

**PREPARATION AND CHARACTERIZATION OF MICROENCAPSULATED
PARAFFIN WAX AS A PCM FOR THERMAL ENERGY STORAGE**

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FACULTY OF ENGINEERING

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**RESEARCH REPORT SUBMITTED IN PARTIAL FULFILLEMENT OF
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**PREPARATION AND CHARACTERIZATION OF MICROENCAPSULATED
PARAFFIN WAX AS A PCM FOR THERMAL ENERGY STORAGE**

Field of Study: **ENERGY**

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ABSTRAK

Mikroenkapsulasi lilin parafin sebagai material penyimpanan energi termal yang disintesis dengan Polianilin (PAn) sebagai material Shell menggunakan metode in-situ polimerisasi. Dalam hal ini, lilin parafin yang bertindak sebagai bahan inti dan PAn digunakan sebagai bahan shell merupakan bahan ramah lingkungan. Struktur kimia, morfologi permukaan, sifat termal dan stabilitas termal dari lilin parafin yang sudah dienkapsulasi ditentukan menggunakan alat berikut, Fourier transform infrared spectrophotometer (FTIR), Field Emission Scanning Electron Microscopy (FESEM), Differential Scanning Calorimeter (DSC), thermogravimetry analyzer (TGA). Hasil FESEM menunjukkan bahwa lilin parafin itu terenkapsulasi dengan baik berbentuk kapsul bola. Analisis DSC menunjukkan bahwa lilin parafin yang sudah dienkapsulasi memiliki penyimpanan energi yang besar dan kapasitas melepas panas ($22-140\text{ J / g}$) tergantung pada perbedaan rasio dari lilin parafin dan PAn. Hasil analisa dengan alat TGA menunjukkan bahwa PAn dapat meningkatkan stabilitas termal lilin parafin terenkapsulasi karena efek sinergis antara lilin parafin dan PAn. Berdasarkan semua hasil tersebut, mikroenkapsulasi lilin parafin sebagai MEPCMs memiliki potensi yang baik untuk tujuan penyimpanan energi termal.

ABSTRACT

Microencapsulation of paraffin wax with Polyaniline (PAn) Shell was synthesized as thermal energy storage materials by in-situ polymerization method. In this preparation, Paraffin wax was acted as the core material and PAn has been used as the shell which is environmentally friendly material. The chemical structure, surface morphologies, thermal properties and thermal stability of the encapsulated paraffin wax have been determined by Fourier transform infrared spectrophotometer (FTIR), Field Emission Scanning Electron Microscopy (FESEM), Differential Scanning Calorimeter (DSC), thermogravimetry analyzer (TGA), respectively. The FESEM results indicated that the paraffin wax was encapsulated well and the shape of the capsules are sphere. The DSC analysis showed that encapsulated paraffin wax has large energy storage and release capacity (22-140J/g) depending on the different ratio of the paraffin wax and PAn. TGA results indicated that the PAn can improve the thermal stability of encapsulated paraffin wax because of the synergetic effect between Paraffin wax and PAn. On the basis of all these results, the microencapsulated paraffin wax as MEPCMs has a good potential for thermal energy storage purpose.

Contents

CHAPTER 1: INTRODUCTION	1
1.1 BACKGROUND OF STUDY	1
1.2 OBJECTIVES OF STUDY	3
1.3 Research Scopes and Methodology	3
1.4 ORGANIZATION OF THIS DISSERTATION	5
CHAPTER 2: LITERATURE REVIEW	6
2.1 Thermal energy storage	6
2.2 Thermal energy storage methods:	6
2.2.1 Sensible heat storage	8
2.2.2 Latent heat storage	8
2.2.3 Comparison of sensible and latent heat storage	8
2.3 Candidate heat storage materials	9
2.3.1 Organic PCM	10
2.3.2 Inorganic PCM	12
2.4 Eutectic mixture	14
2.5 Encapsulation of phase change material	15
2.6 Method of microencapsulation	17
2.6.1 Air suspension	18
2.6.2 Coacervation-phase separation	18
2.6.3 Solvent evaporation technique	20
2.6.4 Spray coating process	20
2.6.5 Interfacial polymerization	22
2.6.6 In-situ polymerization	22
2.6.7 Dip coating	25
CHAPTER 3: MATERIAL AND METHOD	26
3.1 Introduction	26
3.2 Materials	26
3.2.1 Paraffin wax	26
3.2.2 Aniline	27
3.2.3 Ammonium persulfate	27
3.3 Experiment	28
3.3.1 Preparation of samples	28
3.3.2 Synthesis of polyaniline	32

3.4	Characterization.....	33
3.4.1	Differential Scanning Calorimeter	33
3.4.2	Thermo gravimetric analysis (TGA).....	34
3.4.3	Field Emission Scanning Electron Microscopy (FESEM)	35
3.4.4	Transmission electron microscopy (TEM)	36
3.4.5	Fourier transform infrared spectrophotometer (FT-IR)	37
CHAPTER 4: RESULTS AND DISCUSSIONS		39
4.1	Introduction	39
4.2	Thermal performance of encapsulated paraffin wax	39
4.3	Surface morphology	46
4.4	Transmission electron microscopy	48
4.5	Themogarvimetry analysis	49
4.6	Structure stability	52
CHAPTER 5: CONCLUSIONS AND RECOMMENDATION.....		55
5.1	Conclusion.....	55
5.2	Recommendation.....	56
REFERENCES		57

List of Tables

Table 2.1 Comparison between sensible and latent heat storage media	9
Table 2.2 List of published encapsulated PCM systems	17
Table 3.1 The characterization of core.....	27
Table 3.2 The characterization of monomer	27
Table 3.3 The characterization of oxidant.....	27
Table 4.1 DSC data of the paraffin, S1, S2, S3, and S4.....	46

List of Figures

Figure 1.1 Methodology flowchart	4
Figure 2.1 Research area of thermal energy storage (Zalba et al., 2003)	7
Figure 2.2 Classification of energy storage materials (Abhat, 1983)	10
Figure 2.3 Various form of capsules (Banaszek, et al., 1999)	16
Figure 2.4 Schematically of air suspension coating(Yin, 2009)	18
Figure 2.5 Schematic illustrating the process of micro-encapsulation by spray-drying	21
Figure 3.1 Melting of paraffin wax	29
Figure 3.2 Adding ammonim per sulfat	29
Figure 3.3 Filtering of solution by filter paper.....	30
Figure 3.4 The solution after 1h.....	30
Figure 3.5 The solution after 2h.....	31
Figure 3.6 The solution after 3h.....	31
Figure 3.7 The solution after 4h.....	32
Figure 3.8 schematic of typical reaction of polyaniline and Ammonium persulfat.....	33
Figure 3.9 DSC machine	34
Figure 3.10 Thermogravimeter machine.....	35
Figure 3.11 The FESEM machine.....	36
Figure 3.12 TEM machine	37
Figure 3.13 The FT-IR machine.....	38
Figure 4.1 (a) Melting process of paraffin wax (b) Solidifying process of paraffin wax	40
Figure 4.2(a) Melting process of capsule S1 (b) Solidifying process of capsule S1	41
Figure 4.3Figure 4.4 (a) Melting process of capsules S3 (b)Solidifying process of capsules S2	41
Figure 4.4 (a) Melting process of capsules S3 (b)Solidifying process of capsules S3	42

Figure 4.5(a) Melting process of capsule S4 (b) solidifying process of capsule S4	42
Figure 4.6 The melting curve of the paraffin wax, PAn, S1, S2, S3, and S4.....	45
Figure 4.7 DSC solidifying curve paraffin wax, S1, S2, S3and S4	45
Figure 4.8 FESEM results of the (a) capsules S1, (b) capsules S2(c) capsules S3and (d) capsules S4.....	47
Figure 4.9 SPSS analysis	48
Figure 4.10 TEM result of the capsules (a)S1,(b)S2,(c)S3,and(d)S4	49
Figure 4.11 TGA and DTG result of capsule S1.....	51
Figure 4.12 TGA result of paraffin wax, PAn, S1, S2, S3, and S4.....	52
Figure 4.13 FTIR results of the paraffin wax and PAn.....	53
Figure 4.14 FTIR results of capsules S1, S2, S3, and S4.....	54

Nomenclatures

APS	Ammonium peroxydisulfate
DSC	Differential Scanning Calorimeter
DTG	Derivative thermogravimetry
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier transform infrared spectrophotometer
M/F	Melamine–formaldehyde
MEPCM	Microencapsulation phase change material
PAn	Polyaniline
PCM	Phase change material
PETMP	Polythiol pentaerythritol tetrakis 3-mercaptopropionate
PMF	Polymelamine–formaldehyde
SMA	Styrene maleic anhydride
TEM	Transmission electron microscope
TES	Thermal energy storage
TGA	Thermogravimetry analyzer
U/F	Urea–formaldehyde

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND OF STUDY

Nowadays, renewable energy has drawn most attention for scientists. It has been used for providing solar water heating and application for space heating over the few years ago (Hassan E.S, 1995). Otherwise, there are some problems for using renewable energy such as, intermittent of solar radiation because it is completely related to time, weather condition and its latitude. Beside source of energy and demand do not match each other. Thus scientist have been solved this problems by using energy storage. Therefore, thermal energy storage (TES) has been considered by many Scientifics that is one of the technologies for storage of energy (Dincer & Dost, 1996).

TES has a thermal storage mass that can store heat. In general, TES has been classified by sensible, latent and thermo chemical energy. Among these three types of energy storage, the most attractive form is latent heat in the field of phase change material (PCM). Further advantages of energy storage materials include as:

- Decrease in the equipment size,
- More efficient and effective use of equipment,
- Conservation of fossil fuels,
- And reduction in green house gas emissions such as CO_2 (Rosen, 2002).

In the latent heat storage system, choice of the PCM and its selection criteria are the main factors. Most of the researchers have been focused on organic material such as paraffin, non paraffin, salt hydrate and eutectic organic and inorganic compound (G. Lane, 1986).

Between these materials, paraffin wax is more attractive because it has some desirable properties like chemical stability, negligible super cooling, non poisonous, self nucleating, low vapor pressure in the melt and low cost (A.Abhat, 1978). Thereby, in this study paraffin wax has been selected as a suitable PCM.

The application of paraffin wax that used for thermal energy storage (TES) has some limitation. For instance, it has low thermal conductivity around 0.18W/mK, large change in volume during phase transition, oxidation of paraffin wax with air that can toxic our environment (G. Lane, 1986), and one of the properties of paraffin wax particles that was used for thermal storage was its sticky form. Therefore, these particles can stick together and clogging occurs in the storage system of heat (Winters, Bridge, Co, Buildings, & Systems, 1991). Thereby, it is declined energy storage capacity by these limitations.

Many researchers have studied the improvement of heat transfer by using slurries, scrapers and agitator in heat exchanger (Patel, 1968), (Patankar, 1980), (Fouda, Despault, Taylor, & Capes, 1980), and (Yanadori & Masuda, 1989). Therefore, one of the drawbacks of these methods was the high cost and complexity of thermal energy storage application. In order to solve these problems, Hawlader et al. have been reported that PCM should be bounded by a secondary supporting structure and the application of packed/fluidized bed heat exchanger is a better way of heat transfer enhancement (Hawlader, Uddin, & Zhu, 2000). Thus, heat storage material and development of heat exchanger are most important factor for quick charging and discharging heat transfer rate in the latent heat storage process. The suitable surface of heat transfer should be large enough to maintain low temperature gradient over these process (Banaszek, Domański, Rebow, & El-Sagier, 1999) .

Microencapsulation is the process that the droplets of materials (Core) are coated by thin film (coating). Thus, the core has been protected by microencapsulation (Sheu & Rosenberg, 1995). Encapsulation processes have been used in different field of study like

food industry, biomedical, pharmaceutical industry and coating of PCM for high heat storage application.

1.2 OBJECTIVES OF STUDY

The overall objectives of this study are:

- To synthesize microencapsulated paraffin wax
- To determine characterization of encapsulated paraffin wax

1.3 Research Scopes and Methodology

In this report, microencapsulation of paraffin wax with Polyaniline (PAn) Shell was fabricated as thermal energy storage materials by in-situ polymerization method. Short term behavior of the microencapsulated paraffin wax is characterized by DSC, TGA, TEM, FESEM and FTIR. A well-organized methodology is always essential to obtain a good comprehension of what should be done. This can be done by:

- To have a most comprehensive Literature review for beginning the study.
- To prepare the all materials which are needed in present case.
- To fabricate the samples with the mentioned process.
- To characterize and analyze the samples.
- Documentation and thesis preparation.

The methodology of this research is shown in the following flowchart. (Figure 1.1)

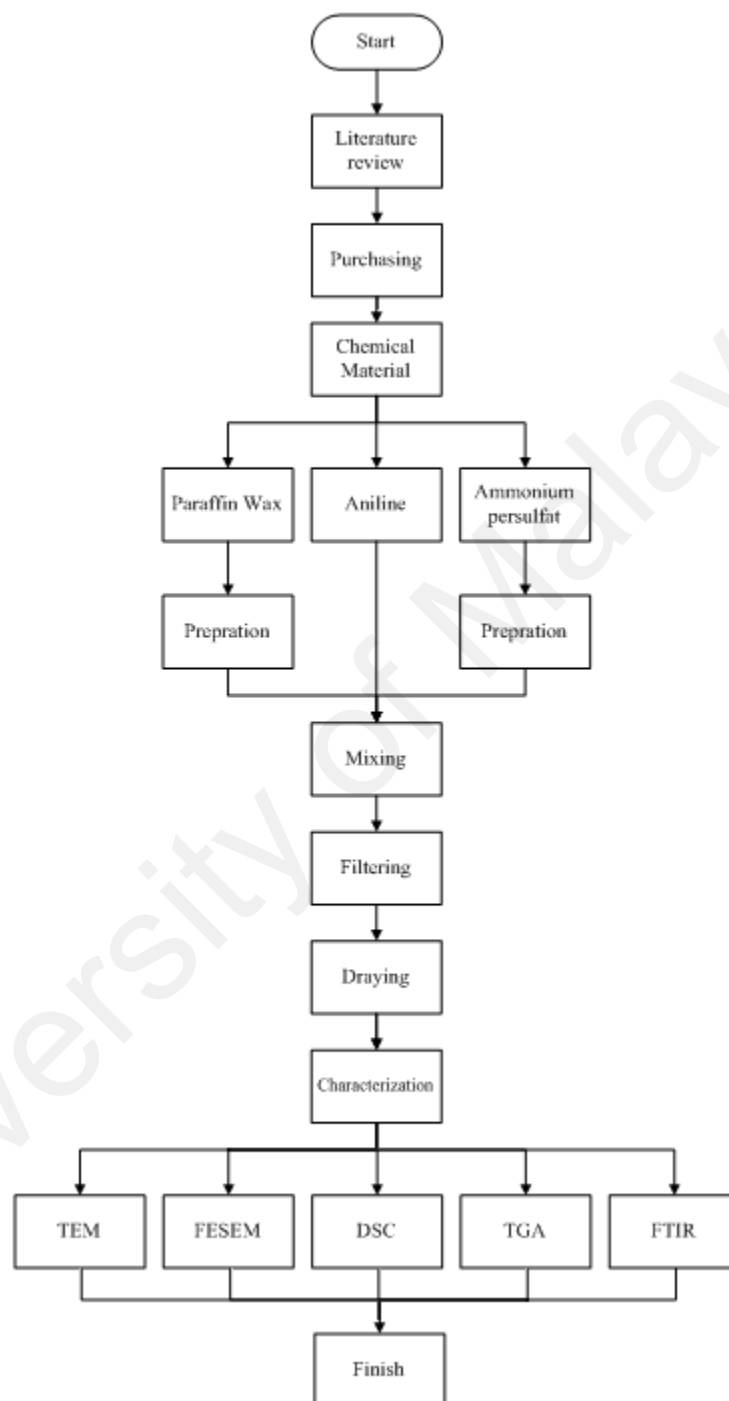


Figure 1.1 Methodology flowchart

1.4 ORGANIZATION OF THIS DISSERTATION

This dissertation adopts a university Malaya style guide to presentation, logically aimed and systematically rendered to enhance understanding of the research.

This thesis is comprised of five chapters including

Chapter one of this study introduced the background and importance of study and objective of study and methodology.

Chapter two presents literature review on renewable energy, thermal energy storage method and the materials that are used for latent heat storage.

Chapter three presents a list of materials used in this experiment, the method of this experiment, the evaluation techniques and the equipments used for characterization of microencapsulated paraffin wax.

Chapter four presents the result and discussion of characterization of encapsulated paraffin wax.

Chapter five summarizes the conclusion of the present work and recommendation for future work.

CHAPTER 2: LITERATURE REVIEW

In this chapter, literature review on some methods of thermal energy storage and their merit and demerit are presented. Furthermore, the study of thermal energy storage, encapsulation of PCMs and the method of encapsulation PCMs have been included.

2.1 Thermal energy storage

A wide variety of thermal energy storage methods have been developed over the last four or five decades for the purpose of conserving fossil fuels and achieving economical benefit. Storage of thermal energy plays an important role in many engineering applications such as space, water cooling and heating and air conditioning (Rosen, 2002). For instance solar energy is available during a sunny day so, we need to collect excess heat during sunshine and later to use during the night. (Zalba et al., 2003) gave a useful area of research in thermal energy storage system that shows in Figure 2.1.

2.2 Thermal energy storage methods:

Thermal energy storage can be classified to two main parts:

- Sensible heat storage
- Latent heat storage

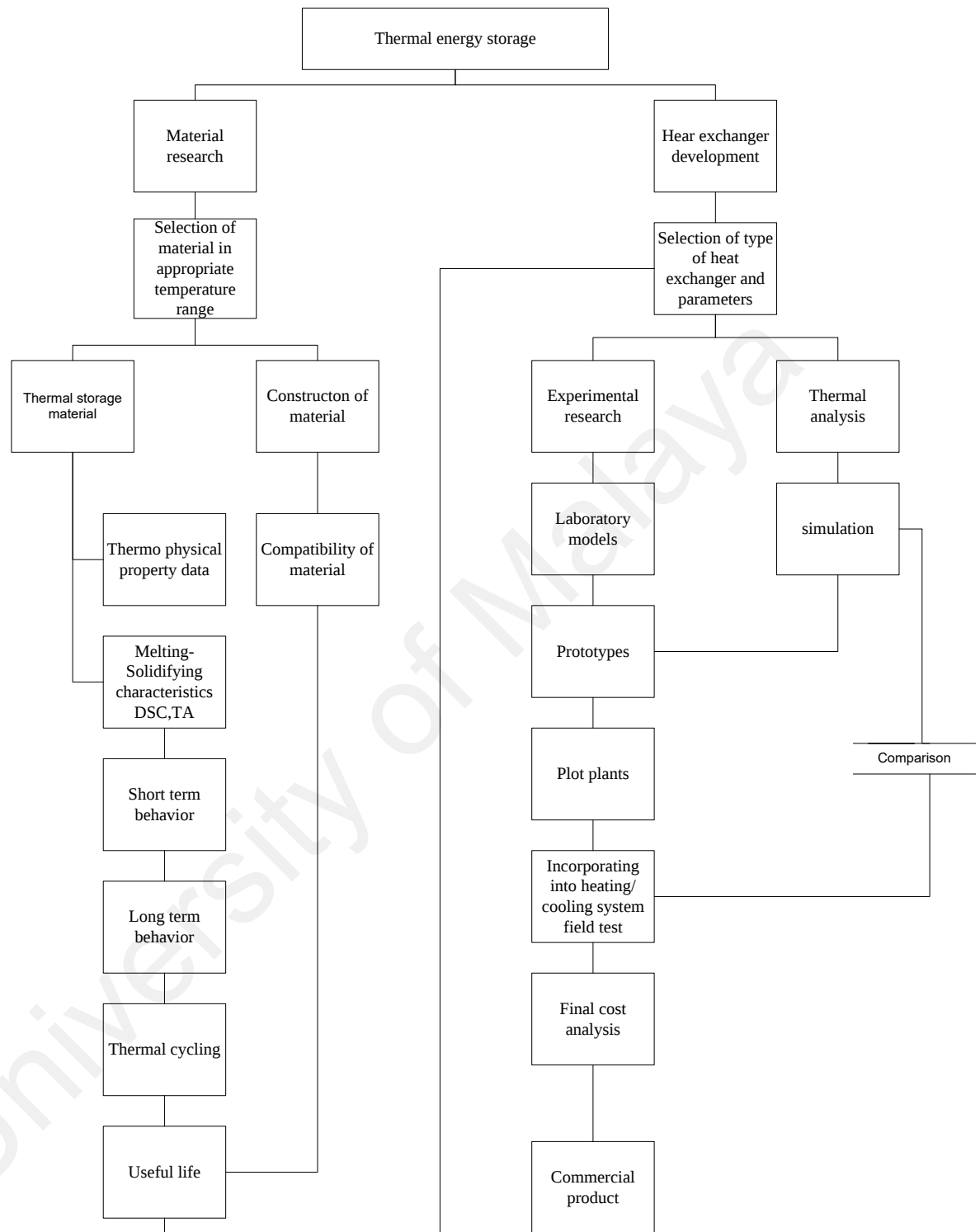


Figure 2.2 Research area of thermal energy storage (Zalba et al., 2003)

2.2.1 Sensible heat storage

The material used for energy storage can be in the form of liquid or solid. This means of energy storage is called sensible heat storage and can happen in material such as water, molten salt, rock and metal. Desirable Storage media should have high heat capacity, long term stability during thermal cycling, compatible with container and low cost. The different factors playing role in amount of heat storage include specific heat, the change in temperature and the amount of storage material. Sensible storage has been classified based on the storage media by solid media storage and liquid media storage. Water has been used for low temperature storage media as liquid medium because it has widely available, cheap and high heat capacity.

2.2.2 Latent heat storage

Storage by phase change like solid to liquid or liquid to vapor could also be another way of thermal energy storage which is called latent heat storage. This mechanism stores energy in a category of materials called phase change materials (PCM) (Hasnain, 1998).

2.2.3 Comparison of sensible and latent heat storage

One of the advantages of latent thermal energy storage is that it provides great energy storage density and has much capacity to store latent heat with a slight temperature range, for instance the required energy for melting 1 kg of ice is 80 times more than that for increasing the temperature of 1 kg of water 1°C.

The heat exchanger size of sensible heat TES can be small because the heat transfer medium can be pumped from the heat exchanger to storage tank. On the other hand, in the latent heat the heat exchanger of the thermal energy storage (TES) system must be incorporated into storage device thus the storage medium must be solid when it charged. So

it could not be pumped. Since the price of the heat transfer area in heat storage part is expensive. Thus one of the challenges in latent heat thermal energy storage is the cost of this part (Lorsch, Kauffman, & Denton, 1975). Table 2.1 shows the comparison between the sensible and latent heat storage media.

Table 2.1 Comparison between sensible and latent heat storage media

	Heat Storage Media			
	Sensible Heat Storage Media		Latent Heat Storage Media	
Properties	Rock	Water	Organic PCM	Inorganic PCM
Storage Mass for Storing $10^6 \text{kJ}(\text{kg})$	67000	16000	5300	4350
Storage Volume for Storing $10^6 \text{kJ}(\text{m}^3)$	30	16	6.6	2.7
Relative Volume	11	6	2.5	1

2.3 Candidate heat storage materials

Most of articles have significant focus on phase change material and classified TES material to organic which includes paraffin, non paraffin and their eutectic compound and inorganic including salt hydrates and their eutectic compound (Abhat et al., 1983; Sharma et al., 2009). On the other hand, there are numerous papers on this topic between the years of 1997 and 2010 like (Agyenim et al., 2010; Cabeza et al., 2011; Mohammed M. Farid, et al., 2004; Hasnain et al, 1998; Sharma, et al., 2009; Zalba, et al., 2003). Figure 2.3 provides the overview of classification of thermal storage material.

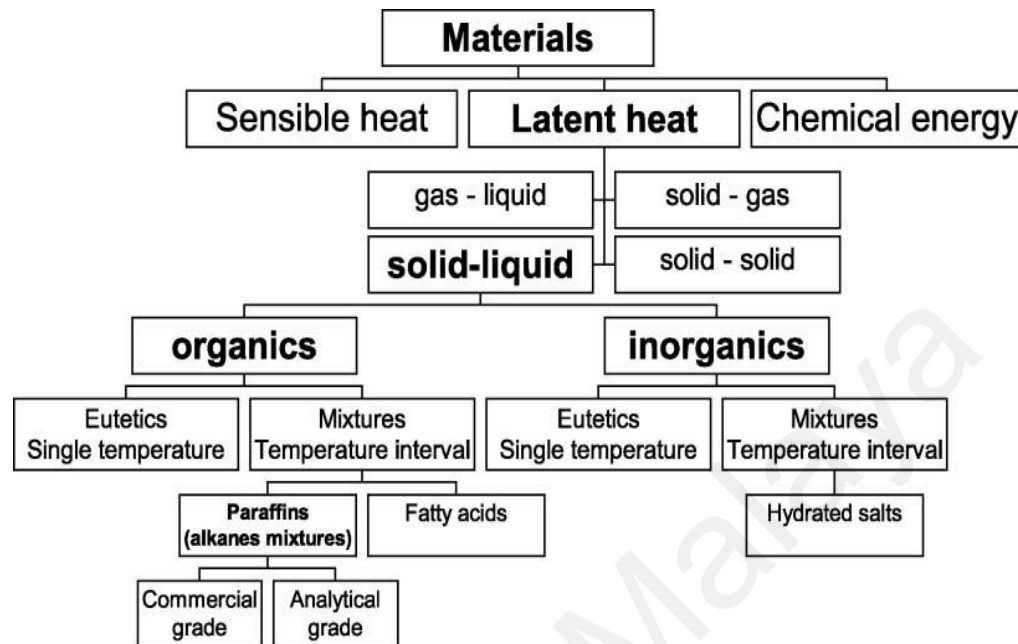


Figure 2.3 Classification of energy storage materials (Abhat, 1983)

2.3.1 Organic PCM

Organic materials are classified to paraffin and non paraffin compound. Most of the organic materials have some properties like melt without any segregation on their phase that called congruent melting and the other one is self nucleating due to the structure of material that is along with no super cooling and some time without any corrosion (Sharma, et al., 2009). We shall examine some of the important components and advantages and disadvantages of organic material.

Paraffins

One of most familiar components is paraffin materials. It is characterized by $C_nH_{2n+2}(CH_3-CH_2-CH_3)$. The rate of melting point and heat of fusion are raising with increase the amount of Carbon. Pure paraffin is so expensive thus we have to use commercial paraffin. Commercial paraffin waxes are inexpensive but have some properties

such as low thermal conductivity, supercooling and segregation in phase change. We can use metallic filler, metal matrix, finned tube, aluminum shaving and embedding aluminum powder in the wax (Mettawee & Assassa, 2007) for improve low thermal conductivity of paraffin wax furthermore to overcome the instability of volume change during melting and freezing plastic container were used (Hasnain, 1998). Beside, properties of some commercial paraffin wax are investigated on (M.M. Farid & Mohamed, 1987; Mohammed M. Farid & Kanzawa, 1989; Mohammed M. Farid, Kim, & Kansawa, 1990; Himran, Suwono, & Mansoori, 1994). Moreover P-116 paraffin wax with melting point 47° and latent heat lower than 210 kJ/kg is considered suitable for solar energy (Lorsch, et al., 1975). The physical properties of some paraffin with a variety of oil content investigated on (A.Abhat, 1978) that found all organic material is non-corrosive and the paraffin with 5% content oil is suitable for freezing.

In general, there are some advantages for paraffin compound such as,

- High heat of fusion (available in vast of temperature range)(Abhat, 1983) ,
- Congruent melting ,
- Non corrosion,
- Good nucleating,
- Less expensive ,
- Chemical stability ,
- Low vapor pressure and without any segregation on the other hand.

Also, there are some disadvantages like

- Low thermal conductivity
- Lower phase change enthalpy
- And Toxicity.

Non paraffin

One of the prominent organic component is Fatty acid that can be showed by $\text{CH}_3(\text{CH}_2)_{2n}\text{COOH}$ with high heat of fusion as well as paraffin compound. Abhat et al. investigated six of fatty acid within the temperature $20^\circ\text{--}80^\circ$ that involved Caprilin, Caprin, Laurin, Myristin, Palmitin and stearin acid (Abhat, 1980). As a result of DSC and TA measurement of six fatty acids has shown that it is suitable for melting and freezing properties. Hasan et al. has been indicated DSC measurement of some fatty acid which is suitable for domestic water heating system (Hasan & Sayigh, 1994). The result has shown that myristic acid and palmitic acid and stearic acid have melting point between 50°C and 70°C . The new form-stable of fatty acid is presented by (Cemil Alkan & Sari, 2008) that is suitable for floor space heating and passive solar space heating. The mixture of lauric acid and capric acid has been investigated by (Dimaano & Watanabe, 2002) which has melting temperature $18\text{--}19.5^\circ\text{C}$. The result has shown that it is suitable for latent heat storage material.

2.3.2 Inorganic PCM

Many of the inorganic components like salt hydrate have some advantages compare to organic materials because of the high latent heat storage per unit volume which is related to greater density of salt hydrate. However, high heat storage density of this material is difficult to maintain and sometimes declines during the cycle. This is because of some irreversibility that happened for salt hydrate.

Salt hydrate

Salt hydrates are renowned materials that are fabricated during the forming of inorganic salt and water and are characterized by $A \cdot nH_2O$. Hydrate salted can be used in thermal energy storage due to their volumetric energy storage around 350 MJ/m^3 , high thermal conductivity, less expensive (to compare the cost of the paraffin wax) (Mohammed M. Farid, et al., 2004). Some of the properties of inorganic salt hydrate which is suitable for solar energy examined by (Lorsch, et al., 1975) like $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with melting point 95°C and great storage density 234 MJ/m^3 is considered. Hasan et al have been selected some fatty acid such as myristic acid, palmitic acid and stearic acid which have the melting temperatures between 50°C and 70°C and also it is suitable for a domestic water heating system (Hasan & Sayigh, 1994). Besides, chemical property of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ are shown that they are corrosive against Cu and Aluminum sequentially (A. Abhat, 1978).

Gluber salt is the name of the sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) therefore, it occurs as white and colorless. Melting temperature and latent heat of gluber salt is 32.4°C and 250 KJ/kg sequentially. Also It has low cost that it is made suitable for use in solar energy and off peak air condition (Lorsch, et al., 1975). Pure Gluber salt have some disadvantage such as incongruently melting point, under cooling and nucleating that can be solve with adding some borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) for prevent nucleating (Marks, 1980). . In conclusion, there are some advantages for salt hydrate such as

- High phase change enthalpy and thermal conductivity,
- Compatibility with plastic (because it is corrosive with aluminum and iron),
- less expensive,
- inflammability,

- And non toxicity.

On the other hand there two main problems for salt hydrate, the primary problem is segregation and the second one is supercooling .

Segregation could be solved by changing the properties of this material with adding to another material that can be prevent the heavier phases. This could be possible with gelling means that cross link material to the salt hydrate like polymer or thickening of salt hydrate means increase the viscosity of salt hydrate by adding the material. Secondly supercooling is another problem that included all the salt hydrate. It obvious when a salt hydrates start to become solid at the temperature below its solidify temperature. It has been solved by direct contact between unmixable heat transfer fluid and the salt hydrate material(Furbo, VERS, DENMARK, & NR, 1980).Another method is using nucleator(Cabeza, et al., 2011). Beside, amount of supercooling could be declined by using glass container and containing a petty bed of the salt hydrate (Abhat, 1980).

2.4 Eutectic mixture

Eutectic materials are blend of two or more component that have different congruent melting and freezing point. Eutectic mixtures have never been segregation because they freeze to intimate mixture of crystal thus don't have any opportunity for separate of component(Sharma, et al., 2009). A wide variety of eutectic mixture have been indicated on(G. A. Lane, 1983). Yoneda et al. have shown thermodynamic properties of inorganic eutectic mixture that is suitable for solar heat storage due to high heat of fusion (Yoneda & Takanashi, 1978) has shown thermodynamic properties of inorganic eutectic mixture that is suitable for solar heat storage due to high heat of fusion. Thermo physical property and DSC measurement of eutectic mixture of palmatic acid and stearic acid have been determined by(Baran & Sari, 2003). The binary system of palmitic and stearic acids in the

mixture ratio of 64.2:35.8 wt% forms a eutectic, which melts and solidifies at an approximately isothermal phase transition temperature of 52.3°C and has a latent heat of 181.7 J/g⁻¹. There is no subcooling during the solidification. Thus, the phase transition temperature and fusion heat of the mixture make it possible to use for heat storage in passive solar space building heating applications and solar domestic water heating with respect to the climate conditions. Thermal properties and conductivity of stable form of the eutectic mixture (expanded perlit with mystric acid and capric acid) are investigated on(Karaipekli & SarI, 2008). The result has shown that the stable form of CA-MA/EP with 10wt% expanded graphite is suitable for low heat thermal energy storage material in building.

2.5 Encapsulation of phase change material

Many researchers have been interested for developing encapsulation of PCM (Zalba, et al., 2003). In general, there are two kinds of encapsulation, micro-encapsulation and macro-encapsulation (Royon, Guiffant, & Flaud, 1997). In order for capsules to have useful properties tiny particle can be surrounded by a coating this process is called micro encapsulation. According to the simple form of microencapsulation is sphere due to uniform wall about it and usually have been used for material smaller than 1 mm in diameter .However it is coated by macro encapsulation that have diameter larger than 1cm (Zalba, et al., 2003). There are varies form of encapsulation like simple coating which is wall for spherical and irregular shape, multi wall structure that is walls of the similar or different composition. Another kind of encapsulation is matrix type which is includes matrix micro particles resemble. Both of the matrix and capsule provides most of the requirements like moisture and physical containment. Moreover the characteristics of

coating material have been shown on (KHIN, 2003). Table 2.2 shows some published encapsulation of PCMs.

The materials have been used for encapsulation PCM should have the following characterization:

- High thermal stability;
- Stable to environment condition;
- Stable to UV exposure, barrier to moisture, air;
- High thermal conductivity;
- Not corrosive of PCM into coating materials;
- No migration of PCM into coating material;
- No reaction between PCM and coating materials.

Generally, there are some advantages for using encapsulation material like

- Rising the rate of heat transfer ;
- Avoiding some problem such as supercooling and phase separation;
- Using PCM with different melting temperature;
- Reducing reaction between the PCM and outside;
- And control the volume of storage material (Mohammed M. Farid, et al., 2004).

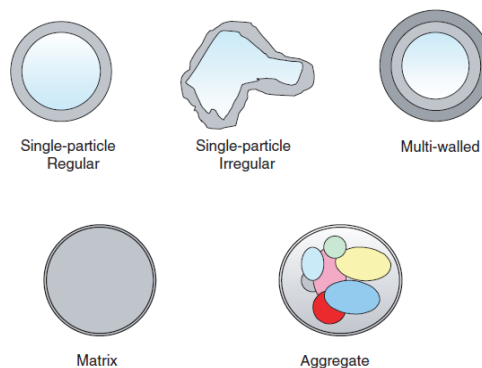


Figure 2.4 Various form of capsules (Banaszek, et al., 1999)

Table 2.2 List of published encapsulated PCM systems

Investigator and year	Core materials	Coating materials	Methods	Type of capsules	applications
Brown et al.1998	Octadecan and paraffin wax	Polymethylene-urea,cross-linked nylon,and gelatin	Interfacial polymerization	Microencapsulation	Gas-fluidized bed
Salyer, 1999	Eutectic PCM	Polyesters resin	Interfacial polymerization	Matrix type microcapsules	Insulation materials for using clothing or bedding articles
Xiao et al.2000	Paraffin wax	Syrene-butadien-styrene copolymer	Interfacial polymerization	Matrix type macro encapsulation	Latent heat storage materials for thermal storage units
Hawllader et al.2002	Paraffin wax	Gelatin and acacia	Complex coaceravation	Matrix type microencapsulation	Packed bed heat exchanger
Jin et al. 2008	Paraffin	Urea-formaldehyde	In situ polymerization	Microencapsulation	Energy conservation
Fang et al.2010	Paraffin	SiO ₂	Sol-gel method	Microencapsulation	Thermal energy storage
Pan et al.2011	Palmitic acid	AlOOH	Interfacial polymerization	Microencapsulation	Thermal energy storage

2.6 Method of microencapsulation

Different methods are used for encapsulation. In general, there are two kind of microencapsulation such as physical and chemical methods. Thus, Spray drying and fluidized bed methods are as a physical process .Also, the chemical method like simple and complex coacervation, in-situ polymerization and interfacial polymerization (Zhao & Zhang, 2011) . The selection of a method depends on economics, properties of the core and wall material, microcapsule size, application and release mechanism. In this study, the overall reviews on the method of microencapsulation are presented.

2.6.1 Air suspension

This method known as the Wurster process or fluidized bed coating involves dispersing solid particulate core materials in a supporting air stream and the spray coating of suspending materials. The flow of particles recirculating through the coating section is affected by the way the chamber and the related parameters are designed. In this section usually a polymer solution would be sprayed into the fluidized particles (Figure 2.5). When a desired coating thickness is achieved, the cyclic process will be stopped. The process is generally considered to be applicable to the encapsulation of solid core materials. Extensive research has been carried out using this method of encapsulation (DeZarn, 1995).

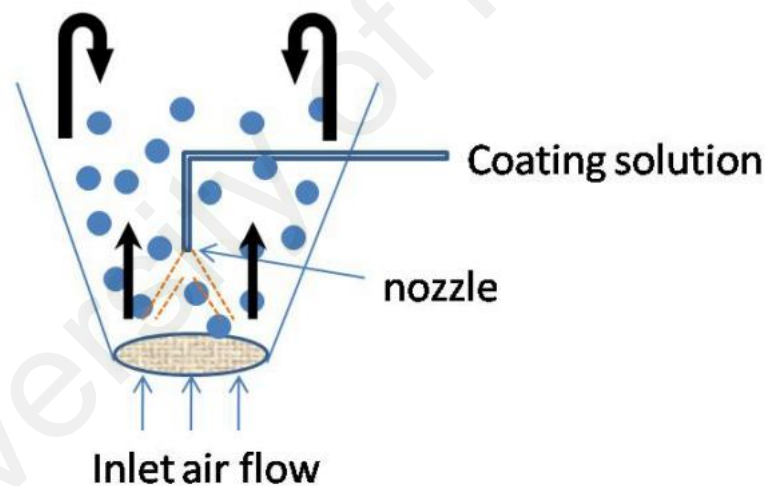


Figure 2.5 Schematically of air suspension coating(Yin, 2009)

2.6.2 Coacervation-phase separation

One of the most popular methods generally focused on is the encapsulation by coacervation. Coacervation includes separating the macromolecular solution into a dense coacervate phase as well as a dilute equilibrium phase. The first phase is concentrated in the molecules and the two mentioned phases are immiscible. The process includes 3 main steps

along with continuous agitation. First step is the dispersion of core material into the coating polymer solution. Second step is to complete the coating deposition by physically mixing of the material in an aqueous phase which is controlled. Final step would be to form microcapsules which are self-sustaining by the use of thermal, cross-linking or desolvation techniques to ruggedize the coating.

Coacervation mainly is classified into two types: simple and complex. Simple coacervation includes using one colloid such as gelatin in water, and removal of the generated water from the dispersed colloid by agents with a greater affinity for water, such as various alcohols and salts.

Simple coacervation is induced by a change in conditions such as the addition of non solvent, the addition of micro ions or a temperature change resulting in molecular dehydration of the macromolecules. Complex coacervation is driven by electrostatic interaction between two or more macromolecules. Complex coacervation is a common method of microencapsulation. On phase separation by complex coacervation, tiny coacervate droplets are formed which coalesce and sediment to form a separate coacervate phase. If a core material is present in a polyion system prior to complex coacervation, then the coacervate will deposit on and coalesce around those particles. Agitation of the coacervate system by stirring or other means can prevent coalescence and sedimentation of the coacervate droplets. The coacervate droplets can be cross-linked to form stable microcapsules by addition of a cross-linking agent, such as glutaraldehyde, or the use of heat.

Complex coacervate formation is dependent on a number of factors such as pH, ionic strength, macromolecular weight, concentration and mixing ratio charge is the most significant factor for complex coacervation. Complex coacervation system

includes gelatin-acacia, carbopol-gelatin, pectin-gelatin, gelatin-gelatin, sodium carboxymethylcellulose-gelatin.

Although successful coacervate microencapsulation systems have been done at specific pH, they require stabilization by the use of cross-linking agent or heat and the extent of cross-linking determines the retention of encapsulate. Gluteraldehyde and formaldehyde are commonly used as cross-linking agents for protein-polysaccharide complex coacervate systems such as gelatin-acacia. A condensation reaction occurs between the amino groups of the protein and the aldehydes. Since the core materials are microencapsulated while being dispersed in aqueous phase, subsequent drying operations are usually required (Luzzi & Gerraughty, 1964).

2.6.3 Solvent evaporation technique

The process is carried out in a liquid manufacturing vehicle. The coating material and core material are dissolved in an immiscible solvent and a coating polymer solution respectively. In order to obtain the suitable size of microcapsule, the core coating material mixture would be dispersed in the liquid phase along with agitation. The mixture can be used in suspension form, coated onto substrates or isolated as powders (Risch, 1988).

2.6.4 Spray coating process

spray drying can be used for microencapsulation, even though traditionally it has been mainly associated with drying of materials. It can be explained as the change of fluid feed form into a dried particulate feed by spraying it into a hot drying medium. This feed can either be a solution, suspension or paste (Newton, 1966).

There are mainly 4 stages in the process of spray drying : one is to atomize the feed to be sprayed. Next is the contact between atomized feed and air also known as mixing and

flow. Third stage is the drying of spray in which moisture evaporates. And finally the dried product will be separated from the air.

The rate of moisture evaporation will be relatively high, causing the temperature of the product to be significantly lower than that of the drying air exiting the drying chamber. The product is thus not subjected to high temperatures and heat degradation (Masters, 1979). Spray congealing and spray drying are similar since they both involve the dispersion of core material into a coating substance in a liquid form. Coat solidification can be done either by congealing the molten coating material or solidifying a dissolved coating material by putting coating-core material mixture into a non-solvent. Afterwards sorption, extraction or evaporation techniques would remove the non-solvent from the mixture. Waxes, fatty acids and alcohols, polymers and sugars, which are solids at room temperature but meltable at higher temperatures, are applicable to spray congealing methods (Blenford, 1986)(Figure 2.6).

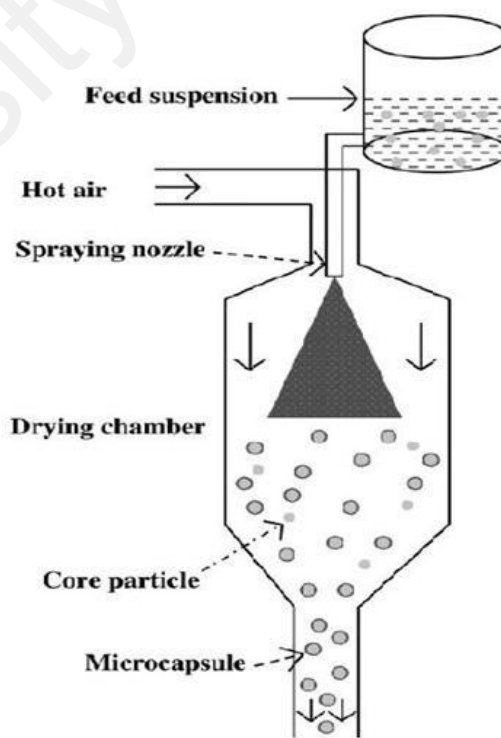


Figure 2.6 Schematic illustrating the process of micro-encapsulation by spray-drying

2.6.5 Interfacial polymerization

When various monomers existing at the interface of two immiscible liquids react to make an encapsulating polymer film for the disperse phase interfacial polymerization occurs. Usually two reactive monomers are employed, one dissolved in the aqueous disperse phase containing a solution or dispersion of the core material, and the other dissolved after the emulsification step in the non-aqueous continuous phase. The water-in-oil emulsion formed requires the stabilizer. The monomers diffuse together and rapidly polymerize at the interface between the phases to form a thin coating, and the by-product of the reaction is neutralized by alkaline buffer. The degree of polymerization can be controlled by the reactivity of monomers chosen, their concentration, the composition of either phase vehicle, and by the temperature of the system. The reaction between monomers is quenched by depletion of monomer, which is frequently accomplished by adding excess continuous phase solution to emulsion .

2.6.6 In-situ polymerization

Generally, In situ polymerization included mixing two immiscible liquids such as water and organic solvent respectively, coating complimentary, direct acting, organic intermediates reacting with each other establishing a solid pre-condensate (Sarier & Onder, 2007). The method of in-situ polymerization and interfacial polymerization are similar to gather however there are no reactants in the core material of in-situ polymerization method. As in interfacial polymerization all polymerization usually takes place in the continuous phase, rather than two phases. Melamine-formaldehyde (M/F) and urea-formaldehyde (U/F) had been applied as the shell material, because of their good chemical stability. However, inevitable remnant formaldehyde may be produced after the shell is formed, which leads to the environmental and health issue during the polymerization process. The

in situ process is capable of yielding microcapsules with the best quality regarding diffusion-tightness of their walls with a size ranging between 5 and 100 μm (Zhao & Zhang, 2011). Therefore, as it can be noted that in situ polymerization method has been commonly implemented in preparation of microencapsulated PCM.

Sarier et al. studied on three kinds of paraffin ($\text{C}_n\text{H}_{2n+2}$), n-hexadecane, n-octadecane and n-eicosane, were preferred for the encapsulation (Sarier & Onder, 2007). Moreover, they are neither toxic, nor corrosive, chemically inert, and odorless. They stated that to improve the thermal capacities of fabrics or to make their phase transition intervals larger, it is preferred to use a combination of microcapsules having different types of PCMs or paraffin waxes instead of those with mixture of them. For the shell material, in situ polymerization microencapsulation process was performed to synthesize the MEPCM with melamine resin and for the core material; n-docosane ($\text{C}_{22}\text{H}_{46}$) was used (Rao, Lin, Luo, Chen, & Wang, 2007). The results showed that to reach a MEPCM particle size of ca. 10 μm , the required stirring speed would be equal to 6000 rpm and in order to get higher microencapsulation efficiency for the core material during the preparation process, the core mass fraction in a single MEPCM particle is below 70%. DSC thermal analysis also demonstrated that the prepared MEPCM with a core mass fraction of 60% owned a high heat of fusion equal to 150 kJ/kg. Li et al. also fabricated microcapsules utilizing n-octadecane as core and M/F as shell along with low remnant formaldehyde content (Li, Zhang, Wang, & Niu, 2007). Incorporating formaldehyde once and melamine three times the employed MF pre-polymer was synthesized. It was outlined that with the rate of the MF pre-polymer being reduced, the flocculation phenomenon of microcapsules also becomes lower and the globular surface becomes smoother; and finally the thermal stability becomes augmented regularly. A narrow diameter distribution were reported and also an average diameter of 2.2 μm for the microcapsules. M/F microcapsules containing with active ingredients for intumescent flame

retardant system were fabricated (Salaün & Vroman, 2008). It was discovered that thermo-physical properties of MEPCM were remarkably dependant on the core content as well as the synthesis conditions; particularly the thermal conductivity were dependant on the chemical structure of the shell while the heat capacity is relevant to the material making up the core. Using curing agent Yuan et al. prepared microcapsules for epoxy with polymelamine-formaldehyde(PMF), high-activity polythiol pentaerythritol tetrakis 3-mercaptopropionate(PETMP) as the shell material and as the core material respectively (Yuan, Rong, & Zhang, 2008). They expressed the appropriate reaction time to be 40–60 min. In order to prevent the microcapsule from collapsing and shrinking reaction temperature should be about 50 °C. The pH value of the capsules was reported to be about 2.9–3.2. The feeding weight ratio of core/shell monomers also is to be adjusted at the value of 2.3. Dispersion rate and emulsifier content were effective on the size of microcapsules. In the experiment by Yu et al. microcapsules containing n-dodecanol using M/F resin and styrene maleic anhydride copolymer (SMA) were fabricated as shell and as emulsifier respectively. It was postulated that thermo-physical properties of MEPCM were strongly influenced by the type as well as the values of SMA. They also showed that if the mass ratio of emulsifier to n-dodecanol were 4.8%, a maximum value of 187.5 kJ/kg and 93.1% for the phase change latent heat and encapsulation efficiency were obtained. A series of microencapsulated phase change materials (Micro-PCMs) based on n-octadecane core and resorcinol-modified melamine-formaldehyde shell was produced by the use of different emulsifiers (Zhang & Wang, 2009). The authors stated that the SMA acted as an optimal emulsifier for preparation of the microcapsules. It was also mentioned that microcapsules having a core/shell weight ratio of 75/25 with SMA owned a compact shell surface and an average particle size lower than 20 µm. This sample demonstrated improved phase change properties along with an encapsulation efficiency of 92%. In the research by Alkan et al. (C.

Alkan, Sari, Karaipekli, & Uzun, 2009) also, microcapsules using docosane and PMMA as the core and material as the shell material subsequently, were fabricated. It was concluded that microcapsules owned smooth and compact surface with mean diameter equal to 0.16 μm . Thermal gravimetric analysis (TGA) showed that microcapsules possessed acceptable chemical stability. The thermal cycling tests as well, demonstrated proper thermal reliability for the microcapsules.

2.6.7 Dip coating

The process is an apparently simple means of encapsulation involves single or repeated dipping of cores into a coating solution, allowing the excess to drain off and drying. However, because of the static nature of the process, the major difficulty encountered is damaged to the coating as cores separate from contact with each other and the mechanical support used to hold them while being coated.

CHAPTER 3: MATERIAL AND METHOD

3.1 Introduction

In this chapter, all the materials which were applied in this experiment and the method of fabrication will be presented. To evaluate mechanical properties of the samples, different mechanical tests such as compressive strength, hardness, elastic modulus, and flexural strength were carried out. SEM, FTIR, TEM, and TG/DTA were also conducted to analyze the samples.

3.2 Materials

The main characterizations of initial powders used in this experiment are paraffin wax, aniline and ammonium persulphate as core, coat and oxidant respectively.

3.2.1 Paraffin wax

Paraffin waxes are saturated hydrocarbon mixtures with general formulation C_nH_{2n+2} . It includes a variety of alkenes that are between $n=20$ and 40 . They are classified by organic materials. Moreover, paraffin wax has properties like odorless, tasteless, waxy solid and nontoxic. Paraffin wax has some properties like simple straight chains, normal-paraffinic hydrocarbons or branched chains, iso-paraffinic hydrocarbons ($CH_3-(CH_2)_n-CH_3$). The suitable paraffin waxes that have been used for thermal energy storage should be

normal paraffin wax (Warth, 1956). The characterization of used paraffin wax that is used in this experiment summarized in Table 3.1.

Table 3.1 The characterization of core

Materials	Vendor (company)	Formula	Properties
Paraffin wax	Griffin & George Limited	C_nH_{2n+2}	melting point: 57-70 °C

3.2.2 Aniline

One of the organic compound that was used in this study as the shell material was Aniline, phenylamine or aminobenzene. The formulation of aniline was C_6H_7N . It was consisted by phenyl group that were attached to amino group. The characterization of used monomer that is used in this preparation summarized in Table 3.2.

Table 3.2 The characterization of monomer

Materials	Vendor (company)	Formula	Properties
Aniline	Sigma Aldrich	C_6H_7N	93.13 g/mol

3.2.3 Ammonium persulfate

The most common synthesis of polyaniline is by oxidative polymerization with ammonium peroxodisulfate as an oxidant. The characterization of used oxidant that is used in this preparation summarized in Table 3.3.

Table 3.3 The characterization of oxidant

Materials	Vendor (company)	Formula	Properties
Ammonium persulfate	Sigma Aldrich	$(NH_4)_2S_2O_8$	228.20g/mol

3.3 Experiment

3.3.1 Preparation of samples

Typically, paraffin wax (0.1 g, 0.2g, 0.3g, 0.7g for S1, S2, S3, S4, respectively) were melted in deionized water (150ml) in a 300 ml beaker at 75°C, followed with stringing for 1h at the speed of 500 RPM (Figure 3.1). The beaker should be keeping on the silicon oil due to uniform heating rate. Next, adding aniline as a monomer (0.9ml, 0.8ml, 0.7ml, 0.3ml, respectively) to the breaker. Then, 2.28 g of the ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) was dissolved in deionized water (100ml) in the 300ml beaker at the same condition of the paraffin wax(Figure 3.2). Then, it was added into the beaker dropwise. The polymerization was performed under static condition at 75°C and 500 RPM. The resultants of microencapsules were filtrated by filter paper (Figure 3.3) and then drying at the room temperature for 24h .The color of the solution started to change gradually from the first hours (Figure 3.4). Initially it was green and after 2 hours the color changed to red(Figure 3.5) and for the third hour the red color became darker (Figure 3.6).Ultimately when the polymerization was completed it became almost black(Figure 3.7).Paraffin wax@PAn microcapsules were prepared by in situ polymerization of adsorbed aniline monomer on the surface of paraffin wax.



Figure 3.1 Melting of paraffin wax



Figure 3.2 Adding ammonim per sulfat



Figure 3.3 Filtering of solution by filter paper



Figure 3.4 The solution after 1h



Figure 3.5 The solution after 2h



Figure 3.6 The solution after 3h



Figure 3.7 The solution after 4h

3.3.2 Synthesis of polyaniline

Preparation of the Polyaniline is typically done by the chemical oxidation of aniline monomers (DC, 1997), ammonium peroxydisulfate (APS) considered as the most common oxidant. Aniline molecules when coupled with oligomeric/polymeric structures, release hydrogen atoms as protons, implying that sulfuric acid is a by-product. Consequently the pH keeps on decreasing in the course of aniline oxidation (Huang & Lin, 2009; Konyushenko et al., 2006). The typical reactions are given in Figure 3.8.

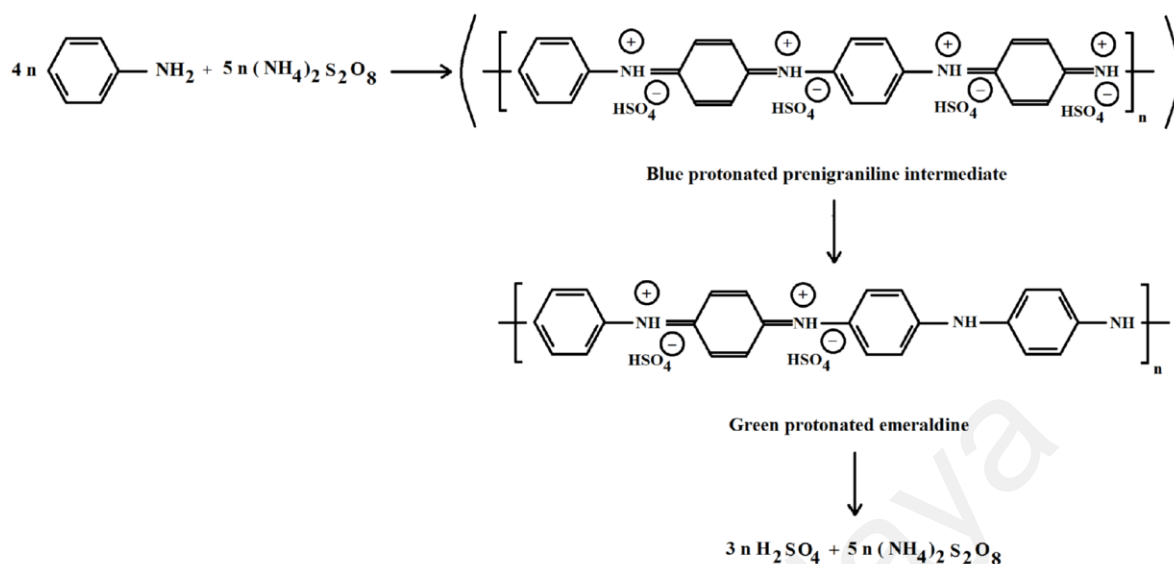


Figure 3.8 schematic of typical reaction of polyaniline and Ammonium persulfat

3.4 Characterization

3.4.1 Differential Scanning Calorimeter

The Differential Scanning Calorimeter (DSC), (Model: Perkin Elmer DSC 6) was used for micro thermal analysis of thermodynamic characteristics of the microencapsulated paraffin wax. In this evaluation, DSC was used to measure heat capacities and melting temperature of the samples.

A small amount of sample (3~20mg) placed in a small aluminium vessel was used for DSC analysis. An empty vessel was used as a reference. After putting samples in aluminium vessel, sample and reference vessels were hermetically sealed and a small hole was made on the cover before being placed on the calorimeter sample chamber. The sample space was purged with nitrogen at a constant flow during the experiments. When the sample was heated at a constant heating rate of 5°C per minute from room temperature, 30°C to 120°C, any kind of change in its calorimetric properties caused a temperature difference between the sample and the reference (empty aluminium

crucible). The measured temperature difference was controlling the electrical power to the sample and the reference in order to keep them at the same temperature. In this technique the difference in power supply to the sample and reference was recorded. The peak area from the output recording directly corresponded to the heat consumed by the sample.

Then, the sample was kept at isothermal condition after it reached 120°C for 10 minutes. After that, the sample was cooled down to 30°C at a constant cooling rate of 5°C per minute. Liquid nitrogen was used as cooling medium. The area between the straight line and that deviated curve represented the energy released for phase change, cooling, which was integrated numerically by a program built in the DSC (Figure 3.9).



Figure 3.9 DSC machine

3.4.2 Thermo gravimetric analysis (TGA)

Thermogravimetry analysis (TGA) is a powerful technique for the characterization of decomposition or weight loss properties of materials. The technique provides the following information:

- Deposition temperature
- Thermal degradation properties
- Oxidative degradation characteristics
- Quantitative weight losses
- Long term stabilities

Here, thermal stability of core material, paraffin wax and the coating materials, PAn were investigated by using thermogravimetry analyzer (Model:Perkin Elmer). With the TGA approach, the microencapsulated paraffin wax was generally heated at a constant rate 10°C per minute and the resulting temperatures and the degradation rate were measured as a function of time or temperature. Nitrogen purging, furnace heating and air-condition cooling were used in this experiment. (Figure 3.10)



Figure 3.10 Thermogravimeter machine

3.4.3 Field Emission Scanning Electron Microscopy (FESEM)

The most widely used procedures to visualize micro particles is Field Emission Scanning Electron Microscopy (FESEM). This technique can be used to determine the

shape and outer structure of micro particles. Sample capsules were mounted on copper stubs with dark double-sided adhesive tape and vacuum-coated with platinum film (Ion Sputtering Device), and then examined by FESEM (Model: INCA Energy 400) and photographed (Figure 3.11). FESEM and conventional microscope do not permit the visualization of internal structure of objects at all.



Figure 3.11 The FESEM machine

3.4.4 Transmission electron microscopy (TEM)

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. What you can see with a light microscope is limited by the wavelength of light. TEMs use electron as “light source” and their much lower wave length makes it possible to get a resolution a thousand times better than with a light microscope.

You can see objects to the order of a few angstroms (10^{-10} m). For example, you can study small details in the cell or different materials down to near atomic levels. The

possibility for high magnifications has made the TEM a valuable tool in both medical, biological and materials research (Figure 3.12)



Figure 3.12 TEM machine

3.4.5 Fourier transform infrared spectrophotometer (FT-IR)

This experiment provided information on the stability of functional groups in the molecule. Paraffin wax contains long chain hydrocarbons, and can oxidize when it contacts with transport medium air. After 0, 500, 1000, 1500 and 2000 thermal cycling, chemical structure stability of microencapsulated was examined by using Fourier transform infrared spectrophotometer (Model: PerkinElmer Spectrum400), (Figure 3.13).



Figure 3.13 The FT-IR machine.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Introduction

In this chapter the results of test conducted to determine the characteristics and performance of microencapsulated paraffin wax prepared by in situ polymerization method are presented.

4.2 Thermal performance of encapsulated paraffin wax

Thermal performance of encapsulated paraffin wax was indicated by its energy storage and release capacities at various cores to coating ratios. They were measured by DSC. The diagrams of the DSC for paraffin wax are shown in Figure 4.1. This figure shows the DSC data characterization, the melting and freezing behavior of paraffin wax at scanning rate of 5 °C/ min from 30°C through 120 °C and from 120 °C to 30°C. There are two peak points in these diagrams. They show a solid to liquid transition and liquid to solid transition. At these temperature ranges, the samples transformed to the crystalline phase. Melting has occurred between 46°C and 60°C. The specified area under and above the curves demonstrate the amount of energy stored and released.

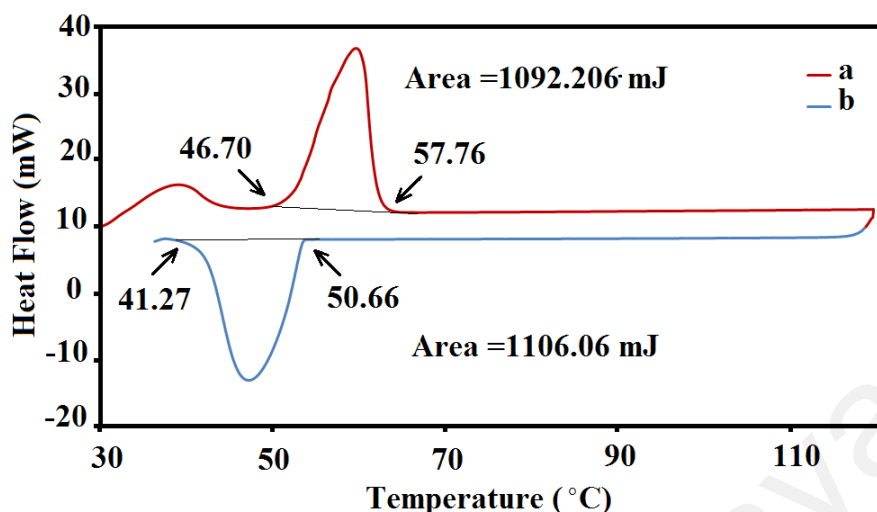


Figure 4.1 (a) Melting process of paraffin wax (b) Solidifying process of paraffin wax

Figure 4.2 reveals the rate of melting temperature during the heating process. As it can be seen from the graph, the melting temperature of the microencapsulated paraffin wax S1 was measured to be 46.57°C by DSC. Figure 4.2 represents the amount of melting temperature during the heating process. Based on the graph, the melting temperature of encapsulated paraffin wax S2 is 46.57 °C. Sharp peaks for discharging mode indicated no supercooling in phase temperature range between 45°C and 60°C for in situ polymerization sample S2. Figure 4.4 also illustrates the solid-liquid and liquid-solid transition of encapsulated paraffin wax S3. Considering the graph, it can be noted that the melting temperature of capsule S3 is 50.24 °C. Figure 4.5 shows the melting and solidifying process of encapsulated paraffin wax S4. As it can be seen from the graph, the rate of melting temperature of capsule S4 is 53.14°C. Moreover, there is a sharp surge during solidifying process due to no supercooling in the process.

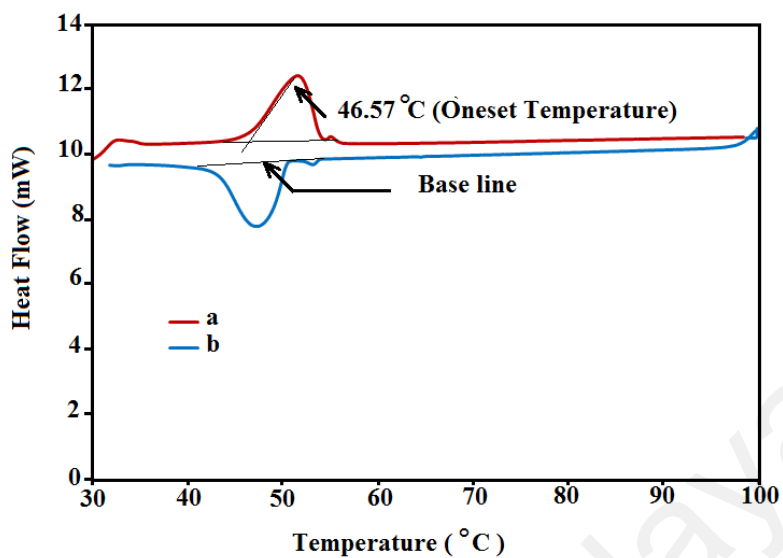


Figure 4.2(a) Melting process of capsule S1 (b) Solidifying process of capsule S1

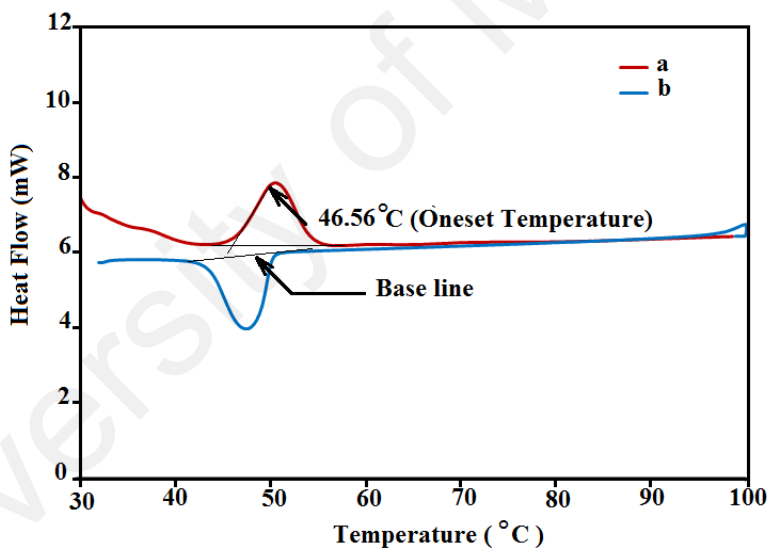


Figure 4.3Figure 4.4 (a) Melting process of capsules S3 (b)Solidifying process of capsules S2

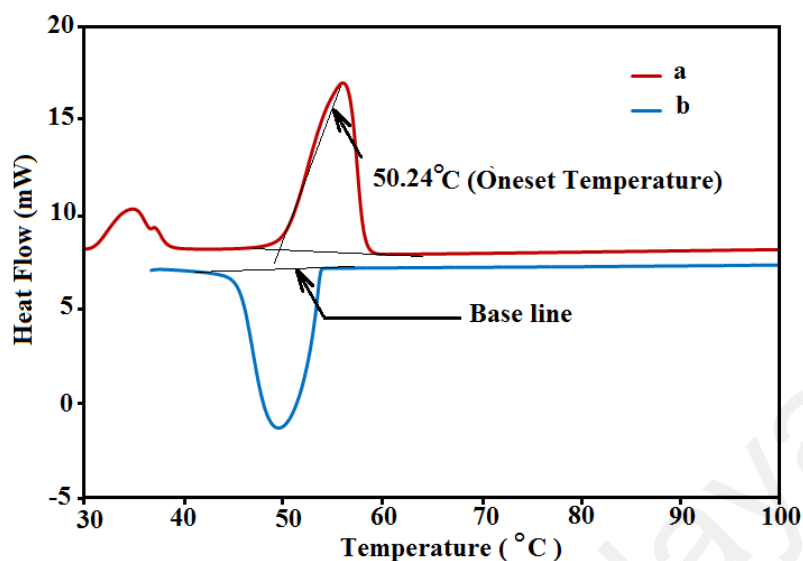


Figure 4.4 (a) Melting process of capsules S3 (b) Solidifying process of capsules S3

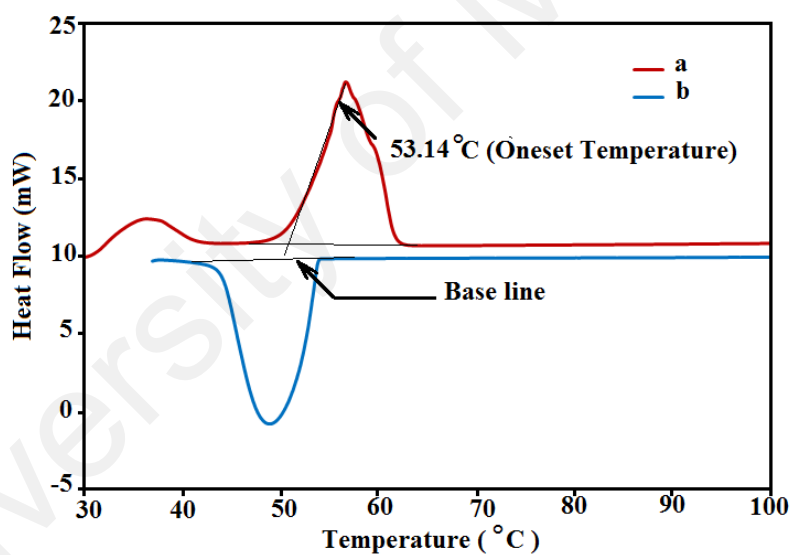


Figure 4.5(a) Melting process of capsule S4 (b) solidifying process of capsule S4

Thermal properties of the pure paraffin wax microencapsulated S1, S2, S3 and S4 are presented in Figure 4.6 and 4.6 and Table 4.1. Figure 4.6 and 4.7 compare the melting and solidifying process of the encapsulated paraffin wax, respectively. As it can be observed, there are two absorbing peaks on DSC analysis of the encapsulated paraffin wax. The first peak signifies solid-solid transition process and the second peak represent

solid-liquid melting process. The DSC analysis for the paraffin wax shows the endothermic and exothermic peaks are located at 59.27°C and 47.37°C. Also the rate of latent heat of paraffin wax was calculated to be as 136.18 J/g. Moreover, the melting peak temperature reduction of 51.61°C and 47.44°C for S1, 50.54°C and 47.61°C for S2, 56.06°C and 49.66°C for S3 and 56.63°C and 48.95°C for S4 were observed. The peak temperature of the capsules S1, S2, S3, and S4 are approximately declined relative to paraffin wax. Also, the melting peak of the capsules S3 and S4. In addition, the amounts of latent heat are decreased to 22.60 J/g for S1, 28.62 J/g for S2, and 89.76 J/g for S3 and 131.95 J/g for S4. The rate of latent heat for S3 and S4 is close to that of paraffin wax, the reason for this can be the fact that the capsulation was not completed. On the other hand, for the case of PAN, there is no endothermic peak is observed in the DSC analysis in for the same temperature range, implying that PAN has no significant effect on the phase change enthalpy of the capsules. Therefore, the low value for the phase change enthalpy of the resulted microcapsules is basically because of the low filling rate of the paraffin wax to the total microcapsules. Besides, Figure 4.7 shows that the difference between the peak temperature and solidifying temperature of the S1, S2, S3, and S4 are 3-5°C which is smaller than that of the paraffin wax. It also shows that the supercooling degrees of the capsules are smaller than that of the paraffin wax, because of the influence of the interior wall of PAN Shells on the surface of paraffin wax acting as nucleation agent.

The content of the paraffin wax in the microcapsules can be determined according to the measured enthalpies (You, Zhang, Wang, Zhang, & Wen, 2010). Based on the Eq(1), ΔH_{PCM} represent the enthalpy of the paraffin wax and ΔH_{MEPCM} shows the enthalpies of the encapsulated paraffin wax as measured by the DSC.

$$\eta\% = \frac{\Delta H_{MEPCM}}{\Delta H_{PCM}} \times 100 \quad (1)$$

Table 4.1 DSC data of the paraffin, S1, S2, S3, and S4 show that melting /solidifying temperature, core content, and enthalpies of the paraffin wax, S1, S2, S3, and S4. As can be seen, the latent heat of the paraffin wax in the form of microencapsulation decreases compared to paraffin wax. This is because the ratio of the paraffin wax is declined to 15.9%, 21.5%, 68.3%, and 79.9% for capsules S1, S2, S3 and S4, respectively. Although, the encapsulation of S1 and S2 done well .However, the latent heat of S1 and S2 have more remarkable decrease compared to that of the other capsules S3 and S4. Because the higher amount of the PAn on S1 and S2 microencapsulation of paraffin wax is concluded. On the other hand, this table show that the melting and solidifying temperature of the capsules are declined by 2-5°C relative to paraffin wax .This in turn implies that the interactions between the paraffin wax molecules and PAn are not strong. This lead to a depression of the phase change temperature of the paraffin wax in the microencapsulation (Fang, Chen, & Li, 2010).

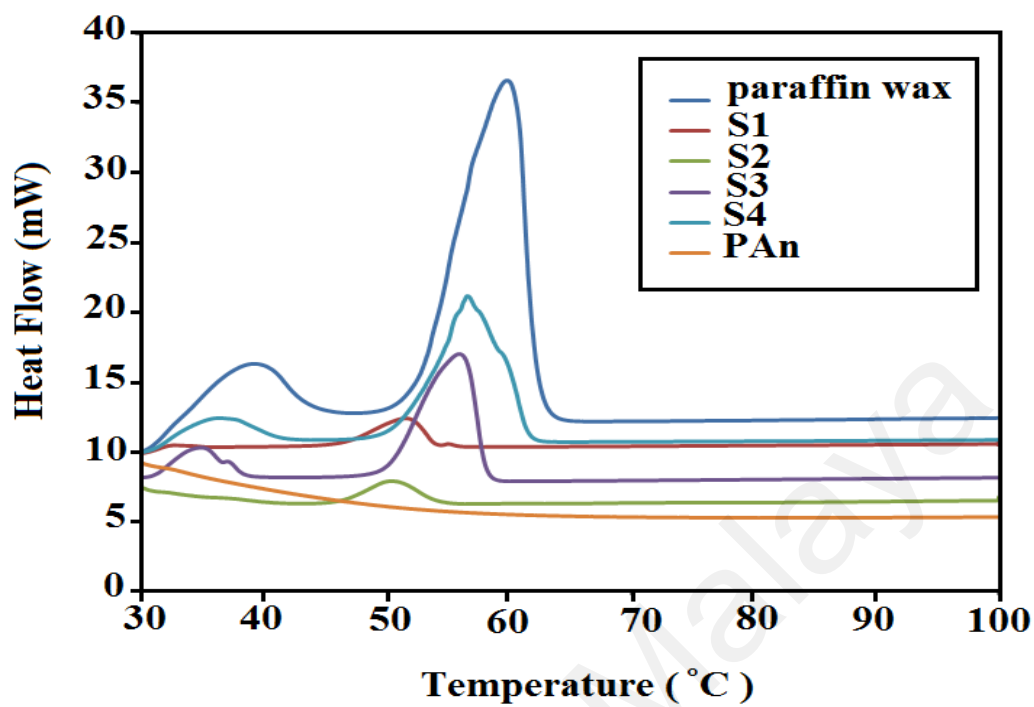


Figure 4.6 The melting curve of the paraffin wax, PAn, S1, S2, S3, and S4

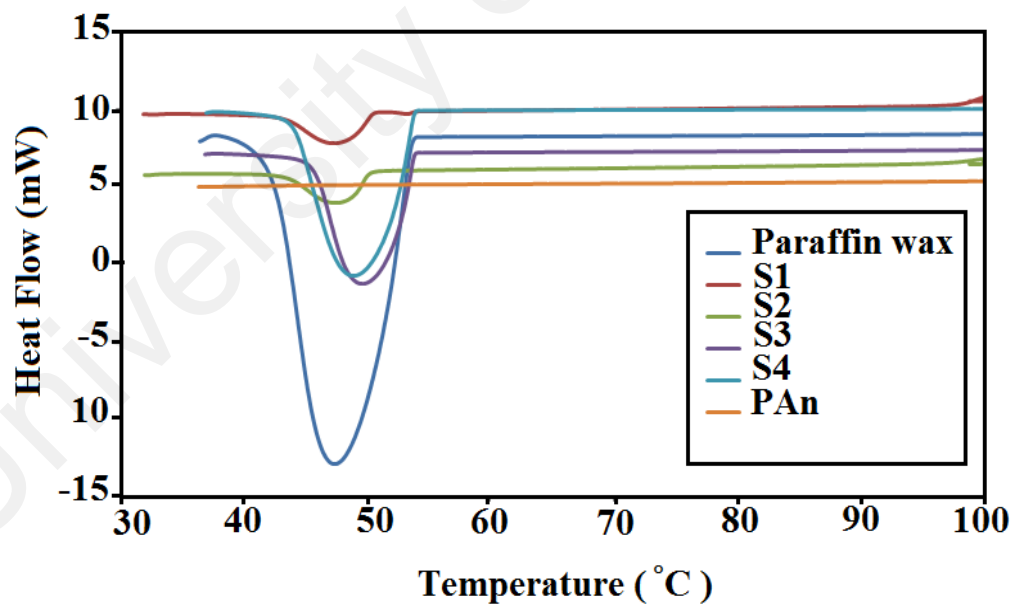


Figure 4.7 DSC solidifying curve paraffin wax, S1, S2, S3 and S4

Table 4.1 DSC data of the paraffin, S1, S2, S3, and S4

Sample no	Paraffin wax content (%)	$T_{om}(^{\circ}\text{C})$	$T_{pm}(^{\circ}\text{C})$	$T_{oc}(^{\circ}\text{C})$	$T_{pc}(^{\circ}\text{C})$	$\Delta H_m(\text{J/g})$	$\Delta H_c(\text{J/g})$
Paraffin	100	52.39	59.27	53.63	47.37	136.18	137.91
S1	15.9	46.57	51.61	50.48	47.44	21.77	22.28
S2	21.5	46.56	50.54	50.67	47.61	29.39	34.66
S3	68.3	50.24	56.06	53.82	49.66	93.06	97.76
S4	79.9	53.14	56.63	53.63	48.95	108.85	121.01

$T_{om}(^{\circ}\text{C})$ Onset temperature on DSC heating curve

$T_{pm}(^{\circ}\text{C})$ Peak temperature on DSC heating curve

$T_{oc}(^{\circ}\text{C})$ Onset temperature on DSC cooling curve

$T_{pc}(^{\circ}\text{C})$ Peak temperature on DSC cooling curve

$\Delta H_m(\text{J/g})$ Enthalpy of heating

$\Delta H_c(\text{J/g})$ Enthalpy of cooling

4.3 Surface morphology

The method of in-situ polymerization was used for microencapsulation. Surface morphology of microcapsules obtained from this method was studied by using a Field Emission Scanning Electron Microscopy (FESEM). Figure 4.8 shows the surface morphology of micro-encapsulation S1, S2, S3, and S4. As can be seen in this figure, the paraffin wax was encapsulated by PAN. However, the encapsulated paraffin wax decreases with growing up the content of the paraffin wax. This figure shows that the surface morphologies of the encapsulation of S1 and S2 are more homogenous than that of the microencapsulated S3 and S4. This is due to the ratio of the paraffin wax in S1 and S2 being smaller than the ratio of the S3 and S4, which resulted in PAN shells well not formed on

the surface of the paraffin wax on S3 and S 4. Beside, It was observed all the samples were globular in shape. Capsules S1 and S2 was found to be more spherical in shape compared capsules S3 and S4. On the other hand, capsules S4 were slightly deformed from spherical shape, because of the large amount of paraffin wax leading to insufficient amount of PAN on the surface of paraffin wax.

On the other hand, SPSS Software can be used to analyze the size of the capsules (Figure 4.9). The average sizes of the capsules are $4.01\mu\text{m}$, 586.96nm , 341.63nm , and 267.47nm for S1, S2, S3 and S4, respectively. It is clear that the encapsulation of paraffin wax owns the best encapsulation in the range of the micro.

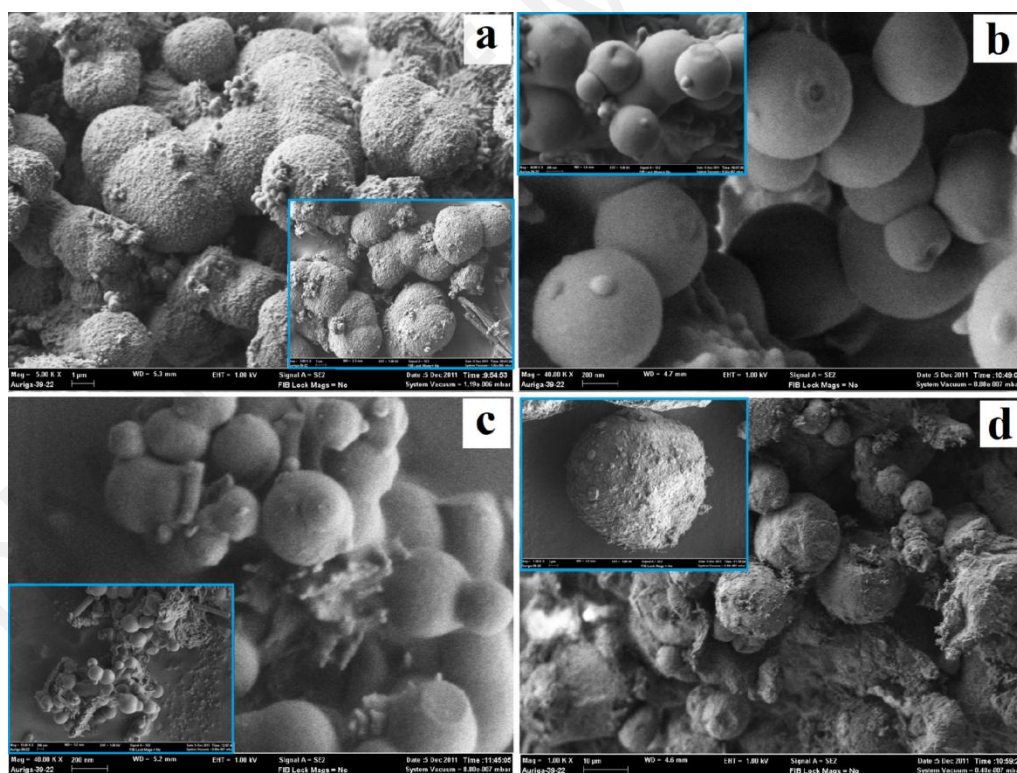


Figure 4.8 FESEM results of the (a) capsules S1, (b) capsules S2(c) capsules S3and (d) capsules S4

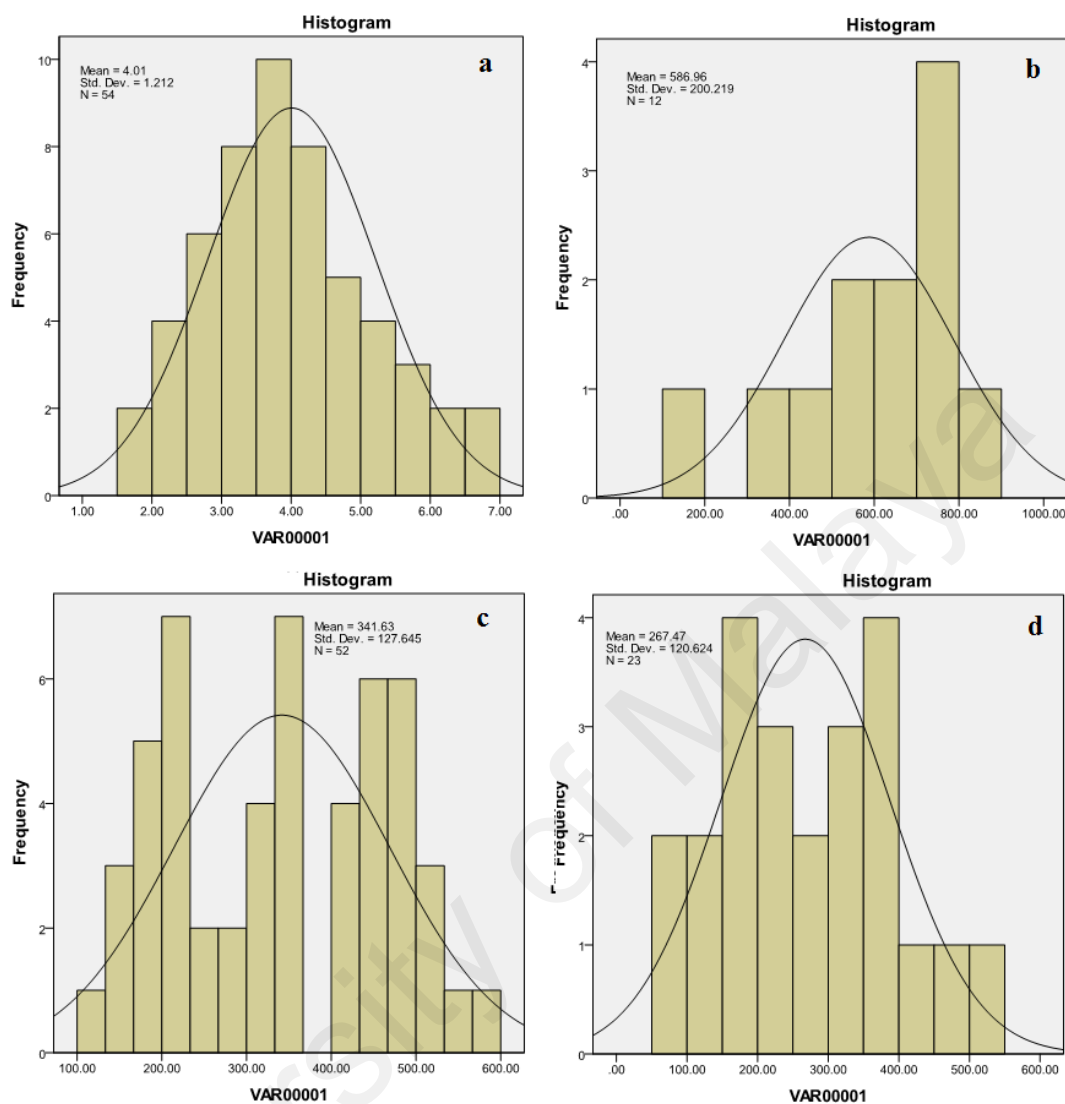


Figure 4.9 SPSS analysis

4.4 Transmission electron microscopy

TEM are used to determine the microstructure of microencapsulated paraffin wax. The powder sample synthesized in the presence at 70°C with different ratio of polyaniline monomer to paraffin was suspended in water under sonication for 1 hour. Figure 4.10 shows the TEM analysis of encapsulated paraffin S1, S2, S3 and S4. As can be considered,

the shape of core shell is spherical. The dark central part shows the core and the grey bright part surrounding the core is the shell.

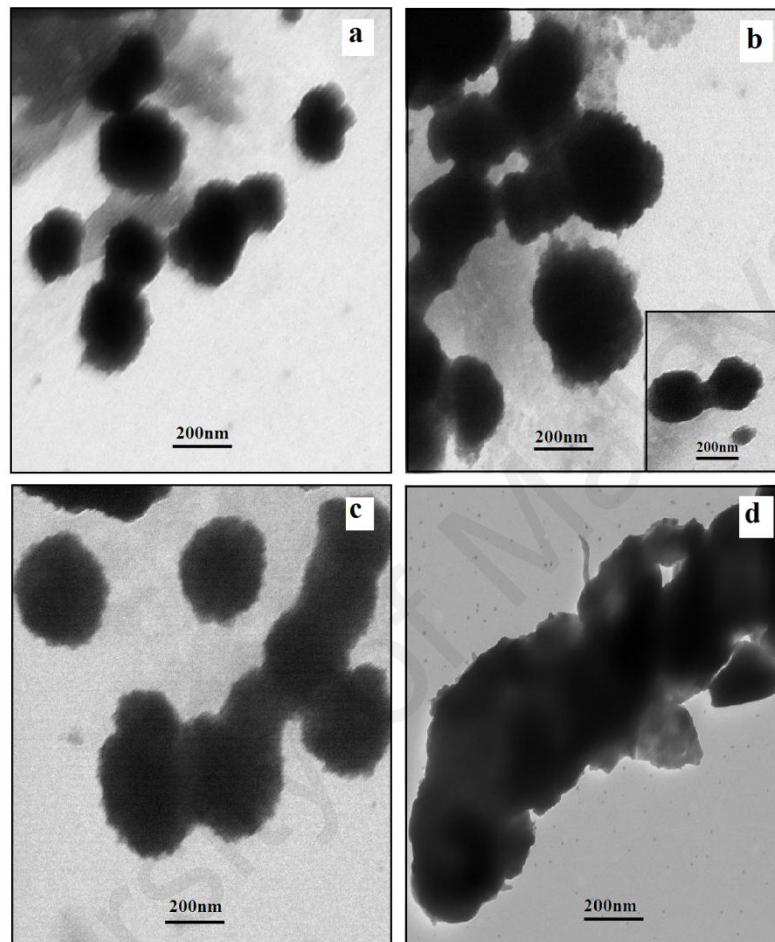


Figure 4.10 TEM result of the capsules (a)S1,(b)S2,(c)S3,and(d)S4

4.5 Thermogravimetry analysis

In order to use microencapsulated PCMs as thermal energy storage, the coating materials have to keep up with requirements for high thermal resistance. TGA was performed on microencapsulated paraffin waxes to find their decomposition temperature. Figure 4.11 shows the TGA test results of in situ polymerization microencapsulated paraffin wax.

In TGA thermograms Figure 4.11 the black curves show the residual weight percent of the sample as a function of temperature. The weight loss for the microcapsules prepared by in situ polymerization started at near the melting point of core material, paraffin wax. Microcapsules showed initial weight loss about 10 % from 50°C to about 200°C, and a subsequent higher weight loss up to about 900°C. The red lines show the derivative of mass change (dm/dT) with respect to temperature T . The area over the derivative thermogravimetry (DTG) curve is directly proportional to the mass change. The height of the DTG peak gives the rate of mass change at that temperature. The TG thermograms obtained for the two samples showed that two highest peak corresponding to maximum degradation rate at temperature T_{max} . The first highest peak corresponded the peak decomposition temperature of core material, paraffin wax around (200 ~ 300°C), the second highest peak showed the decomposition temperature of coating materials around (300 ~ 400°C). The high decomposition temperature evidently indicated high thermal stability of microcapsules. In addition, this decomposition temperature .Also determined the upper limit of temperature that sample could be heated. Furthermore, the decomposition temperature of the coating materials was significantly higher than that of core material so that the coating materials could withstand the phase change process of the core material, paraffin wax. The most reasonable explanation of this phenomenon was the formation of network by two kinds of polymer chains.

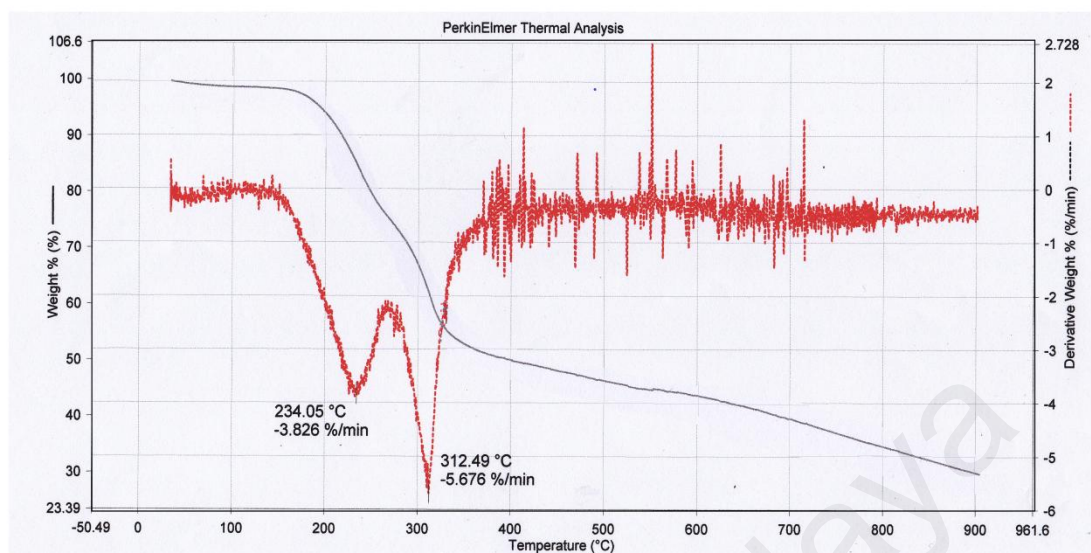


Figure 4.11 TGA and DTG result of capsule S1

Thermal stability of the capsules, pure PAN and pure paraffin have been determined by TGA. Figure 4.12 shows that the TGA result of capsules S1, S2, S3, S4, paraffin wax and PAN. As can be considered, there are not strong mass loss weight at high temperature 200°C for all the capsules. The percentage of decomposition S4 is larger than that S1, S2, and S3. Because the ratios of the paraffin wax in microcapsules S4 are more than S1, S2, and S3, microencapsulation will not form on the surface of all the paraffin wax. The result weight loss percentage for paraffin wax is nearly 100%, in contrast, the weight loss percentage for S1, S2, S3, S4 and PAN is around 60%, 62%, 95%, 96% and 40%, respectively. It is clear that decomposition of the capsules directly depended on the ratio of the core and shell of the capsules.

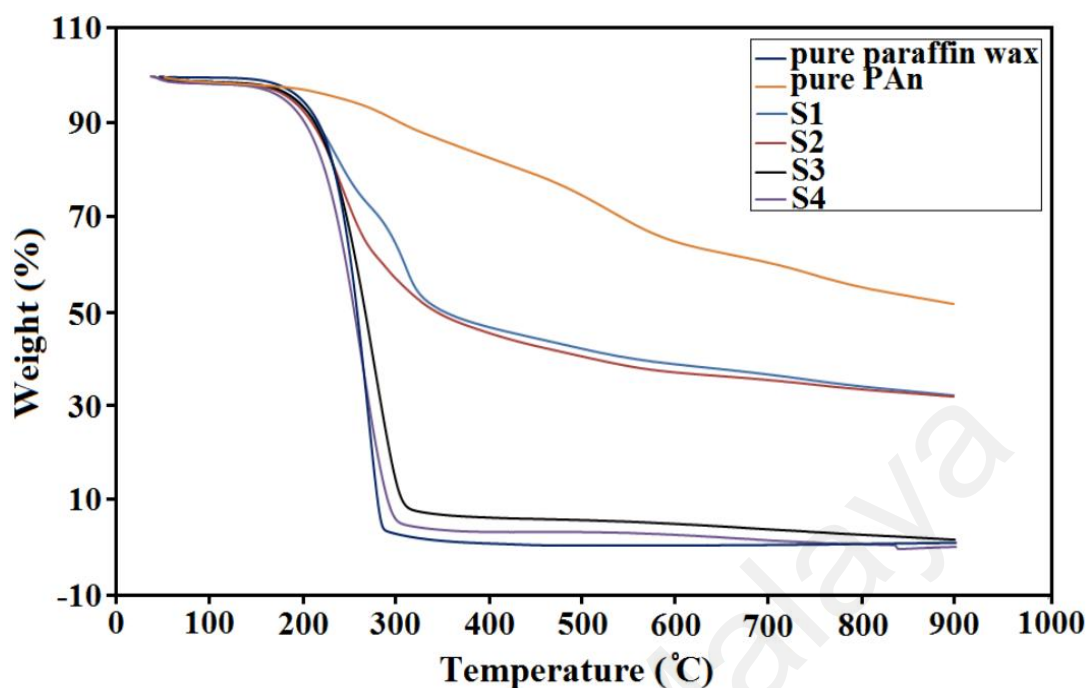


Figure 4.12 TGA result of paraffin wax, PAn, S1, S2, S3, and S4

4.6 Structure stability

FTIR spectra of paraffin wax and polyaniline (PAn) are shown on Figure 4.13 FTIR results of the paraffin wax and PAn. The peaks around 2940-2855 cm^{-1} and 1470 cm^{-1} show carbon hydrogen stretching and bending absorption, respectively. The symmetric C-H bending absorption of the CH_3 group at 1380 cm^{-1} and the CH_2 rocking absorption band at 725 cm^{-1} confirm the linear saturated aliphatic structure of the paraffin wax.

IR spectrum of the polyaniline indicates six principal absorptions at 1590, 1508, 1304, 1210, 1145 and 831 cm^{-1} . The peaks at 1590 and 1508 cm^{-1} are assigned to C-C ring stretching vibrations. The peaks at 1304 and 1210 cm^{-1} correspond to N-H bending and the symmetric component of the C-C (or C-N) stretching modes. The bands at 1145 and 831 cm^{-1} can be attributed to the in-plane and out-of-plane C-H bending modes, respectively. The peaks of the polyaniline salt observed at 1560, 1482, 1306, 1245.9, 1148 and 814 cm^{-1} respectively. On the other hand, the spectrum of the polyaniline salt exhibits

new peaks around 3220, 1653 and 684 cm^{-1} . The peak at 3320 cm^{-1} could be attributed as due to 2 NH stretching mode and the 1653 cm^{-1} band to the 2 NH bending vibration while the 684 cm^{-1} is assigned as due to 2 NH wagging.

Figure 4.14 shows the paraffin wax/PAn spectrum in the different ratios. As we can see, the peak at C-H bending growing up with increases the content of the paraffin wax. The absorption peaks of the polyaniline salt at 1560, 1482, 1306, 1245.9, 1148 and 814 cm^{-1} also appear at S1, S2, S3, and S4. Due to PAn can only formed on the interface of the Paraffin wax. However, the peaks declined with decrease of the PAn. FTIR results show that the PAn shell was formed on the surface of the paraffin wax.

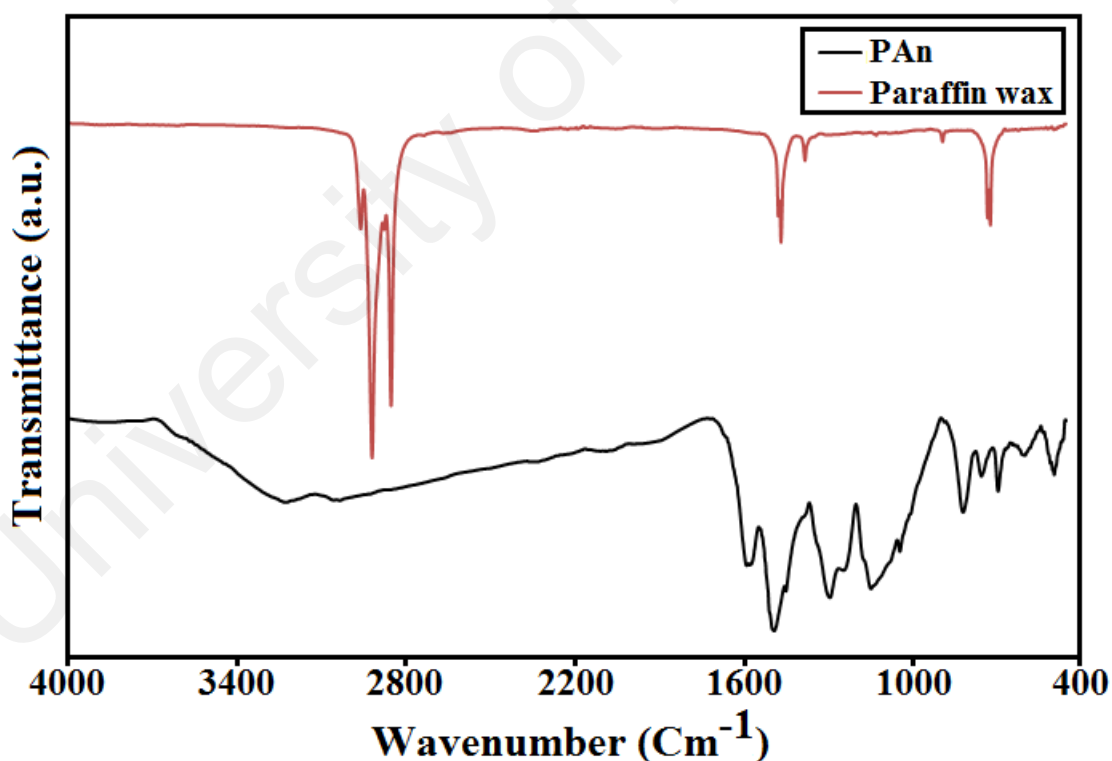


Figure 4.13 FTIR results of the paraffin wax and PAn

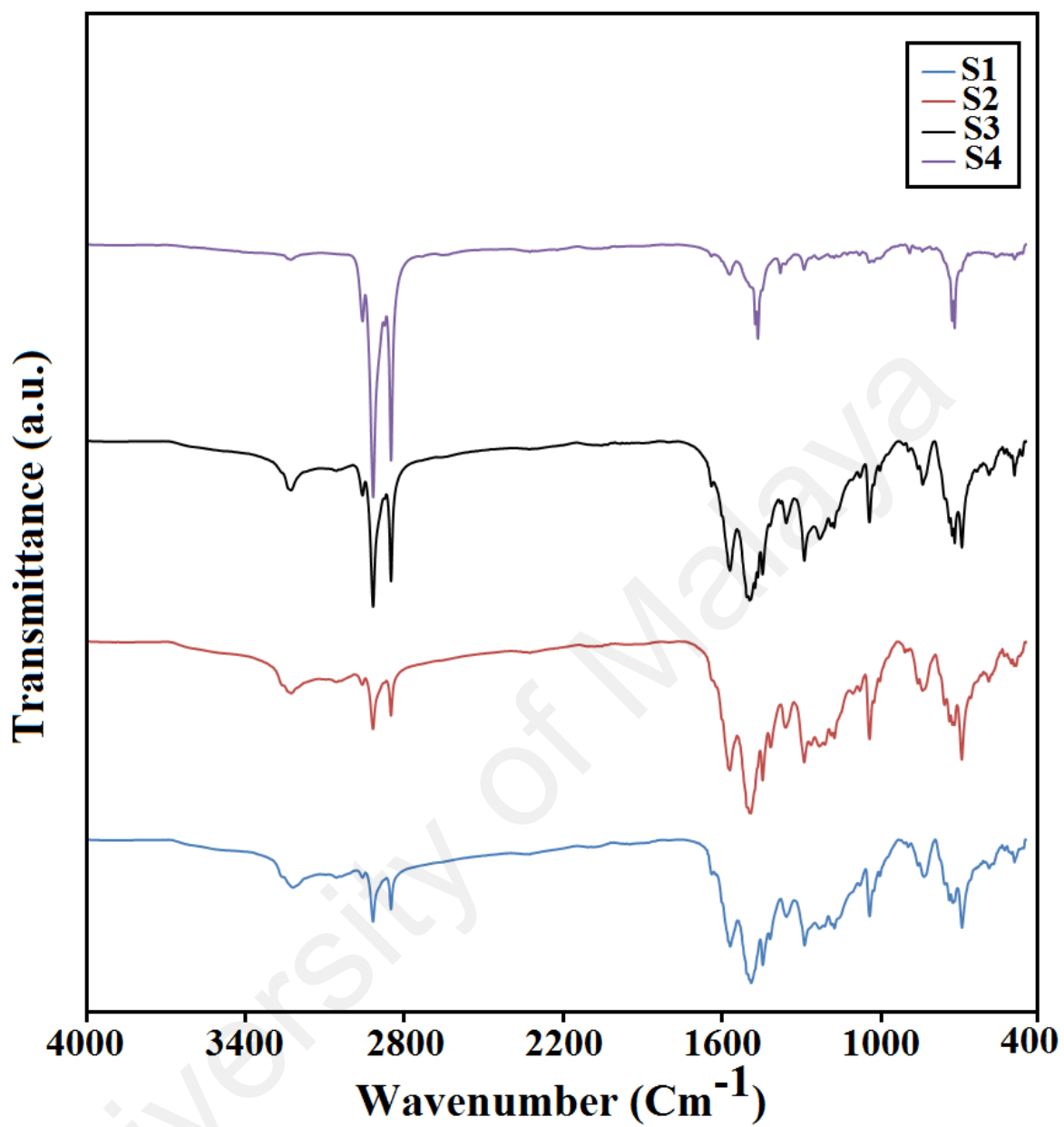


Figure 4.14 FTIR results of capsules S1, S2, S3, and S4

CHAPTER 5: CONCLUSIONS AND RECOMMENDATION

5.1 Conclusion

The present work has been carried out on the preparation and characterization of microencapsulated paraffin wax prepared by in situ polymerization method. From the results of this study, the following conclusion can be drawn.

- Polyaniline can be used for microencapsulation of paraffin wax.
- DSC result showed that the microcapsules prepared by in situ polymerization had high energy storage /release capacities (22-140J/g) and it depended on the core to coating ratio.
- Encapsulation ratio of paraffin wax was measured by enthalpies of capsules S1, S2, S3, S4 and paraffin wax.
- FESEM analysis showed that the microcapsules prepared by situ polymerization method were globular in shape. Beside, the surface morphologies of the encapsulation of S1 and S2 are more homogenous than that of the microencapsulated S3 and S4. This is due to the ratio of the paraffin wax in S1 and S2 are smaller than the ratio of the S3 and S4 which is resulted in PAn shells well not formed on the surface of the paraffin wax on S3 and S4.

- TGA analysis showed high thermal stability for encapsulated paraffin wax. This indicated that the coating materials were suitable for encapsulation of PCM in thermal energy storage at high temperature.
- TEM results showed microstructure of the microencapsulated paraffin wax.
- FTIR results showed that the absorption peaks of the polyaniline at S1, S2, S3, and S4. Due to PAn can only be formed on the interface of the Paraffin wax. However, the peaks declined with decrease of the PAn. FTIR results indicated that the PAn shell was formed on the surface of the paraffin wax.

5.2 Recommendation

On the basis of the present experiments carried out and results obtained the following recommendation are suggested for future studies:

Thermal cycling test is used to determine the thermal stability of the capsules after 100, 200, 300, 400, 500 and 1000 cycles. After the cycling test, characterization of the samples should be performed. If the values of melting point and latent heat remain almost constant, the useful life would be determined.

This study focused on the one method in situ polymerization for microencapsulation of paraffin wax. Hence, further studies on other encapsulation methods such as spray drying, complex coacervation, interfacial polymerization and dip coating.

The encapsulation can be used along with fluidized bed in heat exchangers to improve the performance of the system using PCM.

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