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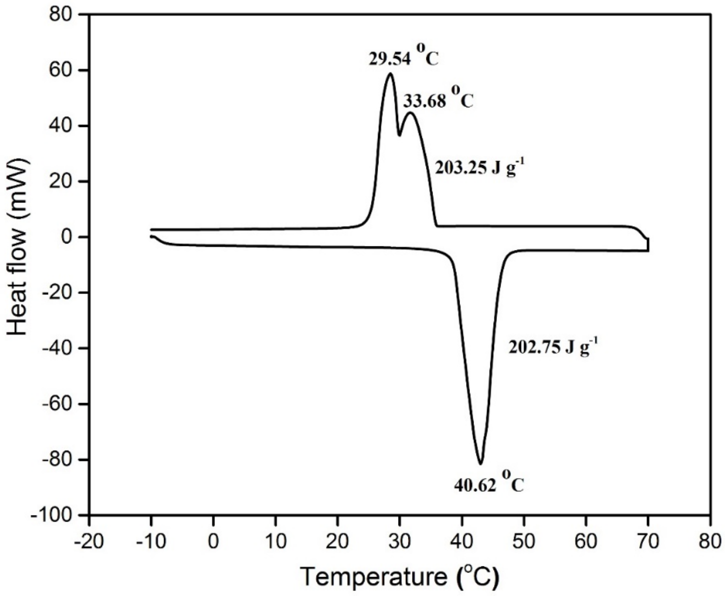
Special Issue on Phase Change Materials



Typical DSC curve of a Phase Change Material

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INSIDE THIS ISSUE

From the Editor's Desk

I am thankful to Dr. A. Sreekumar of Pondicherry University and Dr. Sandip Saha of Indian Institute of Technology, Bombay for contributing articles on Phase change materials in this issue. The readers may find that some information about phase change materials (PCMs) are repeated in these two articles. But the articles have been retained as such as they deal with different aspects of PCMs.

It can be seen that thermal analysis plays important role in the development of such materials. I hope that the articles on PCMs appearing in this bulletin will provide useful information and new directions of research in this area.

I request the ITAS Members to contribute articles on interesting topics in thermal analysis so that we can bring out the Bulletins at regular intervals and also share the new frontiers in this field with fellow members of ITAS.

I also request the members to send me information regarding any event like symposium, workshop etc on thermal analysis and honours and bouquets received by ITAS Members. Let us all be connected through this medium of ITAS Bulletin and share our knowledge in this important area of applied research.

With best wishes from the Editorial Team

Shyamala Bharadwaj

PRESIDENT'S MESSAGE

Greetings to all ITAS members.

As you know that ITAS is publishing thematic bulletin on recent development in the field of thermal analysis and related techniques to update the latest R&D work being carried out in this field. The present bulletin is focused on Phase Change Materials (PCMs). The PCMs have attracted attention in recent years due to wide variety of applications in thermal energy storage, solar cooking, cold energy battery, cooling of food, heat pumps systems, solar power plants, thermal comfort in vehicle etc. The PCMs have very high heat of fusion and capable of storing and releasing large amounts of energy. The heat is absorbed or released when the material changes phases from solid to liquid and vice versa. Different types of PCMs such as : organic, inorganic and eutectic compounds have been studied and each one is having its own advantages as well disadvantages depending upon the specific uses.

I express my deep gratitude to the Editor in Chief. Dr (Mrs) Shyamala Bharadwaj and all other editorial committee members to bring out such a nice bulletin on PCMs. I also wish the contributors, Prof. A. Sreekumar of Pondicherry University and Prof. Sandip Saha of Indian Institute of Technology, Bombay for providing excellent articles on PCMs for this special issue.

I use this opportunity to wish all ITAS members and their family a very happy new year 2018.

Thanking you with regards

(S. Kannan)

Phase change materials for cold thermal energy storage applications in buildings

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1.Introduction

The creation of thermal comfortable space in building is energy intensive, which is estimated to be 40% of total energy consumption. According to a study by the expert group of low carbon strategies for inclusive growth and Bureau of Energy Efficiency - India, the cooling load demand is expected to raise from 75,000 MW to 1,50,000 MW by 2030. Phase change materials (PCM) have received remarkable attention in recent times for its application in latent heat thermal energy storage system. Due to its high potential on energy storage, it has become a popular topic of interest among the research community. Phase change materials can be used for both hot and cold storage depending upon its melting temperature. As the cooling demand increases drastically and conventional technologies are not environment-friendly, PCM for cold thermal energy storage is getting more attraction. PCM based technologies are commercially available nowadays and become inevitable in near future. This article briefly discusses about PCM based thermal energy storage, types of PCM and its application in buildings.

2. Thermal Energy Storage

Thermal energy storage (TES), commonly known as heat or cold storage in which the available heat or cold can be stored in a medium and can be used later when it is needed. In order to retrieve the stored heat or cold, the process of storage should be reversible. The three types of thermal energy storage methods are 1. Sensible storage, 2. Latent storage and 3. Thermo-chemical storage. [1]

2.1 Sensible storage

Sensible storage is a common method of storing heat and cold. The amount of sensible heat stored (Q) in a material is directly proportional to its specific heat capacity (C_p) and change in temperature (ΔT) and mass of the storage material (m). Domestic hot water storage or chilled water storage is an example for this method. The amount of heat stored can be expressed as

$$Q = mC_p\Delta T$$

2.2 Latent storage

Latent storage is a method of storing heat or cold in a material by phase transformation either from solid to liquid or vice versa. The material undergoes phase change at isothermal temperature during which it stores large amount of thermal energy by either absorbing or releasing heat energy being supplied to the material. The materials used in latent heat storage are termed as phase change materials (PCM). The amount of thermal energy stored in the phase change material is directly proportional to the latent heat capacity (H) of the material. The energy stored in this method is expressed by the following equation.

$$Q = mH$$

2.3 Thermo-chemical storage

Thermo-chemical storage is a method to store and retrieve heat or cold by forward and reverse chemical reactions. Energy is stored in forward endothermic reaction and released during reverse exothermic reaction. There are several limitations on this type of thermal storage as it needs special reaction condition and the product of chemical reactions are not stable for longer period.

2.4 Advantages of Latent heat storage

The advantages of latent heat storage are listed below.

- High energy storage density (5 to 10 timesmore energy per unit volume than sensible storage) [1]
- Constant temperature heat storage and heat retrieval
- Smaller in size than sensible storage
- Can be used in wide range of application depends on the melting point of PCM

3. Phase change materials

Phase change materials (PCMs) are energy storage materials used in latent heat thermal storage system. When the temperature is raised, the chemical bonds in the PCM breaks down by absorbing the heat and undergoes phase transition (solid to liquid). Heat absorption during the phase changeis an endothermic process. When the heat is extracted from the material, the chemical bond is again formed and the material undergoes reverse phase transition (liquid to solid). The phase change takes place as an isothermal process with minimum change in temperature. The energy stored during phase change process is in the form of latent heat.

3.1 Classification of PCM

The phase change materials are generally classified as organic, inorganic and eutectic.The detailed classification of PCM is given as chart in Fig. 1.

3.2 Organic PCM

Organic PCMs are carbon based compounds which can be used in latent heat thermal energy storage. It is further classified as paraffins, non-paraffins, fatty acid, poly alcohols etc.The latent heat of the organic PCM depends on number of carbon atoms present in the compound. The advantages of organic PCMs are high stability and high latent heat of fusion. Low thermal conductivity and inflammable at high temperature are notable disadvantages. Some of the organic PCM reported in literature are listed in Table 1.

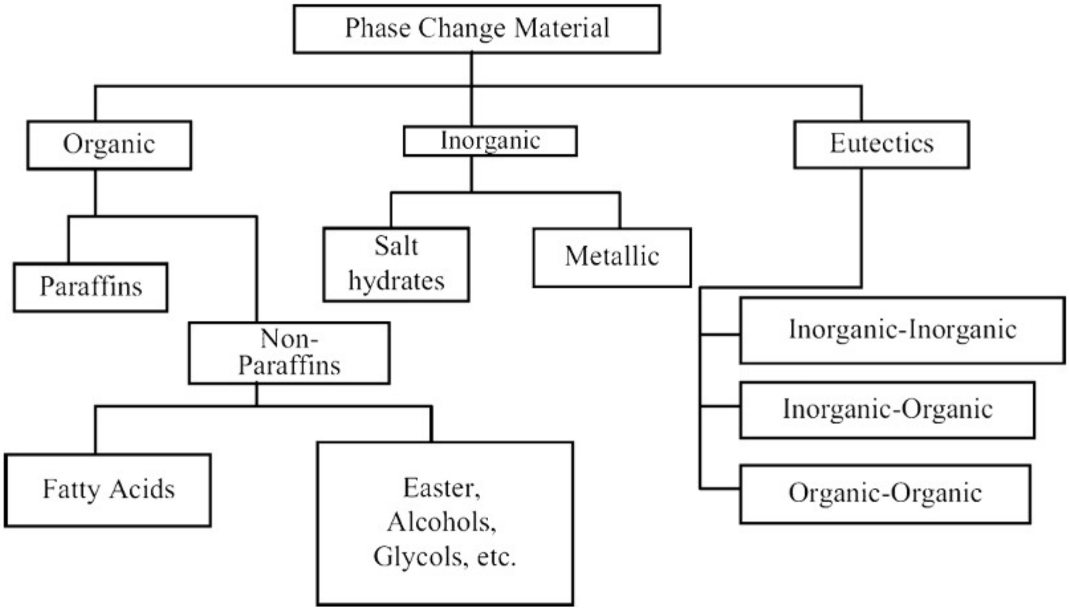

Fig. 1 Classification of PCM [2]

Table 1. Organic PCMs [3,4,5]

Material	Melting point (^{o}C)	Latent heat of fusion (J g^{-1})
n-Hexadecane	18	210-236
n-Heptadecane	19	240
Butyl Stearate	19	140-200
Dimethyl Sabacate	21	120-135
Octadecyl 3-mencaptopropylate	21	143
Paraffin C_{17}	21.7	213
Paraffin C_{16}-C_{18}	20-22	152
Paraffin C_{13}-C_{24}	22-24	189
Ethyl Palmitate	23	122
Lactic Acid	26	184
1-Dodeconol	26	200
OctadecylThioglyate	26	90
Vinyl Sterate	27-29	122
Paraffin C_{18}	28	244
n-Octadecane	28-28.1	245
Methyl Sterate	29	169

3.3 Inorganic PCM

Inorganic PCMs are generally metallic and salt hydrates. The main advantage of this category PCMs are low cost and high thermal conductivity but it is corrosive in nature. The compatibility with the construction materials are to be considered while using this type.Some of the inorganic PCM which are available in literature are listed in Table 2.

Table 2. Inorganic PCMs [3,4,5]

Material	Melting point (°C)	Latent heat of fusion (J g^{-1})
$Na_2CrO_4.10H_2O$	18	-
$KF.4H_2O$	18.5	231
$Na_2SO_4.10H_2O$	21	198
$FeBr_3.6H_2O$	21	105
$Mn(NO_3)_2.6H_2O$	25.8	125.8
$CaCl_2.6H_2O$	29	190.8
$CaCl_2.12H_2O$	29.8	174
$LiNO_3.2H_2O$	30	296
$LiNO_3.3H_2O$	30	189/296

3.4 Eutectic PCM

Eutectic PCMs are mixture of two or more materials which are individually a PCM by itself having different melting point. This is for preparing a new PCM with desirable melting point based on the application requirement. It can be the mixture oforganic-organic, organic-inorganic or inorganic-inorganic. Some of the eutectic PCM mixtures which are available in literature are givenin Tables 3 and 4.

Table 3. Organic eutectic PCMs [3,6]

Material	Melting point (°C)	Latent heat of fusion (J g^{-1})
65 wt%Capric acid+35 wt% Lauric acid	18	120
65wt% Capric acid + 35wt% Lauric acid	18-19.5	140.8-148
61.5wt% Capric acid + 38.5wt% Lauric acid	19.1	132
65-90wt% Methyl Palmitate + 35-10wt% Methyl Sterate	22-25.5	120
76.5 wt% Capric acid + 23.5 wt%Palmitic acid	22.1	153
34wt% $C_{14}H_{28}O_2$ + 66wt% $C_{10}H_{20}O_2$	24	147
Octadecane + Docosane (% of Composition not available)	25.5-27	203.8
Octadecane + Heneicosane(% of Composition not available)	25.8-26	173.93
83 wt% Capric acid + 17 wt% Stearic acid	26.8	152
50wt% CH_3CONH_2 + 50wt% NH_2CONH_2	27	163

Table 4. Inorganic eutectic PCMs [3,6]

Material	Melting point (°C)	Latent heat of fusion (J g^{-1})
45wt% $Ca(NO_3)_2.6H_2O$ + 55wt% $Zn(NO_3)_2$	25	130
66.6wt% $CaCl_2.6H_2O$ + 33.3wt% $MgCl_2.6H_2O$	25	127
50wt% $CaCl_2$ + 50wt% $MgCl_2.6H_2O$	25	95
48wt% $CaCl_2$ + 4.3wt% NaCl + 0.4wt% KCl + 47.3wt% H_2O	26.8-29	190.8
47wt% $Ca(NO_3)_2.4H_2O$ + 53wt% $Mg(NO_3)_2.6H_2O$	30	136
60wt% $Na(CH_3COO).3H_2O$ + 40wt% $CO(NH_2)_2$	30	200.5

3.5 Properties of phase change materials

The essential properties for a material that can be used as phase change material are thermo-physical properties, chemical properties, kinetic properties and economic aspects.[7,8]

Thermo-physical properties

- Melting temperature in the operating temperature of the application
- High latent heat of fusion
- High specific heat capacity
- Good thermal conductivity
- Less volume change during phase change process

Chemical properties

- Chemically stable at elevated temperature
- Thermally reliable on extended operation
- Non-corrosive with the encapsulation material
- Non-toxic
- Non-flammable
- Non-explosive

Kinetic properties

- Melting and freezing process should be stable and at constant temperature
- Low degree of supercooling

Economic aspects

- Easily available
- Cost effective
- Recyclable
- Eco-friendly

3.6 Differential scanning calorimetry (DSC)

DSC is a thermo-analytical calorimetric technique in which the material to be tested is heated and cooled isothermally and the phase transition events are investigated as a function of time and temperature against a standard reference. [9,10]A DSC equipment is shown in Fig.2.The common procedure to be followed in DSC is as follows. The sample has to be prepared before placing it in the sample pan. It has to be weighed and the empty pan weight also to be measured. The sample pan is then placed on the pan press and encapsulated properly. After encapsulation, the reference material has to be prepared. It can be either known material or an empty pan. The sample pan and reference pan are placed on the sample holder.

Fig. 2. DSC instrument (Make: TA Instruments, Model: Q1000) [11]

The sample in the encapsulated pan is heated or cooled from its initial temperature to final temperature with isothermal phase transition in between and then heated or cooled back to its initial temperature. The latent heat of fusion can be calculated using DSC data analysis software. A DSC plot of organic PCM Myristylalcohol generated at Pondicherry University is shown in Fig. 3.

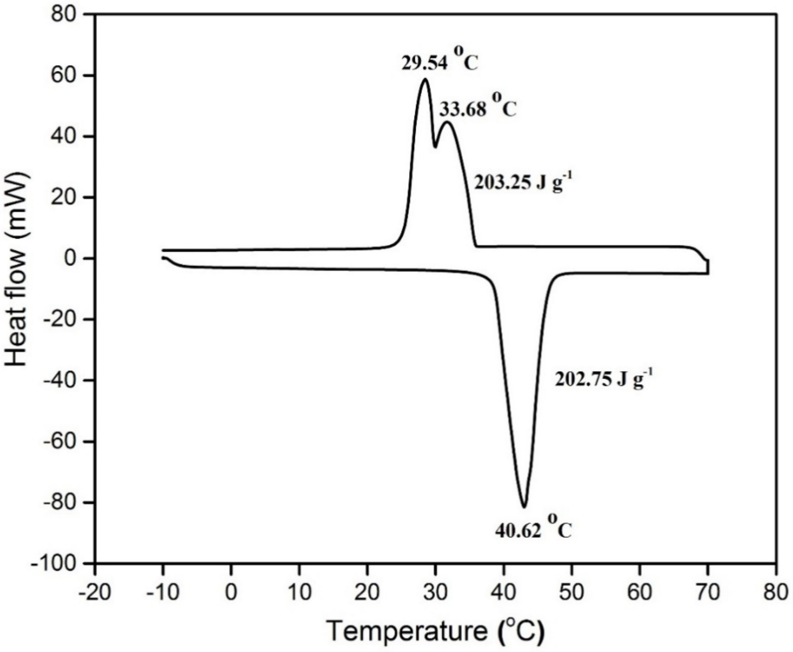

Fig. 3. DSC curve of Myristyl alcohol

Table 5. Properties of Myristyl alcohol from the DSC plot

Material	Melting (^{o}C)	Freezing (^{o}C)		Latent heat of fusion (J g^{-1})	
		First	Second	Melting	Freezing
Myristyl alcohol	40.62	33.68	29.54	202.75	203.25

4. PCM integration for cold storage in buildings

The PCMs are integrated with building and its structure in different ways in order to provide thermal comfort. Before integration, proper encapsulation has to be chosen to hold the PCM. The encapsulation can be of different types based on size, encapsulation material and configuration. Based on size, there are macro, micro and nano encapsulation of PCM. The micro and nanoencapsulation is generally used in PCM slurries and preparation of composite building materials. Macro encapsulation is a common method which is easy to prepare and integrate especially for the application of thermal comfort of buildings. With respect to types of encapsulation material, either metals or polymers are used. Depending upon the application, easy handling and for high efficiency, the PCMs are encapsulated in different configurations such as spherical balls, plates, blocks, etc. Macro encapsulation with different configurations are shown in Fig.4 to Fig. 9.

Fig. 4. PCM panel [12]

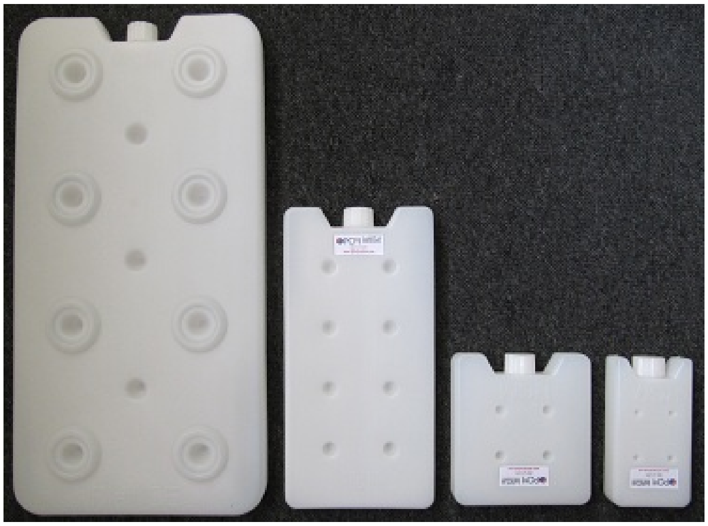

Fig. 5. PCM panels in different size [13]

Fig. 6. PCM capsules [14]

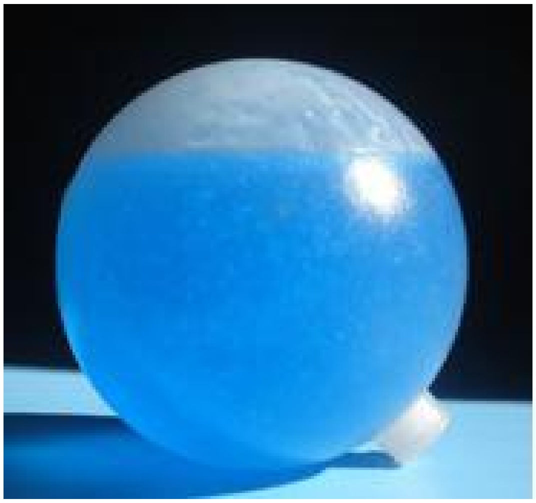

Fig. 7. Spherical balls made of HDPE [15]

Fig. 8. Spherical ball made of Stainless steel [16]

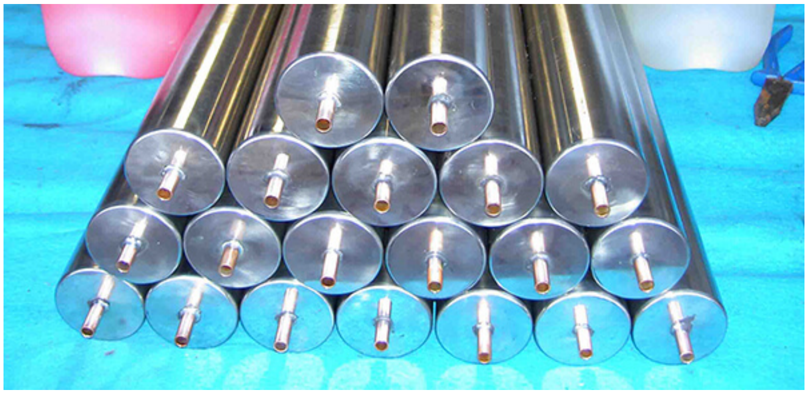

Fig. 9. Cylindrical encapsulation for PCM [17]

In buildings, the encapsulated structures can either be used as building materials or suspended in the space to be cooled. For long term storage, independent system is preferred as the amount of storage is more. In case of short term storage such as peak load demand or temperature fluctuations inside the building space, PCMs are encapsulated in different configurations such as integrated wall, ceiling and floor of the room. Fig. 10 shows the PCM filled polymer tubes fixed in ceiling for maintaining the room temperature. PCM filled panels fixed in ceiling are used in office building is shown in Fig. 11. By using encapsulated PCM, the load to existing air-conditioning system will be reduced.

Fig. 10. PCM filled polymer tubes suspended in ceiling [18]

Fig. 11. Office building with PCM ceiling[18]

5. Conclusion

Low temperature PCMs has potential applications like reduction of cooling load requirement in residential/commercial buildings. There are several practical problems while employing PCM for energy storage application such as heat transfer, stability, supercooling, computability with encapsulation etc. By overcoming these problems with advanced techniques, PCM will be a successful solution for energy efficiency related issues such as peak load levelling, short term storage and utilising ambient energy through free cooling. PCM based technologies will help to make a building energy efficient and eco-friendly. Construction of green building with self-sustainable energy technologies are increasing due to the impact of climate change globally. Advanced PCM technologies provide a better solution in reducing the energy needs of a building.

Acknowledgement

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Phase Change Materials

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Abstract

Latent heat storage systems (LHTES) have attracted considerable attention in recent years. Phase change materials (PCMs) used in LHTES, have turned out to be extremely advantageous in this regard as they absorb high amount of energy without much rise of temperature during phase change. Unfortunately, many PCMs, which have high latent heat capacity, possess low thermal conductivity, hence several enhancement techniques are developed and investigated. This work presents an overview on classification, thermophysical properties, challenges and applications of PCM as energy storage material. In addition, potential PCMs and their problems, heat transfer enhancement techniques and encapsulation methods have been discussed.

1. Introduction

Many available renewable energy sources are intermittent in nature and are available for a certain period during a day, which necessitate the use of energy storage system to bridge the gap between energy demand and supply in various applications. Energy can be stored in different forms, such as, mechanical, thermal, electrical, chemical *etc.* However, thermal energy storage (TES) system utilizing phase change material (PCM) could be a potential solution which is extensively researched in the past decades. It can be used in various applications such as electronic device cooling, solar based systems, heat recovery system, air conditioning application as well as building application for heating and cooling purposes. Thermal energy storage can be classified as short term and long term storage depending on the duration of operation [1]. For example, solar radiation is available only during daytime, hence a short time storage system is required for few hours, while some applications require long time storage system ranging from days to months. In solar application, the excess heat during daytime is stored in thermal energy storage system so that it can be used during nighttime. Similarly, in heat recovery system, thermal energy storage system stores the waste heat which is utilized in different time when it is needed.

Phase change materials (PCMs) are "latent" thermal storage materials and utilize the latent heat of fusion to store energy. In PCMs, heat is stored and released by using their chemical bonds. During transformations from a solid to a liquid or from a liquid to a solid, thermal energy transfer occurs in PCM. The transformation is known as change in state or phase. Initially, below the melting temperature, PCMs behave like a conventional storage material; their temperature rises as they absorb heat in the form of sensible heat. A typical melting curve of an elementary control volume of pure PCM with time is shown in Figure 1. Unlike conventional (sensible) storage material, PCM starts absorbing large amount of heat in the form of latent heat, without much appreciable change in the temperature, after reaching to its melting temperature. When the ambient temperature around the PCM drops, the PCM solidifies, releasing its stored latent heat. PCMs absorb and dissipate heat while maintaining a nearly constant temperature or within a temperature range. They store 3 to 4 times more heat per unit volume than sensible storage materials such as water, sand, concrete, rock, and pebbles. This work provides a review on phase change material, practical difficulties associated with it and different applications as a thermal energy storage system.

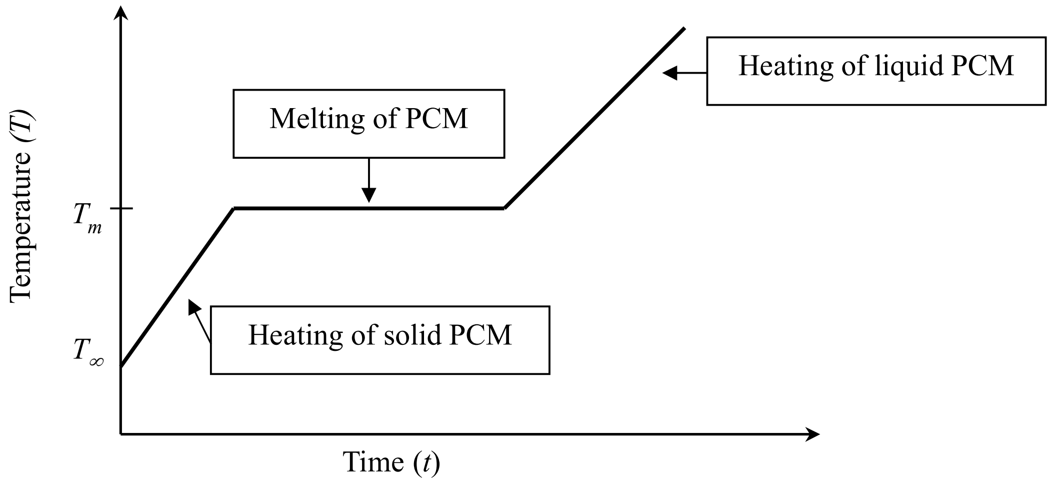

Figure 1: Typical melting curve of an elementary control volume of PCM (the PCM is considered to be a pure material)

2. Classification and properties

Hale et al. [2] reported more than 500 potential PCM candidates and their density and latent heat of fusion, which can be used as energy storage materials. However, only a few materials have actually been well characterized and suitable for the use in storage applications. A phase change material should be selected primarily based on melting temperature and its latent heat of fusion. The selected material must have high latent heat of fusion, so a large amount of energy can be stored in a small amount of PCM; high specific heat, which provides additional sensible heat storage capacity; high thermal conductivity in both solid and liquid phases increases heat transfer in PCM that reduces thermal stratification in PCM and makes the PCM melting and solidification homogenous; high density which reduces the storage size; low vapour pressure; chemically stable, so that the PCM will not be changed periodically; minimum or little subcooling which ensures PCM melts in a small temperature range or at a particular temperature; the PCM must be nonpoisonous; non-flammable; and non-explosive [3]. The PCM should be available widely and inexpensive from economics point of view.

PCMs can undergo solid-solid, solid-liquid, solid-gas and liquid-gas phase transitions isothermally or in a range of temperature. Solid-solid PCM stores and releases heat in the same manner as solid-liquid PCM, however always remains in the solid state under normal conditions, only softens or hardens. Comparatively few solid-solid PCMs are available that are suitable as storage materials. The use of liquid-gas PCMs is not practical yet as storage materials due to volume expansion during phase change from liquid to gas, although they possess high latent heat of transformation. Table 1 gives a comparison of various type of PCMs that experiences solid (S) –solid (S), solid (S)-liquid (L) phase transformation. Examples of PCMs having solid-solid phase change are polyurethanes, polybutadiene and Modified ploy (ethylene glycol) [1, 4].

Table 1: Comparison of some dry PCMs with typical paraffin-based, salt hydrates and metallic-alloy PCMs [5]

Material Type	**Transition**	**Temperature range (°C)**	**Latent Heat (Joule/cc)**	**Density (g/cc)**
Solid-solid Organic Compounds (TCC)	S-S (dry)	21-100	144-212	~1.1
Micro-encapsulated Paraffin (thermosorb)	S-L (dry)	6-101	95-186	~0.9
Paraffin (Eicosane, Docosane, *etc.*)	S-L (wet)	-12-71	128-197	0.75-0.88
Non-Paraffin Organics (Beewax)	S-L (wet)	-13-187	131-438	0.85-1.54
Salt Hydrates ($MgSO_4$-$7H_2O$)	S-L (wet)	28-137	270-650	1.5-2.2
Metallics (Eutectic Bi-Cd-In)	S-L (wet)	30-125	200-800	6-10

Depending on the chemical composition, PCMs are grouped into the families of either organic or inorganic material. Sub-families of the organic materials include paraffin and non-paraffin organics. The basic classification of PCM reported in various literatures is shown in Figure 2 [6, 7]. A comparison of organic and inorganic PCMs with their advantages and disadvantages is shown in Table 2 [6].

Table 2: Comparison of organic and inorganic phase change materials with advantages and disadvantages [6].

	Organic	**Inorganic**
Advantages	No Corrosive Low and non subcooling chemical and thermal stability	Greater phase change enthalpy
Disadvantages	Lower phase change enthalpy Low thermal conductivity Flammability	Subcooling Corrosive Phase separation phase segregation Lack of thermal stability

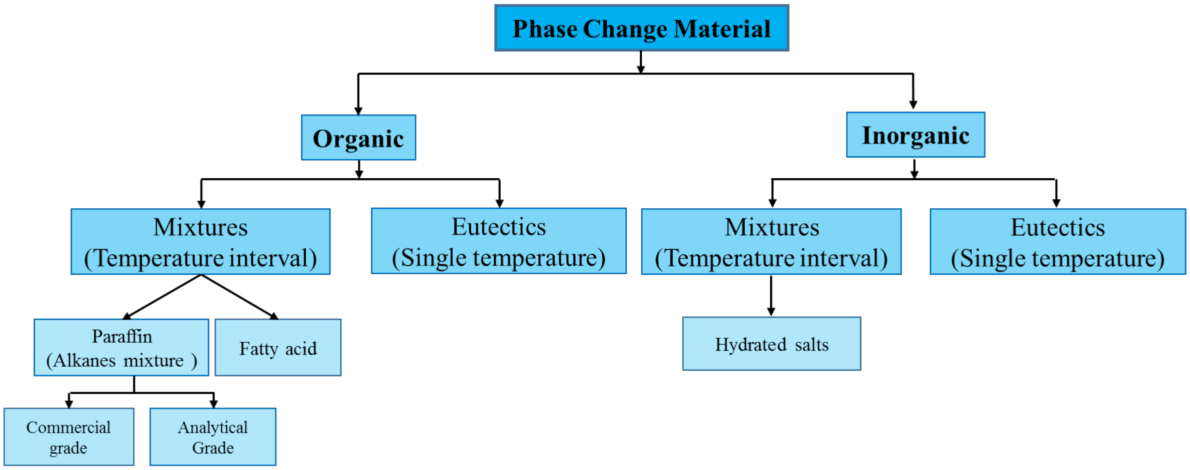

Figure 2: Classification of phase change materials [6, 8]

2.1 Organic and inorganic phase change materials

Organic PCMs are mainly open chain saturated paraffin and alkanes, while inorganics are salts, salt hydrates and alloys. Organic PCMs are non-reactive, non-corrosive, chemically stable, low vapour pressure, negligible subcooling and compatible with container material, however these materials suffer from low thermal conductivity and large volumetric change. The low thermal conductivity causes slow heat charging and discharging in PCM during melting and solidification, hence heat transfer enhancement techniques are employed to improve heat transfer in such PCMs. They also possess high latent heat of fusion and change phase isothermally or within a narrow temperature range. Inorganic materials have better thermophysical properties than the organic materials [9], as shown in Tables 3 and 4, in terms of higher operating temperature range and high thermal conductivity. Although inorganic materials are inexpensive, the chemical stability of these material is an issue, due to corrosiveness with metals and phase segregation and subcooling, especially in case of salt and salt hydrate, that reduces energy storage capacity [6]. However, metals and metallic alloy PCMs, which are used for high temperature applications, do not experience from the above disadvantages. The application-wise organic and inorganic PCMs are elaborately discussed in literatures [3, 9]. A few organic materials are listed in Table 3 [1, 6, 8, 10].

Paraffin: Paraffin is obtained from the petroleum waste product, this is the last product from the petroleum refining process added with some chemical and bleaching agent [11]. Paraffin is the widely used commercial phase change material, and is stable for about 1500 thermal cycles. Paraffin is a mixture of hydrocarbons with straight chain *n*-alkanes (C_nH_{2n+2}) [1]. The melting point of paraffin depends on the length of alkanes chain. For example, *n*-Tetradecane ($C_{14}H_{30}$) has melting temperature of 5.5 °C, whereas the melting temperature of *n*-Eicosane ($C_{20}H_{42}$) is ~36 °C. They have considerable cyclic stability without subcooling problem, hence are the most suitable candidates as energy storage materials, but possess low thermal conductivity. They are non-reactive, non-corrosive, however are similar with plastics in chemical properties.

Salt hydrates: Salt hydrates are inorganic PCMs having water molecules in the integral compound called water of crystallization [12]. They are inexpensive, non-flammable, have high latent heat of fusion, and their higher melting temperatures range making them ideal for many applications [1]. The major disadvantages of salt hydrates as PCMs are corrosiveness, subcooling and phase segregation because of poor nucleating ability and incongruent melting. The thermophysical properties of salt hydrates are listed in Table 4.

Fatty acids:Fatty acids are long hydrocarbon chain ($CH_3(CH_2)_{2n}COOH$) of carboxylic acids, especially occurring as esters in fats and oil [13]. They are corrosive and have undesirable odor which limits the use in building applications. Fatty acids are highly flammable at high temperature and expensive compared to paraffin, which reduces their application [1]. A few examples of fatty acid mixtures are given in Table 5 [14].

*Metals and metal alloys:*A few PCMs can be classified as metal and metallic alloys (eutectics), which have higher melting temperature > 300 °Cand their properties are tabulated in Table 6 [15]. Metallic PCMs have high thermal conductivity and hence any filler material or heat enhancement technique is not required to improve it, which reduces the cost of thermal energy storage. Thermal stability and cyclic performance are better than other PCMs. The main drawback is low heat of fusion per weight, which results in high weight of the storage system. However, the phase segregation and subcooling problems are not associated with this PCMs.Potential metal and metallic alloy PCMs were extensively reviewed by Liu et al. [16].

Table 3: Properties and application of commonly used organic PCM materials [1, 6, 8, 10]

Material	**Type**	**Melting Temprature (°C)**	**Heat of fusion (kJ/kg)**	**Thermal conuctivity (W/mK)**	**Application**
Paraffin	Paraffin	54	184	2.05	Waste heat recovery system
RT42	Paraffin	42	150	0.2	-
Stearic acid	Fatty acid	64.5	196	1.6	-
Malic acid	Fatty acid	51.5-53.6	190-204.5	0.17	Solar space & water heating
Palmitic acid	Fatty acid	61-63	204-212	0.162	Solar space & water heating
Polyurethane Polymer	-	29.8	191	-	PV panel cooling
Erythritol	Organic	118	339.8	0.326	Solar cooing
A164	Organic	168.7	249.7	0.45	Thermal energy storage
Hydroquinone	-	168-173	205	-	Solar cooing
Paraffin C14	Paraffin	4.5	165	-	-
Paraffin C16–C18	Paraffin	20-22	152	-	-
Naphthalene	Paraffin	80	147.7	0.132	-
Tetradecane	Paraffin	5.5	227	0.15	-
Dodecane	Paraffin	-9.6	216		Cold storage
Methyl fumarate	Organic	102	242	-	Solar cooling,
HDPE	Organic	100-150	200	-	-

Table 4: Properties and application of commonly used inorganic PCM materials [1, 6]

Material	**Type**	**Melting Temperature (°C)**	**Heat of fusion (kJ/kg)**	**Thermal conductivity (W/mK)**	**Application**
$CaCl_2.6H_2O$	Salt hydrate	30	170-192	1.08(s), 0.56(l)	Trombe walls, space cooling, greenhouse, PV panels
$Na_2CO_3.10H_2O$	Salt hydrate	33-36	247	-	Trombe wall
$MgCl_2.6H_2O$	Salt hydrate	117	168.6	0.694	Miscellaneous
$KF.4H_2O$	Salt hydrate	18.5	231	-	Space cooling
$Na_2.SO_4.10H_2O$	Salt hydrate	32	251	0.3 (l), 0.15(s)	Trombe walls, solar water heating, greenhouse
$CaBr_2.4H_2O$	Salt hydrate	110		-	

Table 5: Properties and application of commonly used eutectics PCM materials [14]

Material	**Type**	**Melting Temperature (°C)**	**Heat of fusion (kJ/kg)**	**Thermal conductivity (W/mK)**	**Application**
Palmitic acid- stearic acid (64.2/35.8 wt%)	Fatty acidmixture	52.3	182	-	Solar water heating
Lauric acid- stearic acid (75.5/24.5 wt%)	Fatty acidmixture	37	183	-	Solar heating
Capric acid-palmitic acid (76.5/23.5 wt%)	Fatty acidmixture	22.15	173.16	0.14	Greenhouse
Myristic acid+stearic acid (65.7/34.7 wt%)	Fatty acidmixture	44	181	-	Low temperature heat storage

Table 6: Properties and applications of commonly used metal and metal alloys PCM materials [15]

Material	Type	Melting Temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/mK)	Application
Pb	Metal	328	23	35	
Cu	Metal	1083	193.4	386	Solar thermal power plant
Mg (commercial purity)	Metal	648	365	-	
Al–Mg–Zn (60/34/6 wt%)	Metal alloy	443	312	-	
Al-Si (88/12 wt%)	Metal alloy	577	462	181	
Si–Mg (56/44 wt%)	Metal alloy	946	757	-	

2.2 Measurement techniques

The thermophysical properties of PCM are required to determine accurately for designing of effective and efficient thermal energy storage. The morphology of PCM can be studied by scanning electron microscope (SEM). Fourier transform infrared spectrometer (FT-IR) is used to investigate the chemical compatibility of compounds [1]. Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are used to determine the specific heat of PCM and phase change temperature during melting and solidification of PCM. It can also be used to estimate latent heat of fusion of PCM. The dynamic viscosity of PCM is measured by rheometer. The thermal conductivity of PCM is measured either directly using hot wire method or indirectly through thermal diffusivity, specific heat and density, which are measured separately. The volumetric thermal expansion coefficient of PCM can be easily estimated using a slender cylinder made of quartz by measuring the change in volume of liquid PCM at different temperatures [10].

2.3 Challenges with PCMs

2.3.1 Thermal and chemical stability for long term storage

The use of PCMs in thermal energy storage system is limited due to their thermal and chemical stability for long cycles without deterioration of their thermophysical properties. Application of repeated thermal cycles may result in the change in thermal properties of PCM [12]. Also, PCM should be compatible with storage material to prevent the potential damage of thermal properties. The problems associated with the compatibility of PCM with storage system are: (i) inorganic PCM reacts with metal storage container causing corrosion and (ii) plastic storage material losses stability in contact with organic PCM. The corrosion on the surface of storage container can be reduced by applying coating or galvanizing with zinc. Generally, stainless steel (SS316) and carbon based containers are not reactive to most of the PCMs.

2.3.2 Phase segregation and subcooling problems

There are two severe problems associated with PCM, especially with inorganic PCM, *viz.* (i) phase segregation and (ii) subcooling. The storage density of salt hydrate decreases with the thermal cycle due to incongruent melting, that causes the reduction in reversibility of phase change process [12]. At the time of melting, most of the hydrated salts melts congruently with the formation of lower hydrated salt, due to this the process becomes irreversible which results in the continuous drop in their storage efficiency [3, 8]. The drawback of phase segregation can be reduced by the addition of another material as a hinder which sinks heavier phase to the bottom by changing the properties of salt hydrate. This can be achieved by two methods, *viz.* by adding gelling or thickening material [8]. In gelling method, a cross linked material is added to salt for the formation of three-dimensional network that holds the salt hydrate together. Another method for the prevention of phase separation is the addition of material (nucleator) to increase the viscosity, which helps to hold the salt hydrate together called thickening.

The phenomenon of subcooling occurs when salt hydrate starts solidifying at lower temperature than the congealing temperature. To prevent from subcooling, several methods are used; one method is the use of salt hydrate with direct contact heat transfer between immiscible heat transfer fluid (HTF) and salt hydrate and another solution is the use of nucleator with salt hydrate [3]. Nucleators used with salt hydrate to prevent subcooling reported in literatures are as follows:

a. *Intrinsic nucleator*: Solid PCM particles are kept separately from the PCM to prevent these particles from melting andthereby, becoming inactive.
b. *Extrinsic nucleator*: These are the chemicals with similar crystal structures as the solid PCM. These chemicals have similar phase transition temperatures as the PCM, and thus become deactivated very close to the phase change temperature of PCM [8].

2.3.3 Heat transfer enhancement method

Most of the organic PCMs have unacceptably low thermal conductivity, hence enhancement methods are required to enhance heat transfer in PCM. Various methods are proposed to enhance heat transfer between HTF and PCM and within PCM, which can be broadly classified as, (i) increase of the heat transfer area and (ii) improvement of the effective thermal conductivity. Figure 3 shows a layout of different techniques for enhancing heat transfer in PCM. A brief description on each enhancement technique is presented next.

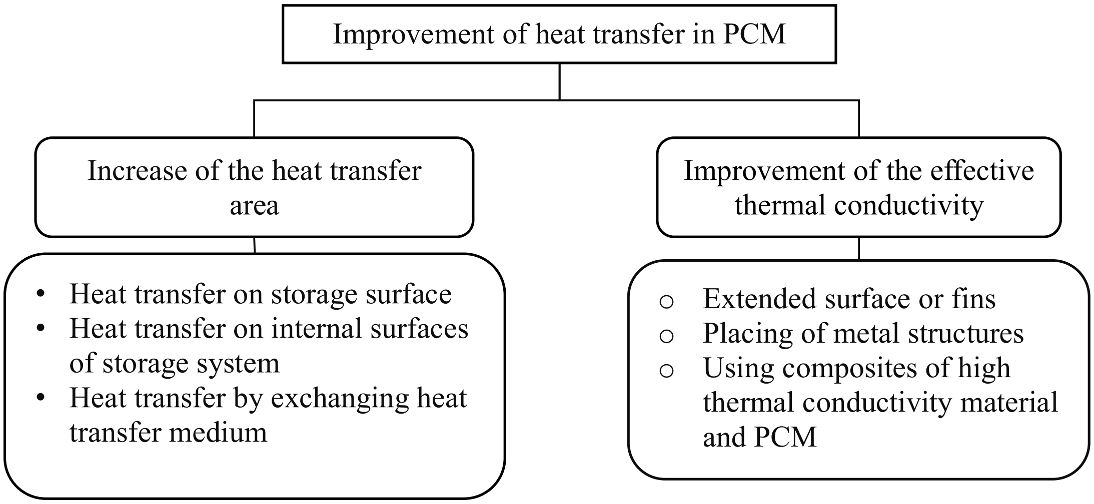

Figure 3: Different heat transfer enhancement techniques in PCM

(a) Increase of heat transfer area:

The storage is designed in such a way that the heat transfer surface increases. Thermal energy storage can be classified into three types based on the heat transfer surfaces, *viz.* 1) on the storage surface, 2) on the internal surfaces of storage and 3) by exchanging heat storage medium.

Heat transfer on storage surface: A few studies have been carried out on the thermal performance of this type of storage system and also at low temperature (< 120 °C). Examples of this techniques are: (i) cylindrical energy storage tank which consists of PCM filled cylindrical vertical tubes surrounded by a cylindrical jacket through which heat transfer fluid is flowing [1, 17], (ii) PCM based storage in graphite foam [5, 18].

Heat transfer on internal surfaces of storage system: Several designs are developed either in laboratory or commercially under this category. The most widely studied domain is the shell-and-tube geometry [6, 19], where the PCM is stored in the annulus and heat transfer fluid (HTF) flows through the pipe, however opposite arrangement is also investigated [8, 20].

Heat transfer by exchanging heat transfer medium: The third way of transferring heat is to use small encapsulated PCMs flowing within the heat transfer fluid. The encapsulation of PCM ensures compatibility with outside environment. These encapsulated PCMs are so small that it can leave the system. The advantages of using encapsulated PCMs are:

a. Larger surface area than volume
b. Subcooling and segregation of few PCMs during the thermal cycling can be overcome
c. Shorten the heat transfer times during charging/ discharging
d. Protection of PCM from exposure and corrosive heat transfer fluid

However, the problems with encapsulated PCMs are compatibility of encapsulation with PCM and the processes of encapsulating PCM here the volume change during phase transformation needs to be accounted.

There are mainly two techniques for encapsulating PCM, *viz.* macro encapsulation and micro encapsulation [1]. In macro encapsulation technique, phase change material is clenched into pockets, such as spheres, tubes, thin plates of other material. This technique is used to protect PCM against the environmental degradation and also it provides volume control and easy to use in building application. This technique has leakage issue and disadvantages of poor heat transfer characteristics and thermal stratification, which limits its use. The disadvantages of macro encapsulation technique can be reduced using micro encapsulation technique, which increases the application range. In this technique, capsules are formed by coating the PCM material with very thin layer of other material such as polymer. It reduces the problem of leakage, volumetric change during phase change and reactivity to the environment, while it improves the strength and compatibility with outside heat transfer material. Two methods are used for micro encapsulation, physical and chemical encapsulation. The physical encapsulation technique is cheaper and easy, while chemical methods costly and complex but provides desired properties with distinct particle structure and therefore used widely [21]. The advantages and disadvantages of these techniques are shown in Table 7 [1].

Table 7: Comparison of macro and micro encapsulation with advantages and disadvantages [1]

Category	Advantages	Disadvantages
Macro encapsulation	• Good compatibility with material. • Easy PCM handling. • Prevent changes in composition with surrounding. • Use as a heat exchanger directly. • Thermal reliability is considerably increased.	• Thermal conductivity is poor. • Manufacturing problem like leakages. • Poor heat transfer performance.
Micro encapsulation	• Improved heat transfer performance. • Improved chemical stability • Prevent from leakage.	• Lead to subcooling effect • Strength of microcapsule shell material could be affected. • Costly process. • Reduces the effect of natural convection which affects the solidification process.

(b) Improvement of the effective thermal conductivity:

One important issue needs to be addressed, is the thermal conductivity of organic PCM, which is low (~0.2 W/m.K) and as a result, heat transfer rate is slow within PCM during melting and solidification. The improvement of heat transfer can be achieved by inserting high thermal conductivity materials, known as thermal conductivity enhancer (TCE) into the PCM. The TCE could be in the form of metal matrix, fins, graphite flakes, copper foam with fin, circumferentially positioned fin, lauric acid based nanocomposites using chemically functionalized graphene nanoplatelets, carbon nanostructures, carbon nanotubes, nanoparticles of metallic (Ag, Al, C/Cu and Cu) and metal oxide (Al_2O_3, CuO, MgO and TiO_2) and silver nanowires,dispersion of metallic particles in PCM, multi-tube, rings and bubble agitation in PCM [22].

3 Major applications

3.1 Solar thermal application:

In today's energy scenario, solar energy is considered as one of the potential energy sources and can be used effectively in large scale with the use of thermal energy storage.

Latent heat based energy storage technique are effective to store the solar energy during daytime, which can be used to reduce the fluctuations due to clouds as well as can be utilized during nighttime. PCM can be used in two major applications, (i) low temperature, and (ii) high temperature. The detailed review of solar energy application can be found elsewhere [23], however a brief is presented here.

A. **Low temperature applications:** The operating temperature range is 0 to 80 °C. Solar water heating, air heating applications and dryer are considered in this category [1]. Solar water heating system is simple in manufacturing and inexpensive. The use of PCM for storing heat in solar water heating system is extensively studied by several authors in recent years [24].

B. **High temperature applications:**Solar thermal power plant using concentrated solar collector or Fresnel solar collector is considered as the high temperature solar application with the operating temperature above 120 °C. The concentrated solar power (CSP) based high temperature solar application integrated with latent heat thermal energy storage using PCMs is currently an active research area. Solar radiation is intermittent in nature during daytime, hence excess energy from solar radiation can be stored in PCM based thermal energy system which is utilized during fluctuations and useful to extend the energy generation during nighttime [25].

3.2 HVAC system and food industries:

Solar absorption cooling system is new technology developed in air conditioning and refrigeration applications. There are two main methods of refrigeration absorption using electricity and using thermal energy. Thermal approach can be thermo chemical or sorption, in which sorption methods have various types *viz.* adsorption, absorption and chemical adsorption. Solar absorption system is mostly used in cooling application in recent years because of high energy efficiency and economic feasibility. This system is working on a vapor refrigeration cycle, generator and absorber are used in compression of refrigerant to produce cooling effect. Solar energy is used to heat the low-pressure refrigerant from generator to convert it into vapour at high pressure. The process of generating high pressure vapour in absorption system with the use of solar energy is known as solar absorption system [26]. There are two types of absorption refrigeration systems, (a) continues and (b) intermittent absorption system. Solar absorption system needs continuous operation for various applications, however due to fluctuations in solar radiations, there is a need of thermal energy storage system in solar absorption system. Thermal energy storage system also improves the thermal performance and reliability of the system.

PCMs are used in food industry to preserve, pack and transport the foods and fruits. Several PCM based storage systems are studied, *viz*. shelf integrated with PCM and heat pipes [27], rapid temperature balancing container with PCM [28], submicro-encapsulated PCM plate [29].

3.3 Thermal management of building

Suitable PCMs are used in cooling and heating of buildings for thermal comfort of human and thus significant electricity consumption can be saved by utilizing energy during peak period that was stored during off peak period. According to American Society of Heating, Refrigeration, Air-conditioning Engineers (ASHRAE), the room temperature should be in the range of 23.5-25.5 °C in summer and 21-23 °C in winter, which can be maintained by PCMs with melting temperature range 20-30 °C. For this purpose, encapsulated PCMs can be used in three different ways, *viz.* (i) in building walls, (ii) in building floors or ceiling and (iii) external heat or cold storage units. The charging and discharging of PCMs, in first two cases, can automatically happen based on the ambient temperature. PCMs fixed with external wallboard, *e.g.* plaster, gypsum, are used in building walls. Floors and ceiling are also used for cooling and heating of room, and the use of heat pipes and PCMs can make it easy to install the system [1]. Another method of maintaining temperature of building is the use of external heat or cold storage units, which require external source for charging and discharging. Refrigerator with PCMs is an example of such system.

3.4 Thermal management of electronics

Thermal management issues for electronic devices arise because of their high heat dissipation rates. Even if the power levels are low, the heat dissipation rates are usually high because of the compactness and complexity in electronic packaging. For these high heat dissipation rates, traditional cooling techniques such as natural convection or forced convection are no longer sufficient and they may increase the frequency of failures. Various cooling techniques are broadly classified into two groups, *viz.* (a) active cooling and (b) passive cooling. Active thermal management requires external energy to be applied to remove heat from an electronic device. In case of passive techniques, the removal of heat from an electronic device does not need any external energy to maintain the coolant flow. Phase change cooling is one of such technique, which has been widely used as an alternative cooling method for numerous applications such as power electronics, communication equipment, wearable computers, space craft and avionics *etc.*, where heat dissipation is time-varying or periodic. This is the case in many of the above-mentioned applications.

3.5 Textiles

Clothing plays an important role to maintain the body temperature within a comfortable temperature range. Fabric cotton, polyesters, wool, polyacrylic fibers can be used to produce the insulation effect [1], which can also be obtained by the use of some external materials for insulation and this type of insulation is called active insulation in textile application. These active materials are used as a heat storage using PCM [30], and can be easily incorporated with micro encapsulation or by coating on cloths. Spherical microcapsules containing liquid PCMs can be used in protective clothing such as sportswear and shoes, blankets, thermal insulators *etc.* [1]. When the environmental temperature changes, the encapsulated material absorbs or releases heat which helps to maintain temperature in cyclic cooling and heating. Organic PCMs are the most common materials used in textile application.

3.6 Automobiles

PCMs can be an attractive solution in automobiles for improving the overall performance. Various organic PCMs can be used in cooling of automobile engine, which increases the overall efficiency. Erythritol is one of the best PCMs for this purpose [31]. PCMs are used in the thermal management system of automobiles, especially in cold weather. An exhaust heat recovery with LHTES system can be useful in battery heating at the time of cold start of the engine. Mostly, paraffin based materials are used for this type of application [32]. Also, PCMs are useful in thermal comfort of passengers and pre-heating of catalytic convertor.

4. Conclusion

This work focuses on thermophysical properties, development challenges and application of PCMs. PCM based thermal energy storage systems can be used to reduce the mismatch between energy demand and generation. Several issues associated with PCM, such as subcooling, phase segregation, poor thermal conductivity, can be overcome by suitable techniques. Different encapsulation techniques and their advantages and disadvantages are discussed. Organic PCMs are found to be the most suitable storage material as they offer higher energy density and marginal subcooling. However, there is a need for extensive research on the development of new PCMs and the feasibility of using PCMs as storage material in different applications.

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Report on THERMAWORK – 2016

Indian Thermal Analysis Society organisedFirst DAE-BRNS Workshop on Thermal Analysis, THERMAWORK-2016, during 20-21 December, 2016 at Multipurpose Hall, Training School Hostel, Anushaktinagar, Mumbai-400094. With an aim to keep up pace with the development in the subject area and to expose young researchers to a variety of topics related to basic and applied aspects of thermal analysis that are of interest to DAE and industry, the Indian Thermal Analysis Society (ITAS) organized the workshop on Thermal Analysis, THERMAWORK-2016. More than 150 delegates including invited speakers/ session chairman, participated in the workshop. Eminent scientists from academic, research and industrial organizations were invited to deliver lectures during the workshop. There were fifteen workshop lectures which covered basic and applied aspects of Thermal Analysis, instrumentation and methods and applications of thermal analysis in characterizing nuclear materials, alternate energy materials, composites, ceramic, alloys, polymeric materials, glasses, catalysts and nanomaterials. The gist of workshop lectures was compiled in the form of an abstract book and was made available to the participants of the workshop.

From Left to Right: Dr. A. M. Banerjee, Secretary, Thermawork-2016, Dr. K. I. Priyadarsini, Head, Chemistry Division, Dr. B. S. Tomar, Director RC&I Group & Head RACD, Dr. S. Kannan, Head Fuel Chemistry Division, Chairman, Thermawork-2016 and President ITAS, Dr. Mrinal R. Pai, Convener, Thermawork-2016.

The workshop was inaugurated with introductory remarks by Dr. B. S. Tomar, Director, Radiochemistry and Isotope group, Head Radio-Analytical Chemistry Division, and Abstract book was released by Dr. K. I. Priyadarsini, Head Chemistry Division. The workshop began with a keynote address by Dr. G. K. Dey, Director Materials Group, Head Materials Science Division on “Some Novel Applications of Thermal Analysis”. He focussed on fascinating applications of thermal analysis in the field of material science, for instance how to delineate the magnetic transition occurring simultaneously with a structural transformation in the same range of temperature using an inductively heated dilatometer in case of invar. Many other important innovations and novel studies were also mentioned in the keynote address. Invited speakers presented their research work and perspectives on several thermal analysis techniques for diverse applications.

The workshop concluded with a valedictory function chaired by Dr. V. Venugopal, Ex-Director, RC&I Group, BARC.Other senior members involved in conducting the valedictory function were Dr. K. Ananthasivan, Head, Fuel Chemistry Division, IGCAR, Kalpakkam, Prof. A. Pratap, MSU, Baroda, Dr. A. K. Tyagi, Head, Solid State Chemistry Section, Chemistry Division, BARC and Dr. Renu Agarwal, Head, Actinides Thermochemistry Section, FCD, BARC.Many participants gave their feedback about the workshop and appreciated the indepth basic aspects, instrumentation and applications of thermal analysis in various industrieswere dealt in the topics. The workshop offered an excellent platform for young researcher to discuss among delegates and experts in the field. This could lead ways to strengthen their research by interdisciplinary and multi-institutional cooperation.