-Stabilized Phase Change Materials for High-Efficiency Thermal Energy Storage Applications”, *Journal of Energy Storage* (I.F.=9.8) (SCIE) (Elsevier) (under review)

Additional Publications

1. Raminder Kaur, Pooja Singh, Surya Tanwar, **Gunjan Varshney** and Sarla Yadav (2022), “Assessment of Bio-Based Polyurethanes: Perspective on Applications and Bio-Degradation”, *Macromol*, 2, 284–314, DOI: <https://doi.org/10.3390/macromol2030019> (I.F.= 4.4) (Scopus Indexed) (MDPI)
2. Pooja Singh, **Gunjan Varshney** and Raminder Kaur (2024), “Primary Microplastics in the Ecosystem: Ecological Effects, Risks, and Comprehensive Perspectives on Toxicology and Detection Methods”, *Journal of Environmental Science and Health, Part C*, 42(4),314–365, DOI: <https://doi.org/10.1080/26896583.2024.2370715> (I.F.= 2.5) (SCI indexed) (Taylor and Francis)
3. Sarla Yadav, Pooja Singh, **Gunjan Varshney**, Saurabh, Poonam Singh, Raminder Kaur (2025) “Photocatalytic degradation of crystal violet dye using phytofabricated zinc oxide nanoparticles from anthocyanin extract”, *Microchemical Journal*, 213, 113681, DOI: <https://doi.org/10.1016/j.microc.2025.113681> (I.F.= 5.1) (SCIE indexed) (Elsevier)
4. Surya Tanwar, **Gunjan Varshney**, and Raminder Kaur (2025), “Fatty acid filled polyaniline nanofibres with dual electrical conductivity and thermo-regulatory characteristics: Futuristic material for thermal energy storage”, *e-Polymers*, 25(1), 20250003, DOI: <https://doi.org/10.1515/epoly-2025-0003>.e-polymer.2025 (I.F.= 3.2) (SCIE indexed) (De Gruyter)
5. Pooja Singh, Manpreet Kour, **Gunjan Varshney** and Raminder Kaur (2025), “Non-isocyanate polyurethane (NIPU) Foams: Overcoming challenges and embracing sustainability”, *Polymer*, 333, 128658, DOI: <https://doi.org/10.1016/j.polymer.2025.128658> (I.F.= 4.5) (SCIE indexed) (Elsevier)

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6. **Gunjan Varshney**, Sarla Yadav, Monika Duhan, Devvrat Tiwari, Raminder Kaur (2026), "Polyaniline Nanofibers as a Sustainable Adsorbent for Cr (VI) and Hg (II) Ions Detoxification", *Chemistry Select*, 11(5), e03770, DOI: <https://doi.org/10.1002/slct.202503770> (I.F.= 2) (SCIE indexed) (Wiley)
 7. Saurabh, Sarla Yadav, **Gunjan Varshney**, Pooja Singh, Raminder Kaur, "Potential Impacts of Renewable Energy for Next Generation Materials Challenges via Green Chemistry Approaches" (under Revision)
 8. Saurabh, Pooja Singh, Sarla Yadav, **Gunjan Varshney**, Raminder Kaur, "Environment-Friendly pH-Sensitive Intelligent Film for detecting spoilage in Beverages" (under Revision)

Book Chapters

1. Pooja Singh, **Gunjan Varshney** and Raminder Kaur (2024), Arsenic Contamination in Drinking Water and Health, Chapter 3, Arsenic Toxicity Remediation: Sustainable Nexus Approach. Emerging Contaminants and Associated Treatment Technologies, 125-142, Part-II (Health Risks Linked to Arsenic Exposure in Food and the Environment), ISBN 978-3-031-52614-5, ISSN 2524-6410, Springer Cham, DOI: https://doi.org/10.1007/978-3-031-52614-5_7
2. Sarla Yadav, **Gunjan Varshney**, Manisha Yadav, Raminder Kaur (2025), Geochemical Characterization and Assessment of Fluoride Sources in Groundwater, Chapter 1, Fluorides in Drinking Water: Source, Issue, and Mitigation Strategies. Environmental Science and Engineering, 3-34, Part- I (Sources and Distribution of Fluoride in Water Ecosystem), ISBN 978-3-031-77247-4, ISSN 1863-5539, Springer, DOI: https://doi.org/10.1007/978-3-031-77247-4_1
3. Sarla Yadav, **Gunjan Varshney**, Pooja Yadav, Riya Malik, Raminder Kaur (2025), Biotribology of articular cartilage, Chapter 5, Biotribology: Friction, Wear and Lubrication in Biological Systems. Green Tribology and Tribochemistry, 121-146, eBook ISBN: 9783111563176; Hardcover ISBN: 9783111562940, De Gruyter, DOI: <https://doi.org/10.1515/9783111563176-005>.
4. Sarla Yadav, **Gunjan Varshney**, Raminder Kaur, Microbial Biofilm as Natural Pesticides in Crop Protection, Chapter 6, Microbial Biofilm Engineering: Harnessing Microbial Power for Agriculture, Environment, and Industry (accepted)

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5. Sarla Yadav, **Gunjan Varshney**, Pooja Yadav, Riya Malik, Raminder Kaur, Combinations of various thermo-chemical and biochemical processes for various biomass feedstock also in combination with other traditional and existing biomass conversion routes, Chapter 4, Biohydrogen from Organic Material: Options, solutions, and their assessment (**accepted**)
 6. **Gunjan Varshney**, Pooja Singh, Raminder Kaur, Oleaginous Yeasts: Single Cell Oil from Lignocellulosic Biomass as a Feedstock for Biofuels, Chapter 6, Advances in Fermentation Technology and their Practical Implications (**accepted**)

Conferences

1. **Gunjan Varshney** and Raminder Kaur, (2022), **Poster Presentation** on title: “Encapsulation of Phase Change Material (PCM) for thermal energy storage system”, International Conference on Emerging Trends in Biotechnology and Sustainable Chemistry: (ETBSC-2022), organized by Baba Farid College, Bathinda in collaboration with Central University of Punjab, Bathinda, India, April, 27-29, 2022.
2. **Gunjan Varshney**, Raminder Kaur and Manish Jain (2022), **Poster Presentation** on title: “Advancement in Phase Change Materials for Thermal energy storage applications: An Overview” 2nd Indian Analytical Congress (2nd IAC-2022), jointly organised by Indian Society of Analytical Scientists Delhi Chapter (ISAS-DC), Graphic Era University, and CSIR Indian Institute of Petroleum, Dehradun, Uttarakhand, India, May, 26-28, 2022.
3. **Gunjan Varshney** and Raminder Kaur (2022), **Poster Presentation** on title: “An Overview of Recent Developments in Phase Change Materials for Thermal Energy Storage Applications”, 2nd International Conference on Green and Sustainable Chemistry Conference (GSCC-2022), organised by Manav Rachna University, Faridabad, Sponsored by Science and Engineering Research Board (SERB)- Department of Science and Technology India, NHPC Faridabad and DRDO India, November 17-19, 2022.
4. **Gunjan Varshney**, Raminder Kaur (2022), participated in the International Conference on “Nanotechnology: Opportunities & Challenges (ICNOC-2022)”, organized by Department of Applied Sciences & Humanities, Faculty of Engineering & Technology, Jamia Millia Islamia University, New Delhi, India, November, 28–30, 2022.
5. **Gunjan Varshney** and Raminder Kaur (2023), **Oral Presentation** on title: “Recent Advancements in Phase Change Materials and their Utility”, International Conference on

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- “Chemical & Allied Science and their Applications, organized by Delhi Technological University, New-Delhi, India, January 20, 2023.
6. **Gunjan Varshney**, Mohammad Zulfequar and Raminder Kaur (2024), **Oral Presentation** on title: “Cutting-Edge Approach for Latent Heat Storage: Fabrication of Organic Phase Change Materials with Polymer Shells” International Conference on Emerging Techno-Economic Development for Sustainable Environment (ETDSE-2024) organized by IPS Academy Institute of Engineering & Science, Indore, Madhya Pradesh, India, January, 12-13, 2024.
 7. **Gunjan Varshney**, Mohammad Zulfequar and Raminder Kaur (2024), **Oral Presentation** on the title: “Fabrication and Assessment of eicosane/poly(styrene-co-butylacrylate) microencapsulated phase change materials using an ultrasonicated mini-emulsion approach”, International Conference on Current Environmental Technologies for Sustainable Development (ICCETSD2024), organized by the Department of Environmental Science, Graphic Era (Deemed to be University), Dehradun, Uttarakhand, India, December 9-10, 2024.
 8. **Gunjan Varshney**, Mohammad Zulfequar and Raminder Kaur (2024), **Oral Presentation** on the title: “Production and assessment of eicosane/poly(styrene-co-butylacrylate) microencapsulated phase change materials using ultrasonicated mini-emulsion method”, National Conference on Indian Knowledge System: Traditional to Modern Nanotechnology jointly organized by the Special Centre for Nano Science, JNU, School of Biotechnology, JNU and Department of Chemistry, Gurukula Kangri Deemed University, New Delhi, India, December 13, 2024. **Awarded by Best Oral Presentation.**
 9. **Gunjan Varshney**, Mohammad Zulfequar and Raminder Kaur (2025), **Poster Presentation** on the title: “High-Performance Eicosane Microcapsules with Poly(Styrene-co-Butylacrylate) Shell via Ultrasonic Mini-Emulsion for Thermal Energy Storage” International Conference on Chemistry for Sustainability (ICCS-2025) organized by the Chemistry in association with the Greenko School of Sustainability, Indian Institute of Technology, Hyderabad, India, July 13-16, 2025.

Workshops Attended

1. Short-Term Program on Bio-Privileged and Sustainable Chemistry, conducted by the Department of Chemistry, Manav Rachna University, Faridabad, from 17th – 21st January 2022.
2. Five-Day Skill Enhancement Workshop on Beyond Industry 4.0: Energy and Environment, organized by University School of Chemical Technology, Guru Gobind Singh Indraprastha University, New Delhi, from 25th – 29th July 2022.
3. IP Awareness/Training Program under National Intellectual Property Awareness Mission (NIPAM), organized by the Intellectual Property Office, Government of India, held on 30th November 2022.
4. Three-Day INUP-i2i 6th User Awareness Workshop on Fabrication and Characterization Facility for Nanotechnology, organized by the Indian Institute of Technology Delhi (IIT Delhi), from 4th – 5th March 2023.
5. Two-Day Hands-On Training Workshop on Thermal Analyses (DSC/TGA/ITC), conducted by the University Science Instrumentation Center (USIC), University of Delhi, on 11th – 12th November 2024.
6. Workshop on Samerpan: Sustainable Action & Mobility for Emission Reduction & Promoting Awareness Nationwide, organized by the Department of Environmental Engineering, Delhi Technological University in collaboration with Alfatech Services, on 26th November 2024.
7. School on Microscopic Characterization Techniques (TEM/SEM/AFM), organized by Inter-University Accelerator Center (IUAC), New Delhi, from 9th – 12th December 2024.
8. Two-Day Workshop on Structural Analysis (XRD, Rietveld Refinement, HRTEM & SAED), organized by the Centre for Nanoscience and Nanotechnology, International Research Centre & Advanced Characterization Facility, Sathyabama Institute of Science and Technology, Chennai, during 24th – 25th February 2025.
9. Five-Day International Workshop on Sophisticated Instrumentation Techniques, organized by the Department of Chemistry, School of Advanced Sciences (SAS), VIT-AP University in association with the Institute of Physical Sciences (ICF), National Autonomous University of Mexico (UNAM), held from 17th – 21st March 2025.

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10. Training Workshop on Safety from Hazards: Fire, Chemical and Biological and Natural Disasters, organized by Shriram Institute for Industrial Research, Delhi, India held on 11th June 2025.

Seminars Attended

1. One-Day Industry-Academia Seminar on “Petrochemicals in Today’s World”, organized by the Department of Applied Chemistry in association with Just Polymer Solutions and PLUSS Advanced Technologies, held on 21st April 2023.
2. Webinar on “Higher Study Opportunities & Latest Research in Portable Sensor, Bio-Chip, Metal Catalysis, Atomic & Electronic Structure”, organized by National Sun Yat-Sen University (NSYSU) & EduCare Taiwan, on 9th June 2023.
3. Webinar on “Breaking Barriers: Addressing Gender Gaps in STEM Education, Careers, and Research”, organized by the Department of Biotechnology, Delhi Technological University, held on 11th February 2025.

Publications from the Thesis

Chemical Engineering Journal 500 (2024) 156994



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Fabrication and evaluation of eicosane/poly(styrene-co-butylacrylate) microencapsulated phase change materials through ultrasonicated mini-emulsion technique

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Microencapsulation
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 n-ESE
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ABSTRACT

This study reports the synthesis and characterization of Microencapsulated Phase Change Materials for the pertinence of latent heat storage. Eicosane/ Poly(Styrene-co-Butylacrylate) [ESE/Poly(Sty-co-BA)] microcapsules were synthesized by encapsulating n-Eicosane (n-ESE) with a shell made of Poly(Styrene-co-Butylacrylate) [Poly(Sty-co-BA)] via employing ultrasonic-assistant mini-emulsion polymerization technique. The properties of the synthesized ESE/Poly(Sty-co-BA) microcapsules were analyzed by Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), Transmission electron microscopy (TEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy. DSC results indicated that ESE/Poly(Sty-co-BA) exhibited a melting and crystallizing temperature of 35.72 and 32.27 °C, and latent heat of 220.53 and 218.57 J/g, respectively. The ESE/Poly(Sty-co-BA) microcapsules prepared in this work unveiled an effective encapsulation ratio (91.93 %), encapsulation efficiency (91.59 %) and displayed excellent thermal storage capacity (99.63 %). Various models such as Kissinger's, Augis and Bennett's approximation, Mahadevan and Arvami theory were employed to determine the effective activation energy value alongside the crystal growth of n-ESE and ESE/Poly(Sty-co-BA). TGA analysis revealed that ESE/Poly(Sty-co-BA) demonstrated three step degradation and exhibited good thermal stability. The findings of the work manifested a novel technique for producing the phase transition materials for TES that can be applied to a wide range of instances, including smart textiles, thermo-sensitized functional coatings, passive space cooling or heating.

1. Introduction

The rapid population growth and booming economies all over the world have contributed to a spike in the use of non-renewable energy sources like petroleum, natural gas, and coal. This has not only reduced the availability of these fossil fuels but also increased air pollution, global warming, and CO₂ emissions [1]. It has been proposed that enhancing energy efficiency and developing renewable energy sources would be an alternate course of action to reduce dependency on fossil fuels for energy production. The use of phase change materials (PCMs) in thermal energy storage (TES) has been scientifically developed as a means of storing latent heat and providing resilient energy management through controlled heat release in appropriate environments [2]. PCMs are a heat-storage materials that can change its state from a solid to a

liquid and vice-versa, by absorbing and releasing a significant quantity of latent heat energy at a constant temperature. PCMs have a greater TES density than traditional heat-storage materials, and they can minimise energy waste by bridging the gap between energy availability and usage [3].

Many traditional PCMs, such as fatty acid [4], fatty alcohol [5], paraffin [6], and polyethylene glycol [7] have been investigated and reported by researchers in the last few decades. Among these, paraffin is considered to be an excellent potential material for latent heat thermal energy storage (LHTES), which shows high latent heat storage (LHS), and high thermal stability [8]. The enhanced properties of these materials gaining more attention in both industrial and domestic areas; however, their phase transition poses certain challenges, such as low thermal conductivity-induced thermal hysteresis, absorption of

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Review article

A review on unleashing the potential solution of thermal comfort: Exploring the cutting-edge progress of advanced engineering application of phase change materials integrated textiles

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ARTICLE INFO

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Sustainable energy
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ABSTRACT

Conventional fabrics often fail to regulate temperature effectively, leading to discomfort for the wearer. Under fluctuating environmental conditions, the discomfort in textiles may pose a challenge, specially, in outdoor apparel; sportswear and healthcare. Phase Change Materials (PCMs), have emerged as a game-changer in textile engineering due to the pursuit of novel solutions in the realm of thermal comfort. Owing to their abilities of absorbing, storing, and releasing heat during phase transitions, PCMs provide a more controlled thermal environment. PCMs, considered as excellent contenders for thermal energy storage as they can store and release latent heat energy over a narrow temperature range and are available at various phase change transition temperatures. This review explores the integration of PCMs into textiles, known as PCMs incorporated textiles (PCMTs), which are designed to enhance thermal regulation in fabrics. The study reports a detailed classification of PCMs and textiles structures, along with an evaluation of incorporation techniques such as lamination, coating, and spinning. Analytical techniques like Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and mechanical property assessments are thoroughly reviewed to measure the effectiveness of PCMT. Additionally, a detailed analytical study has been conducted on the categorisation of PCMT according to PCM type, textile structure, and their potential to transform thermal comfort solutions across a range of applications. Furthermore, critical research gaps and future directions for optimising PCMT for enhanced durability, breathability, and thermal regulation across a wide range of applications have also been discussed.

Introduction

Overview of thermo-regulated fabrics

Traditional textiles often fail to provide adequate insulation or cooling across fluctuating temperatures, making the wearer uncomfortable. This challenge is especially prominent in outdoor gear, sportswear, and medical textiles, where temperature regulation can directly impact performance and well-being. Thermo-regulated fabrics address the critical issue of maintaining thermal comfort in dynamic environmental conditions. In this instance, the demand for temperature-regulating textiles has dynamically gained more attention. Additionally, the performance of such textiles has been improved and expanded in recent years through the innovation of functional textiles. A thermo-regulated textile, which adjusts its temperature based on external

conditions, is an example of an intelligent textile. The human body starts experiencing discomfort beyond $\pm 4.5^\circ\text{C}$ variation to its ideal temperature (35°C) [1]. Even though skin adjusts itself to the changes in the ambient temperature, the extreme swings can be fatal because they can result in horripilation, excessive sweating, nose secretions, and other symptoms that interfere with thermoregulation [2].

Phase Change Materials (PCMs) utilised in producing thermo-regulated textiles (either incorporated on the fabric's surface or encapsulated and integrated within it), can effectively enhance thermal comfort. The temperature difference between the body and the outer layer of clothing causes PCMs to change phase and release or absorb heat accordingly [3]. During the cooling phase, PCMs can release latent heat that they have absorbed and stored throughout the heating phase and offer adaptive heat management. The growing interest in PCMs-incorporated textiles (PCMTs) can be ascribed to the materials'

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Fabrication and assessment of *n*-eicosane/poly(stearylmethacrylate-co-butylacrylate) nanocapsules: impact of long alkyl polymer chains on thermal performance and stability

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The objective of this study is to develop, characterise, and analyse thermal energy storage (TES) properties of *n*-eicosane/poly(stearylmethacrylate-co-butylacrylate) [ESE/P(SMA-co-BA)], a novel nanoencapsulated phase change material (NPCM). The NPCMs were produced via mini-emulsion polymerisation of a polymer shell, poly(stearylmethacrylate-co-butylacrylate) [P(SMA-co-BA)], around *n*-eicosane [ESE], which served as the core material. The thermal behaviour and thermal stability of ESE/P(SMA-co-BA) were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). According to DSC results, ESE/P(SMA-co-BA) has melting and crystallisation temperatures of 37.4 °C and 25.1 °C and latent heat values of 224.6 J g⁻¹ and 191.7 J g⁻¹, respectively. The ESE/P(SMA-co-BA) nanocapsules exhibited an effective encapsulation efficiency (87.2%), encapsulation ratio (93.6%), and excellent thermal storage capacity (93.1%). The TGA study revealed the exceptionally good thermal stability of ESE/P(SMA-co-BA), with degradation in two stages. The chemical structure and crystallinity of the prepared ESE/P(SMA-co-BA) were verified using Fourier transform infrared (FTIR) spectroscopy and powder X-ray diffraction (PXRD) analysis. The results obtained from field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and polarized optical microscopy (POM) indicated that the synthesized ESE/P(SMA-co-BA) had a spherical morphology with a mean particle diameter of 195.3 nm, as determined by particle size distribution (PSD) analysis. This research highlighted a novel technique for fabricating phase transition materials for TES, which can be used in a variety of applications, including food storage containers, smart textiles, and building, medical and electronic materials.

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1. Introduction

Energy from various renewable sources, including solar, biomass, geothermal and tidal power, has garnered immense attention in recent years as a means of curbing environmental pollution and promoting sustainable development.^{1,2} Thermal energy accounts for about 60%–70% of global energy consumption, though it is quite challenging to convert it into mechanical work or electricity due to high entropy and significant losses. Excessive waste and intermittent thermal energy supply typically result in low energy utilisation efficiency and create a mismatch between supply and demand. Since the last

century, numerous thermal energy storage (TES) technologies have been developed to enhance utilisation efficiency and accomplish the requisite regulation of thermal energy.^{3,4} Latent heat storage based on phase change materials (PCMs) is one of the most actively explored TES technologies, owing to its operational simplicity as well as substantial energy storage density at constant temperature. PCMs are substances capable of storing and releasing thermal energy during the phase transition process within a specific temperature range. PCMs are becoming more prevalent in a variety of applications, including automotive battery energy management systems,⁵ thermal-regulated textiles,⁶ solar energy storage systems,⁷ industrial waste heat utilization⁸ and energy-efficient buildings.⁹ PCMs are divided into three categories based on their state aggregations: solid–solid, solid–liquid, and liquid–gas. Among these three categories, solid–liquid PCMs are the most promising for TES and thermal management due to their high energy storage capacity, isothermal behaviour, and minimal volume variation during phase transitions.¹⁰

The direct use of PCMs with solid-to-liquid phase transitions in TES systems is undesirable because of their

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Research Papers

Fabrication of ZnATH-(O) NPs -Integrated microencapsulated phase change materials (MEPCMs) for improved heat storage capacity

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ABSTRACT

A novel microencapsulated phase change materials (MEPCM) was synthesized via mini-emulsion polymerization technique by introducing zinc oxide (ZnO) nanoparticles (NPs) into the PCM matrix, and encapsulated within the polymer shell of poly(styrene-co-butylacrylate) (PS-co-PBA) crosslinked with Divinylbenzene. The nano ZnO dopant utilizes anthocyanin (ATH) extract derived from red cabbage that acts as reducing, capping and stabilizing agent which optimizes the thermal behavior and stability of the prepared MEPCM. A series of MEPCMs were prepared by mixing different weight percentage (wt%) of NPs. The thermal behavior, stability, reliability, microstructure and chemical composition of the resultant MEPCMs were investigated by Differential Scanning Calorimetry (DSC), Thermogravimetry Analysis (TGA), Infrared Thermography (IFT), Field Emission Scanning Electron Microscopy (FE-SEM), Fourier transform infrared (FT-IR) spectroscopy and Powder X-ray Diffraction (PXRD) respectively. From the DSC result, it was observed that the optimal microcapsule performance was achieved at a 1:1 core-to-shell ratio, with ZnATH-(O) NPs doped at 7 wt%, resulting in a maximum encapsulation ratio of 77.9 % and an encapsulation efficiency of 77.8 %. TGA analysis revealed that all the MEPCMs demonstrated two step deterioration and exhibited good thermal stability. FE-SEM images confirmed that the produced microcapsules exhibited spherical shape with a smooth surface, but as the wt% of NPs increases, agglomeration appears. The results highlighted that ZnATH-(O) NPs integrated MEPCMs have substantial potential as thermal energy storage materials for moderate-temperature applications within the temperature range of 30–40 °C.

1. Introduction

The expanding global energy demand, rising greenhouse gas emissions and depletion of fossil fuel reserves have highlighted the importance of effectively utilising renewable energy resources. Solar energy is one of the most potential substitutes among these. However, a major drawback of solar energy is that it is only available for short period of time, and rhythms of energy generation and consumption frequently diverge [1,2]. Thermal energy storage (TES), for both short- and long-term uses, has emerged as a feasible method to address the supply-demand imbalance. Phase change materials (PCMs) have received a lot of attention for TES applications due to their distinctive ability to absorb, store, and release enormous amount of latent heat

during phase transitions [3]. PCMs are categorised as solid-solid, solid-liquid, solid-gas, or liquid-gas based on the type of phase transition. The solid-liquid type is the most extensively used, owing to its large latent heat storage (LHS) capacity, consistent phase transition temperature, and stable performance over multiple cycles. Solid-liquid PCMs are widely classified into organic and inorganic materials [4,5].

Inorganic PCMs, which are predominantly made up of salts, metals, and alloys, have a high volumetric energy storage capacity but have downsides such as corrosiveness, significant volume changes, and probable phase separation [6]. Organic PCMs, on the other hand, such as fatty acids, paraffin wax (PW), and lipid derivatives, have several advantages, including non-corrosion, negligible supercooling, chemical stability, low cost and compatibility with a wide range of applications

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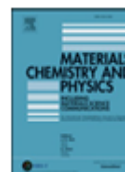
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Tailoring thermal properties and structural integrity of n-Eicosane/Poly(Styrene-co-Butylacrylate) microcapsules with divinylbenzene cross-linker

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HIGHLIGHTS

- Effect of DVB cross-linking agent on the thermal behavior of the microcapsules.
- DVB concentrations of 0.5%, 1%, 2%, 3%, and 5% were incorporated into the polymer shell.
- A 3-D polymer network was formed between the Poly(Styrene-co-Butylacrylate) shell and the DVB cross-linker.
- The incorporation of DVB significantly enhanced the thermal stability of the synthesized microcapsules.

ARTICLE INFO

Keywords:

Phase change materials
Microencapsulation
Mini-emulsion
Eicosane
Divinylbenzene

ABSTRACT

Crosslinkers play a vital role in defining the structural stability and thermal reliability of microencapsulated phase change materials (MPCMs). This study reports the microencapsulation of n-Eicosane as a PCMs using Poly (Styrene-co-Butylacrylate) as a shell by means of mini-emulsion polymerisation technique. The cross-linker, divinylbenzene (DVB), was employed at different concentrations to investigate its effect on the properties of the synthesized microcapsules such as thermal performance, thermal stability and morphology. The structural, morphological, thermal behaviour and thermal stability of the microcapsules was determined using Powder X-ray diffraction (PXRD), Fourier transform infrared spectrophotometry (FT-IR), Field emission scanning electron microscopy (FE-SEM), Differential scanning calorimetry (DSC) analysis, and Thermogravimetric analysis (TGA). FE-SEM images showed that the prepared microcapsules produce a smoother and more compact surface as incorporated the DVB with the ratio of 0.5 to 5%. DSC results indicated that enthalpy progressively rise as the cross-linker concentration increased by 5%, but above 5% substantial decrease in the enthalpy was observed. Thereby, the core percentage value ranged from 43.52 to 71.10%. TGA analysis revealed the two-step degradation of the produced microcapsules. By the incorporation of DVB, the weight loss percentage of the microcapsules improves as the temperature rise. After 50 thermal cycles, the latent heat of MPCMs remains stable, indicating high thermal reliability.

1. Introduction

The continuing rise in greenhouse gas emissions and associated environmental problems necessitates more efficient use of renewable energy [1,2]. The global transition toward renewable energy has become a major area of research. However, the development of sophisticated energy storage systems is equally important to provide a

steady and efficient energy supply. These technologies substantially enhance the performance and reliability of energy networks and mitigate the imbalance between supply and demand. Thermal energy storage (TES) for latent, sensible and thermochemical heat has garnered significant interest in the last few decades [3]. One potential method for TES is the use of phase change materials (PCM). Due to their superior capacity for reversible storage of thermal energy, PCMs have been

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Review

Assessment of Bio-Based Polyurethanes: Perspective on Applications and Bio-Degradation

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Abstract: Among numerous synthetic macromolecules, polyurethane in its different forms has proven its sheer dominance and established a reputation as a reliable and trusted material due to its proficiency in terms of superior properties, which include: high mechanical strength and abrasion resistance, good durability, good adhesion, good thermal stability, excellent chemical and weathering resistance. Synthetic polyurethane materials are non-biodegradable, poisonous, and use petrochemical-based raw materials, which are now depleting, leading to a surge in polyurethane production costs. Bio-based polyurethanes (PU) have been synthesized by researchers in recent decades and have mostly overtaken petrochemical-based PU in terms of challenges such as solid pollution, economic effectiveness, and availability of raw materials. Enormous kinds of available bio-renewable sources as predecessors for the production of polyols and isocyanates have been explored for the development of “greener” PU materials; these bio-based polyurethanes have significant potential to be used as future PU products, with a partial or total replacement of petroleum-based polyurethanes, due to increasing concern about the environment, their relatively low cost and biodegradability. This critical review concentrates on the possibilities of renewable sources to be used for polyurethane production and gives a clear perspective on the journey, utilization, and recent advancements in the field of different bio-based polyurethane polymers that have arisen over the last decade.

Keywords: polyurethanes; non-isocyanate polyurethanes; adhesives; coatings; recycling; biodegradation



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1. Introduction

Polyurethanes (PU) represent nearly 8% of the total plastics production and stand tall as the 6th most widely used polymer in the world, with total production reaching 18 Mton in 2016 [1] and still progressing. The superior properties of PU, such as flexibility, corrosion, resistance to chemicals, high automatic strength, low-temperature comfortability, adhesiveness, and chemical structure adaptability, etc. account for their considerable popularity among researchers. PU have urethane groups as major repeating units along their main backbone chains, which are derived by reacting hydroxyl (–OH) terminated chemical entities, with isocyanate (–NCO) terminated compounds, as represented by a generalized scheme shown in Figure 1. In addition, some other functional groups may also be present in the end constitutions of the PU chains, including ethers, esters, urea, biuret, and aromatic moieties [2].



Figure 1. Formation of Urethane Linkage.



Primary Microplastics in the Ecosystem: Ecological Effects, Risks, and Comprehensive Perspectives on Toxicology and Detection Methods

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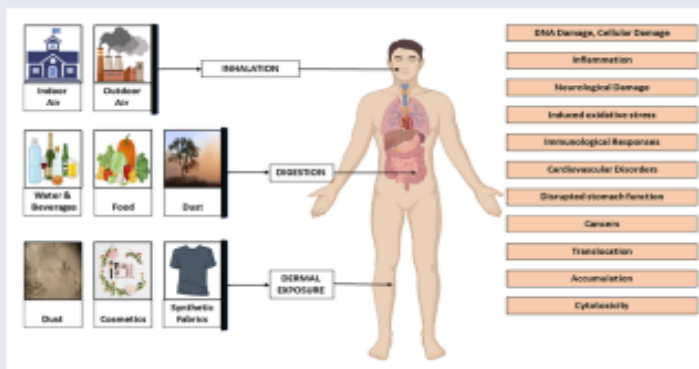
ABSTRACT

Recent discoveries of microplastics in cities, suburbs, and even remote locations, far from microplastic source regions, have raised the possibility of long-distance transmission of microplastics in many ecosystems. A little is known scientifically about the threat that it posed to the environment by microplastics. The problem's apparent size necessitates the rapid development of reliable scientific advice regarding the ecological risks of microplastics. These concerns are brought on by the lack of consistent sample and identification techniques, as well as the limited physical analysis and understanding of microplastic pollution. This review provides insight regarding some unaddressed issues about the occurrence, fate, movement, and impact of microplastics, in general, with special emphasis on primary microplastics. The approaches taken in the earlier investigations have been analyzed and different recommendations for future research have been suggested.

KEYWORDS

Primary microplastics;
ecological risk;
identification techniques;
bioaccumulation;
microplastic toxicity

GRAPHICAL ABSTRACT



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Photocatalytic degradation of crystal violet dye using phytofabricated zinc oxide nanoparticles from anthocyanin extract

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ARTICLE INFO

Keywords:

Phyto-fabrication
Zinc oxide nanoparticles
Anthocyanin extract
Photocatalysis
Crystal violet dye
Water treatment

ABSTRACT

This study investigates a coprecipitation method for the production of zinc oxide nanoparticles (ZnO NPs) using anthocyanin (ATH) extract derived from red cabbage (RC) that acts as a reducing, capping and stabilising agent. The efficacy of these NPs in the photocatalytic degradation of crystal violet (CV) dye is assessed thoroughly considering all the relevant influencing parameters such as pH levels, catalytic dosage, and dye concentration, among others. The structural, morphological, surface charge and presence of different functional groups of the synthesized NPs were then analysed using XRD, SEM-EDX, BET, and FTIR. The average particle size of the synthesized ZnO NPs and ZnATH-(O) NPs was 31.12 nm and 27.91 nm, respectively. The BET analysis determined that the surface area of ZnO NPs was 15.685 m²/g, and that of ZnATH-(O) NPs was 25.187 m²/g. In contrast to ZnO NPs, ZnATH-(O) NPs exhibit efficient photocatalytic degradation of CV dye. This is due to their improved stability, reduced size, increased surface area and optimized structure. The influence of various parameters like initial dye concentration, catalyst dosage, pH and ionic strength was also assessed under 90 min visible light irradiation. It was observed that ZnATH-(O) NPs show maximum photocatalytic degradation of CV dye in 90 min of visible light irradiation with a degradation efficiency of 96.12 %. This green synthesis method mitigates the environmental consequences associated with conventional chemical synthesis and utilizes the plentiful and renewable resources present in RC, thereby offering a sustainable alternative to a deteriorating environment.

1. Introduction

The rapid industrialization and urbanization of recent decades have led to a significant increase in the release of synthetic dyes into aquatic environments [1–3]. Among these, crystal violet (CV) dye, which is frequently used in printing, textiles, and other sectors, presents a significant risk because of its high toxicity, persistence, and possible carcinogenicity [4–6]. Conventional techniques used to treat water contaminated with dye, such as coagulation [7], flocculation and adsorption frequently lack effectiveness, cost-efficiency, and environmental sustainability [8]. Therefore, the quest for inventive and environmentally friendly methods to reduce the detrimental impacts of these contaminants has become a crucial area of attention in environmental research.

Photocatalysis, capable of harnessing light to activate semiconductor materials that can degrade organic pollutants, emerges as a promising solution [9,10]. Zinc oxide nanoparticles (ZnO NPs) have gathered considerable interest in this field because of their distinctive optical and

electrical characteristics, such as a broad energy gap (3.37 eV), a high exciton binding energy (60 meV), and a robust photocatalytic activity [5,11]. These properties enable ZnO NPs to generate reactive oxygen species (ROS) such as hydroxyl radicals (OH[•]) and superoxide (O₂^{•-}) anions under UV irradiation, which can effectively degrade complex organic pollutants, including dye molecules, into less degraded entities like CO₂²⁻, NO₃²⁻ and H₂O [12]. Moreover, ZnO NPs are biocompatible, easy to synthesise, and non-toxic, making them an ecologically benign choice for water treatment and other applications [13,14].

Conventional methods adopted to synthesize ZnO NPs frequently employ toxic compounds like sodium hydroxide, zinc nitrate, and other organic solvents. Additionally, these approaches need energy-intensive procedures such as sol-gel, hydrothermal, and chemical vapour deposition (CVD) techniques [15]. These technologies not only give rise to environmental and safety concerns but also provide obstacles in achieving constant NPs size and morphology, which are crucial for achieving optimal photocatalytic performance. As an outcome of these challenges, the field of green synthesis has gained prominence,

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Research Article

Surya Tanwar, Gunjan Varshney, and Raminder Kaur*

Fatty acid filled polyaniline nanofibres with dual electrical conductivity and thermo-regulatory characteristics: Futuristic material for thermal energy storage

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Abstract: This study emphasizes on the production of nano-encapsulated phase change materials for the application of thermal energy storage (TES). The core is undecylenic acid (UA), a renewable latent heat storage material, which is encased inside the polyaniline (PANI) nanofibres (NFs) synthesized by interfacial polymerization technique. The morphological and structural features of the prepared NFs were examined by high-resolution transmission electron microscopy and Fourier transform infrared spectroscopy. According to differential scanning calorimetry analysis, the latent heat values were observed as 56 ± 1.4 and $57 \pm 1.3 \text{ J-g}^{-1}$, while the melting and freezing temperatures were recorded as $18 \pm 0.2^\circ\text{C}$ and $14 \pm 0.3^\circ\text{C}$, respectively. Thermogravimetric analysis revealed a multi-step deterioration pattern, demonstrating the developed nano-encapsulated-phase change material's (PCMs) exceptional thermal stability. In addition to exhibiting reliable thermal performance over numerous cycles, PANI/UA NFs showed excellent TES and release rates. This work addresses key challenges in TES applications by introducing a PCM based on renewable materials that offers enhanced thermal reliability and efficiency. The results contribute in the development of compact and environmentally friendly thermal management systems for utilizing in the applications of electronic device cooling, building energy systems, and renewable energy storage.

Keywords: phase change materials, nano-encapsulation, polyaniline, undecylenic acid, thermal energy storage

1 Introduction

The dwindling fossil fuel reserves and increasing energy demand have heightened the urgency for efficient and sustainable energy storage solutions (1,2). A promising option is phase change materials (PCMs) for thermal energy storage (TES), which have the capacity to both absorb and release thermal energy during phase transitions (3). PCMs are latent heat storage systems that use phase transitions, such as solid-liquid, solid-solid, liquid-gas, and solid-gas transformations, to store and release energy (4). Solid-liquid PCMs are the most extensively used due to its exceptional versatility, better efficiency and high adaptability for a variety of applications because of their benefits, which includes a high energy storage density, uniform heat transfer during phase transition at constant temperature, and a wide range of operating temperatures. The aforementioned features make PCMs suitable for energy-efficient systems like textiles, air conditioning, electronics cooling, building materials, and renewable energy storage (5–9). Despite their potentials, PCMs are difficult to execute in real life, especially the organic PCMs experiencing solid-liquid transitions, due to the problems like poor thermal conductivity and risk of material seepage during phase transition (10). Encapsulation techniques have been used to circumvent these limitations, resulting in the formation of encapsulated PCMs (EPCMs) (11). PCMs shielded by this technique acquire a core-shell configuration, which also inhibits leakage and regulates variations in volume during phase transitions. In particular, nano-encapsulation has attracted a lot of interest because of its exceptional thermal performance. Nano-encapsulated PCMs are interesting candidates for TES applications owing to their high surface area-to-volume ratio, which facilitates

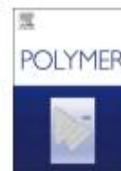
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Non-isocyanate polyurethane (NIPU) Foams: Overcoming challenges and embracing sustainability

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ARTICLE INFO

Keywords:
NIPU foams
Blowing agent
Self-blowing
Transurethanisation
Thermal carbamate decarboxylation

ABSTRACT

Polyurethane (PU) foams are widely acknowledged for their versatility and utility across numerous industries, owing to their remarkable properties. However, concerns regarding the toxicity associated with isocyanates have driven the imperative for Non-Isocyanate Polyurethane (NIPU) foams. NIPU foams offer a promising alternative, harnessing greener synthesis routes to mitigate environmental and health risks. However, the production of NIPU foams poses significant difficulties due to the challenges of substituting alternate reagents for isocyanates. This review examines the complex field of NIPU foam synthesis, exploring various methodologies such as transurethanisation and thermal carbamate decarboxylation. The diverse biomass sources such as carbohydrates, terpenes and oleochemicals are examined for their potential in advancing sustainable foam production. Furthermore, this paper comprehensively discusses the technological advancements necessary to overcome hurdles in NIPU foam synthesis. It elucidates the role of different blowing agents and the utilization of characterization techniques, such as rheological analysis and microscale combustion calorimetry, among others, in elucidating foam properties. The environmental and economic considerations surrounding NIPU foam production are addressed, highlighting the potential for cost-effectiveness and sustainability. This review offers valuable perspectives on the current state and future prospects of NIPU foams, illuminating pathways towards their widespread adoption across diverse applications.

1. Introduction

Polyurethanes (PU) have held significant importance in engineering sectors since its discovery by Wurtz and Hoffman in 1849, followed by Otto Bayer in 1937, after which it was commercially utilized [1]. Owing to their exceptional versatility and robust physical and mechanical attributes, PUs are ranked as the 6th most widely used polymers globally. Since its discovery, it has found multifaceted applications in numerous sectors, such as the construction, automotive, and electrical industries, in the manufacturing of mattresses, furniture, car seats, thermal insulations, and packaging materials. Furthermore, they are employed in producing coatings, adhesives, sealants, flexible and rigid foams, paints, varnishes, synthetic leathers, rubbers, films, and bio-mimetic materials. Notably, the largest segment of PU utilization is in the form of foams, accounting for over three-quarters of the global consumption of PU products [2]. PU foams (PUF) is the third most commonly used foam for industrial and commercial applications after polyvinyl chloride and polystyrene foams. PUF offer superior thermal and acoustic insulation

and impressive energy-absorbing capabilities, making them valuable in cushioning and packaging, particularly in automotive and electronics.

PUs are synthesized using addition reactions between polyols and polyisocyanates, both of which pose significant challenges. This reaction is exothermic and results in the formation of urethane groups (Fig. 1). Industrial PUF production involves polyaddition reactions of polyols and poly-isocyanates, facilitated by a blowing agent like CO₂.

The in-situ generation of CO₂ through the reaction between water and isocyanates, allows the formation of gaseous cells inside the polymer matrix (Fig. 2) [3]. This process produces a range of PUF, from rigid to flexible variants. Synthesizing PUF at an industrial scale involves simultaneous polymerization reactions and foaming reactions. Water is a common blowing agent and its reaction to isocyanates gives urea and CO₂, facilitating foam expansion. Physical blowing agents, such as hydrofluoroolefins (HFO), hydrofluorocarbons (HFC), and hydrocarbons (HCs), contribute to expansion through vaporization [1]. Their cellular structure, predominantly gas, reduces the need for polymeric mass, and they can be manufactured across a range of densities,

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RESEARCH ARTICLE

Polyaniline Nanofibers as a Sustainable Adsorbent for Cr(VI) and Hg(II) Ions Detoxification

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Keywords: Cr(VI) removal | heavy metal adsorption | Hg(II) removal | polyaniline nanofibers | wastewater treatment

ABSTRACT

Heavy metal pollution in water presents a significant environmental and health hazards, seeking for effective and sustainable remediation methods. This research examines the adsorption efficacy of polyaniline nanofibers (PANI-NF) for the uptake of chromium (Cr(VI)) and mercury (Hg(II)) ions from dilute solutions. The synthesized PANI-NF was characterized by using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) isotherm, and zeta potential analysis to elucidate its structural and physicochemical properties. The adsorption efficiency was methodically assessed under different experimental parameters; including reaction time, initial heavy metal ion concentration, adsorbent dosage, and pH of metal ion solution. Different mathematical models further examined the adsorption mechanism to evaluate adsorption isotherms and kinetic behavior. The synthesized PANI-NF, devoid of any structural alterations like doping or nanocomposite integration, exhibited maximum adsorption capacity and outstanding removal efficiency of 142.85 mg g⁻¹, 97% for Cr(VI) and 166.66 mg g⁻¹, 91% for Hg(II), respectively, under optimum adsorption conditions (contact time (45 min), initial metal ion concentration (20 mg L⁻¹), adsorbent dosage (20 mg), and pH (7)), indicating its excellent efficacy in removing heavy metal ions as compared to previously reported studies. Electrostatic interactions and surface binding processes primarily govern the adsorption process. The findings of the present work demonstrate that PANI-NF is a viable and economical adsorbent material for wastewater treatment applications. This research advances sustainable adsorption technologies and establishes a basis for future investigations to enhance the adsorption efficiency of PANI-based materials for environmental remediation.

1 | Introduction

Heavy metals represent a class of metals and metalloids with atomic weights ranging from 63.5 to 200.6 g mol⁻¹ and densities above 5 g cm⁻³ [1, 2]. The release of these heavy metal ions (Pb²⁺, As³⁺, Hg²⁺, Cd²⁺, Zn²⁺, Cu²⁺, Ag⁺, Fe³⁺, Ni²⁺, Pd²⁺, and Pt²⁺) in significant quantities from human-related activities, including mining, mineral processing, metallurgical operations,

electroplating, fuel production, painting, battery manufacturing, paper production, pigments, photographic materials, and explosives manufacturing into water bodies is a primary concern of researchers [3, 4]. Most of these heavy metals are non-biodegradable and can bioaccumulate into higher trophic levels via food chains, damaging living organisms, flora and fauna. Among various heavy metal ions, hexavalent chromium (Cr(VI)) and mercury (Hg(II)) are eminent due to high level of toxicity



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RESEARCH INTERESTS:

Phase Change Material, Thermal Energy Storage, Encapsulation, Nanomaterials, Polymer Blends & Composites

ACADEMIC QUALIFICATIONS:

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2019	B.Sc. Chemistry Hon.	Amity University, Uttar Pradesh	8.59

TECHNICAL SKILLS

- Analytical Techniques:** DSC (DSC 8000, Perkin Elmer; TA DSC Q200); TGA (Perkin Elmer, TGA 4000; TA TGA 5500); UV-Vis Spectrophotometer (Agilent Technologies; Cary Series); Zeta potential (Malvern Zetasizer Nano); Fluorescence Microscopy (Motic BA410E); Refractometer
- Software & Data Tools:** Origin-Pro, TA Universal Analysis, X'Pert HighScore Plus, PowDLL Converter, PowderX, ChemDraw, Image J

ACADEMIC RESEARCH GUIDANCE

Worked alongside and mentored M.Sc. Chemistry and B.Tech. students at Delhi Technological University under the guidance of Dr. Raminder Kaur.

PUBLICATIONS:

➤ Peer-Reviewed Journals

- Gunjan Varshney**, Raminder Kaur, Mohammad Zulfequar (2026), “Tailoring thermal properties and structural integrity of n-Eicosane/Poly(Styrene-co-Butylacrylate) microcapsules with divinylbenzene cross-linker”, *Materials Chemistry and Physics*, 359,

- 132549, DOI: <https://doi.org/10.1016/j.matchemphys.2026.132549> (I.F.= 4.7) (SCIE indexed) (Elsevier)
2. **Gunjan Varshney**, Sarla Yadav, Raminder Kaur, Mohammad Zulfequar (2026), "Fabrication of ZnATH-(O) NPs-Integrated Microencapsulated Phase Change Materials (MEPCMs) for Improved Heat Storage Capacity", *Materials Research Bulletin*, 195, 113884, DOI: <https://doi.org/10.1016/j.materresbull.2025.113884> (I.F.= 5.7) (SCIE indexed) (Elsevier)
 3. **Gunjan Varshney**, Sarla Yadav, Monika Duhan, Devvrat Tiwari, Raminder Kaur (2026), "Polyaniline Nanofibers as a Sustainable Adsorbent for Cr (VI) and Hg (II) Ions Detoxification", *Chemistry Select*, 11(5), e03770, DOI: <https://doi.org/10.1002/slct.202503770> (I.F.= 2) (SCIE indexed) (Wiley)
 4. **Gunjan Varshney**, Raminder Kaur, Mohammad Zulfequar (2025), "Fabrication and assessment of n-eicosane/poly (stearyl methacrylate-co-butylacrylate) nanocapsules: impact of long alkyl polymer chains on thermal performance and stability", *Nanoscale*, 17(46), 26923-26934, DOI: 10.1039/D5NR04183J (I.F.= 5.1) (SCIE indexed) (RSC)
 5. Pooja Singh, Manpreet Kour, **Gunjan Varshney** and Raminder Kaur (2025), "Non-isocyanate polyurethane (NIPU) Foams: Overcoming challenges and embracing sustainability", *Polymer*, 333, 128658, DOI: <https://doi.org/10.1016/j.polymer.2025.128658> (I.F.= 4.5) (SCIE indexed) (Elsevier)
 6. Surya Tanwar, **Gunjan Varshney**, and Raminder Kaur (2025), "Fatty acid filled polyaniline nanofibres with dual electrical conductivity and thermo-regulatory characteristics: Futuristic material for thermal energy storage", *e-Polymers*, 25(1), 20250003, DOI: <https://doi.org/10.1515/epoly-2025-0003> (I.F.= 3.2) (SCIE indexed) (De Gruyter)
 7. Sarla Yadav, Pooja Singh, **Gunjan Varshney**, Saurabh, Poonam Singh, Raminder Kaur (2025) "Photocatalytic degradation of crystal violet dye using phytofabricated zinc oxide nanoparticles from anthocyanin extract", *Microchemical Journal*, 213, 113681, DOI: <https://doi.org/10.1016/j.microc.2025.113681> (I.F.= 5.1) (SCIE indexed) (Elsevier)
 8. **Gunjan Varshney**, Pooja Singh, Sarla Yadav, Raminder Kaur (2024) "A Review on Unleashing the Potential Solution of Thermal Comfort: Exploring the Cutting-edge Progress of Advanced Engineering Application of Phase Change Materials Integrated Textiles", *Sustainable Energy Technologies and Assessments*, 72, 104089, DOI: <https://doi.org/10.1016/j.seta.2024.104089> (I.F.= 7.1) (SCI indexed) (Elsevier)
 9. **Gunjan Varshney**, Raminder Kaur and Mohammad Zulfequar (2024) "Fabrication and Evaluation of Eicosane/Poly(Styrene-co-Butylacrylate) Microencapsulated Phase Change Materials through Ultrasonicated Mini-Emulsion Technique", *Chemical Engineering Journal*, 500, 156994, DOI: <https://doi.org/10.1016/j.cej.2024.156994> (I.F.= 13.3) (SCIE indexed) (Elsevier)
 10. Pooja Singh, **Gunjan Varshney** and Raminder Kaur (2024), "Primary Microplastics in the Ecosystem: Ecological Effects, Risks, and Comprehensive Perspectives on Toxicology and Detection Methods", *Journal of Environmental Science and Health, Part C*, 42(4), 314–365, DOI: <https://doi.org/10.1080/26896583.2024.2370715> (I.F.= 2.5) (SCI indexed) (Taylor and Francis)

11. Raminder Kaur, Pooja Singh, Surya Tanwar, **Gunjan Varshney** and Sarla Yadav (2022), “Assessment of Bio-Based Polyurethanes: Perspective on Applications and Bio-Degradation”, *Macromol*, 2, 284–314, DOI: <https://doi.org/10.3390/macromol2030019> (I.F.= 4.4) (Scopus Indexed) (MDPI)

➤ Book Chapters

1. Sarla Yadav, **Gunjan Varshney**, Pooja Yadav, Riya Malik, Raminder Kaur (2025), Biotribology of articular cartilage, Chapter 5, Biotribology: Friction, Wear and Lubrication in Biological Systems. Green Tribology and Tribochemistry, 121-146, eBook ISBN: 9783111563176; Hardcover ISBN: 9783111562940, De Gruyter, (11/2025), DOI: <https://doi.org/10.1515/9783111563176-005>.
2. Sarla Yadav, **Gunjan Varshney**, Manisha Yadav, Raminder Kaur (2025), Geochemical Characterization and Assessment of Fluoride Sources in Groundwater, Chapter 1, Fluorides in Drinking Water: Source, Issue, and Mitigation Strategies. Environmental Science and Engineering, 3-34, Part- I (Sources and Distribution of Fluoride in Water Ecosystem), ISBN 978-3-031-77247-4, ISSN 1863-5539, Springer, (1/2025), DOI: https://doi.org/10.1007/978-3-031-77247-4_1.
3. Pooja Singh, **Gunjan Varshney** and Raminder Kaur (2024), Arsenic Contamination in Drinking Water and Health, Chapter 3, Arsenic Toxicity Remediation: Sustainable Nexus Approach. Emerging Contaminants and Associated Treatment Technologies, 125-142, Part-II (Health Risks Linked to Arsenic Exposure in Food and the Environment), ISBN 978-3-031-52614-5, ISSN 2524-6410, Springer Cham, (3/2024), DOI: https://doi.org/10.1007/978-3-031-52614-5_7.
4. **Gunjan Varshney**, Eksha Guliani, Christine Jeyaseelan (2022), Graphene from Natural Sources, Chapter 9, Graphene from Natural Sources: Synthesis, Characterization, and Applications, 117-137, eBook ISBN 9781003169741, CRC Press, (07/2022), DOI: <https://doi.org/10.1201/9781003169741-9>.

CONFERENCES:

1. **Gunjan Varshney**, Mohammad Zulfequar and Raminder Kaur (2025), **Poster Presentation** on the title: “High-Performance Eicosane Microcapsules with Poly(Styrene-co-Butylacrylate) Shell via Ultrasonic Mini-Emulsion for Thermal Energy Storage” International Conference on Chemistry for Sustainability (ICCS-2025) organized by the Chemistry in association with the Greenko School of Sustainability, Indian Institute of Technology, Hyderabad, India, July 13-16, 2025.
2. **Gunjan Varshney**, Mohammad Zulfequar and Raminder Kaur (2024), **Oral Presentation** on the title: “Production and assessment of eicosane/poly(styrene-co-butylacrylate) microencapsulated phase change materials using ultrasonicated mini-emulsion method”, National Conference on Indian Knowledge System: Traditional to Modern Nanotechnology jointly organized by the Special Centre for Nano Science, JNU, School of Biotechnology, JNU and Department of Chemistry, Gurukula Kangri Deemed University, New Delhi, India, December 13, 2024. **Awarded by Best Oral Presentation.**

3. **Gunjan Varshney**, Mohammad Zulfequar and Raminder Kaur (2024), **Oral Presentation** on the title: “Fabrication and Assessment of eicosane/poly(styrene-co-butylacrylate) microencapsulated phase change materials using an ultrasonicated mini-emulsion approach”, International Conference on Current Environmental Technologies for Sustainable Development (ICCETSD2024), organized by the Department of Environmental Science, Graphic Era (Deemed to be University), Dehradun, Uttarakhand, India, December 9-10, 2024.
4. **Gunjan Varshney**, Mohammad Zulfequar and Raminder Kaur (2024), **Oral Presentation** on title: “Cutting-Edge Approach for Latent Heat Storage: Fabrication of Organic Phase Change Materials with Polymer Shells” International Conference on Emerging Techno-Economic Development for Sustainable Environment (ETDSE-2024) organized by IPS Academy Institute of Engineering & Science, Indore, Madhya Pradesh, India, January, 12-13, 2024.
5. **Gunjan Varshney** and Raminder Kaur (2023), **Oral Presentation** on title: “Recent Advancements in Phase Change Materials and their Utility”, International Conference on “Chemical & Allied Science and their Applications, organized by Delhi Technological University, New-Delhi, India, January 20, 2023.
6. **Gunjan Varshney**, Raminder Kaur (2022), participated in the International Conference on “Nanotechnology: Opportunities & Challenges (ICNOC-2022)”, organized by Department of Applied Sciences & Humanities, Faculty of Engineering & Technology, Jamia Millia Islamia University, New Delhi, India, November, 28–30, 2022.
7. **Gunjan Varshney** and Raminder Kaur (2022), **Poster Presentation** on title: “An Overview of Recent Developments in Phase Change Materials for Thermal Energy Storage Applications”, 2nd International Conference on Green and Sustainable Chemistry Conference (GSCC-2022), organised by Manav Rachna University, Faridabad, Sponsored by Science and Engineering Research Board (SERB)- Department of Science and Technology India, NHPC Faridabad and DRDO India, November 17-19, 2022.
8. **Gunjan Varshney**, Raminder Kaur and Manish Jain (2022), **Poster Presentation** on title: “Advancement in Phase Change Materials for Thermal energy storage applications: An Overview” 2nd Indian Analytical Congress (2nd IAC-2022), jointly organised by Indian Society of Analytical Scientists Delhi Chapter (ISAS-DC), Graphic Era University, and CSIR Indian Institute of Petroleum, Dehradun, Uttarakhand, India, May, 26-28, 2022.
9. **Gunjan Varshney** and Raminder Kaur, (2022), **Poster Presentation** on title: “Encapsulation of Phase Change Material (PCM) for thermal energy storage system”, International Conference on Emerging Trends in Biotechnology and Sustainable Chemistry: (ETBSC-2022), organized by Baba Farid College, Bathinda in collaboration with Central University of Punjab, Bathinda, India, April, 27-29, 2022.
10. **Gunjan Varshney** (2019), **Poster Presentation**, International Conference on Recent Trends in Materials and Devices (ICRTMD-2019) jointly organised by Amity Institute of Applied Sciences and Amity Institute of Advanced Research Studies (Materials & Devices), Uttar Pradesh, Noida, December, 18-19, 2019.

WORKSHOPS ATTENDED

1. Training Workshop on Safety from Hazards: Fire, Chemical and Biological and Natural Disasters, organized by Shriram Institute For Industrial Research, Delhi, India held on 11th June 2025.
2. Five-Day International Workshop on Sophisticated Instrumentation Techniques, organized by the Department of Chemistry, School of Advanced Sciences (SAS), VIT-AP University in association with the Institute of Physical Sciences (ICF), National Autonomous University of Mexico (UNAM), held from 17th – 21st March 2025.
3. Two-Day Workshop on Structural Analysis (XRD, Rietveld Refinement, HRTEM & SAED), organized by the Centre for Nanoscience and Nanotechnology, International Research Centre & Advanced Characterization Facility, Sathyabama Institute of Science and Technology, Chennai, during 24th – 25th February 2025.
4. School on Microscopic Characterization Techniques (TEM/SEM/AFM), organized by Inter-University Accelerator Center (IUAC), New Delhi, from 9th – 12th December 2024.
5. Workshop on Samerpan: Sustainable Action & Mobility for Emission Reduction & Promoting Awareness Nationwide, organized by the Department of Environmental Engineering, Delhi Technological University in collaboration with Alfatech Services, on 26th November 2024.
6. Two-Day Hands-On Training Workshop on Thermal Analyses (DSC/TGA/ITC), conducted by the University Science Instrumentation Center (USIC), University of Delhi, on 11th – 12th November 2024.
7. Three-Day INUP-i2i 6th User Awareness Workshop on Fabrication and Characterization Facility for Nanotechnology, organized by the Indian Institute of Technology Delhi (IIT Delhi), from 4th – 5th March 2023.
8. IP Awareness/Training Program under National Intellectual Property Awareness Mission (NIPAM), organized by the Intellectual Property Office, Government of India, held on 30th November 2022.
9. Five-Day Skill Enhancement Workshop on Beyond Industry 4.0: Energy and Environment, organized by University School of Chemical Technology, Guru Gobind Singh Indraprastha University, New Delhi, from 25th – 29th July 2022.
10. Short-Term Program on Bio-Privileged and Sustainable Chemistry, conducted by the Department of Chemistry, Manav Rachna University, Faridabad, from 17th – 21st January 2022.
11. Five-Day Online Workshop on Advanced Skills in Research and Protection of IPR, conducted by the Amity Institute for Applied Sciences, from 7th – 11th June 2021.
12. International e-Workshop on Computational Approaches in Drug Design and Therapeutics, organized by Drug Discovery and Development Cluster in collaboration with Amity Institute of Biotechnology, Amity University Chhattisgarh, held on 20th February 2021.

SEMINAR/ WEBINAR:

1. Webinar on “Breaking Barriers: Addressing Gender Gaps in STEM Education, Careers, and Research”, organized by the Department of Biotechnology, Delhi Technological University, held on 11th February 2025.
2. Webinar on “Higher Study Opportunities & Latest Research in Portable Sensor, Bio-Chip, Metal Catalysis, Atomic & Electronic Structure”, organized by National Sun Yat-Sen University (NSYSU) & EduCare Taiwan, on 9th June 2023.
3. One-Day Industry-Academia Seminar on “Petrochemicals in Today’s World”, organized by the Department of Applied Chemistry in association with Just Polymer Solutions and PLUSS Advanced Technologies, held on 21st April 2023.
4. National Webinar on “Selective Transformation of Biomass-Derived Substrates to Chemicals”, organized by the Department of Chemistry, Faculty of Humanities and Science, Adayalampattu Phase-II Campus, on 9th October 2020.
5. National Webinar on “Ozone Layer: Closing the Gap”, organized by the Postgraduate and Research Department of Zoology, Nirmala College, Muvattupuzha, Kerala, India, on 16th September 2020.
6. International Webinar on “Nanostructured Semiconducting Materials for Energy Applications (NSME-2020)”, organized by the Department of Applied Chemistry, Defence Institute of Advanced Technology (Deemed to be University), sponsored by SPARC MHRD, from 15th – 17th September 2020 — attended and delivered an oral presentation.

AWARDS & HONORS

1. Commendable Research Excellence Award- Delhi Technological University (2025)
2. Best Oral Presentation – JNU & Gurukula Kangri Conference (2024)
3. Verbal Commendation – IMUN Online Conference (2020)
4. Cultural Excellence Award – Amity University (2019–2021)

INTERNSHIP/ TRAINING:

1. FTN Training (FSSAI Food Law and Regulations, FSSAI Labelling and Display Regulations, Laboratory Management Systems - ISO/IEC 17025:2017, Quality Assurance and Quality Control with Food Allergy Management in Factory, Hazard Analysis and Critical Control Points, Food Safety Management Systems), FTN Training and Services Pvt. Ltd. (Dec 2024)
2. Laboratory Accreditation (ISO/IEC 17025:2017), MSME Technology Centre, Sitarganj (Nov 2024 – Jan 2025)
3. Project: Thermo-Regulating Fabric using PCMs, Shriram Institute for Industrial Research (Jan–May 2021)
4. Springfest Internship Program, IIT Kharagpur (Oct 2020)
5. Water Audit & Conservation, Centre for Science and Environment, New Delhi (Jul–Aug 2020)
6. Open Research Lab Internship, Chem Academy (Jul–Sep 2020)

EXTRA CURRICULAR ACTIVITIES:

1. Secured 3rd Position in the Poster Making Competition on “*Swachh Bharat Mission*”, organized by Kugelblitz Club, Amity Institute of Applied Sciences (AIAS), held on 2nd October 2020.
2. Successfully completed the Think India–YOLO Certificate Course on “Cyber Space”, conducted on 27th September 2020.
3. Volunteered/Interned at Youth Online Learning Organisation (YOLO) from 29th August to 31st December 2020.
4. Completed a Two-Week Certificate Course on Nanotechnology, organized by Scienceplace – A Pioneer Institute for STEM Education, affiliated with Vigyan Prasar, Department of Science and Technology (Government of India), in 2020.
5. Participated in Organizing “SANGATHAN 2019” – 21st Inter-Amity Institutions Sports Meet, in celebration of Founder’s Day, held on 24th October 2019.
6. Actively Participated in Organizing a Chemistry Club Event, held on 8th August 2019.