

Design and Development of Temperature-History Setup

4.1 INTRODUCTION

Phase change materials (PCMs) are widely used for thermal energy storage applications because of their high energy storage density, and heat storage/release in small temperature window near melting temperature. Such requirements compel to design and develop materials with high latent heat of fusion for thermal energy storage applications. The knowledge about the major thermal properties of PCMs is important for engineers to design efficient LHTESS [Shansundar and Sparrow, 1975; Cabeza et al., 2014; Kant et al., 2016; Sobolciak et al., 2016; Nasiru et al., 2017; Salunkhe et al., 2017]. Calorimetric methods such as differential scanning calorimeter (DSC) and Differential Thermal Analysis (DTA) are being widely used to determine thermal properties of materials [Hohne et al., 2003; Mehling and Cabeza, 2008]. DSC is the most popular method among all calorimetric methods and is used widely for understanding the thermal properties such as melting and solidification point, latent heat, specific heat of solid and liquid phases, glass transition temperature etc. of materials [Feldman et al., 1995; Cho and Choi 2000; Alkan, 2006; Baran and Sari 2003; Hawlader et al., 2003; Kakiuchi et al., 2003; Lamberg et al., 2004; Rusell et al. 2004; Cai, et al. 2006; Akgun et al., 2007; Sarier and Onder 2007; Sun et al. 2007; Zhang et al., 2007]. However, characterization of PCMs using DSC has certain limitations such as, (i) measurements are carried out on small quantities of samples (few milligrams), which may lead different thermal response against bulk materials used in TESSs; (ii) enthalpy versus temperature measurements of PCM cannot be carried out at different supercooling temperatures; (iii) latent heat of fusion, specific heat, degree of supercooling , thermal conductivity and thermal diffusivities of numerous materials samples cannot be measured simultaneously; (iv) the response is heating and cooling rate dependent; and (v) complex and costly [Yinping et al., 1999; Marin et al., 2003; He et al. 2004; Arkar and Medved, 2005; Genovese et al., 2006; Vyazovkin, 2006; Castellon et al., 2008; Gunther et al., 2009; Barreneche et al., 2012].

To overcome the shortcomings of conventional measurement techniques, Yinping developed a novel method for characterization of PCMs' thermophysical properties and is known as temperature-history (T-History) method [Yinping et al., 1999]. The T-History method is getting more attraction because of its applicability for characterizing PCMs' thermophysical properties. This can be used with large sample amounts (10-50 g), in conjunction with a possibility of characterizing numerous samples simultaneously. This is a simple method and relatively economical if compared with conventional DSC measurement techniques. The T-history method can provide more realistic results about volume dependent properties such as supercooling and phase separation, heating and cooling rates comparable to real applications. The Yinping method was further improved to extract PCMs' enthalpy-temperature response with reduced measurement errors [Marin et al., 2003; Hong et al. 2003 and 2004]. Lazaro et al., 2006 discussed a methodology to verify the applicability of T-History method using three standard material, gallium, water and hexadecane and observed that this method can be used for such applications. Sandnes and Rekstad proposed a different T-History experimental procedure to measure PCMs' thermophysical properties [Sandnes and Rekstad, 2006]. The temperature dependent heat loss from reference sample test tube was determined in advance and does not measure with PCM samples each time. Gunther et al., 2009 discussed about the required

accuracy of T-History method for determining enthalpy as a function of temperature. Sole et al. 2013 reviewed T-history methods to measure thermal properties of PCMs. Recently, Cabeza et al. 2014 reviewed all unconventional experimental techniques used for characterization of thermal properties of pristine and composite PCM systems. Rathgeber et al., 2014 discussed a methodology to calibrate T-history setup for measuring PCMs' enthalpy in 40- 200 °C temperature range.

T-History method has been used by many researchers for characterization of thermophysical properties of PCMs such as paraffins, salt hydrates, RT21, granular PCM composites etc. [Rady et al.; 2010; Chiu et al., 2012; Li et al., 2012; Stankovic and Kyriacou, 2012]. However, standard T-history measuring system is not available commercially. We have attempted to design and fabricate a T-history setup at IIT Jodhpur for characterization of PCMs and used in the present work.

4.2 DESIGN DETAILS of T-HISTORY SETUP

A T-History setup consisting a temperature controlled air chamber, temperature measuring sensors, and data logger connected with computer is designed and fabricated for T-history measurements of PCM developed in the present work. The actual photograph of experimental test set-up is shown in Figure 4.1 (a). The air bath is selected against water bath to improve T-history results by reducing the heat transfer rate from PCM to ambient and to carry out both heating and cooling experiments in the range of 0-100 °C in same chamber. The internal dimensions of air-bath chamber are 60cm (Length) x 32cm (Width) x 30cm (Height). A 500 W heating and 600 W refrigeration system are used for heating and cooling of material in 0 to 100 °C temperature range. A double stage refrigerating compressor is used for better temperature stability inside the chamber. The temperature stability inside air chamber is ± 0.5 °C. A variable speed air circulating system is integrated with air chamber to ensure the spatial temperature uniformity and to achieve uniform temperature across the PCM container. The temperature uniformity around the PCM container is required to get uniform heat transfer across the entire test tube length and to minimize temperature gradients inside samples under investigation. Additionally, a provision for stainless steel mesh has been made to slow down the air circulation, if required to achieve desired heat transfer from test tube. The temperature response for these PCM samples has been recorded using calibrated K-type thermocouples (~15 cm (length) and 0.5 mm diameter). The temperature sensors are connected with 40 channel data logger (Make: Agilent; Model: 34972A), connected to the computer, for automation. The Cylindrical glass test tubes of size 20 cm (length) X 2 cm (diameter) X 1 cm (thickness) used for measurements. The temperature uniformity (minimum temperature gradient) within the PCM sample inside the container is important to limit heat loss by the tube surface to air rather than by internal heat transfer process [Goose, 1986]. To ensure the same and to apply lump capacitance model, Bi number for material container should be less than 0.1 to calculate thermophysical properties more accurately [Marin et al., 2003; Sandnes and Rekstad, 2006]. Hence, we used effective thermal insulation around the sample under investigation and the reference sample test tubes. The cylindrical insulation made of expanded polypropylene (EPP) of size 28 cm (Length) X 15 cm (Diameter) is used, shown in Figure 4.1(b). The EEP insulating material is used for insulation because of its thermal stability up to 120° temperature, low thermal conductivity (0.04 W/m.K) and lower heat capacity. This insulation provides lower heating and cooling rates for sample and reference materials as compared to that of measurements without insulation. Further, it helps to reduce the temperature gradients inside the sample and reference materials. In addition to above, a very low rate of heat transfer to the ambient is achieved during these experiments.

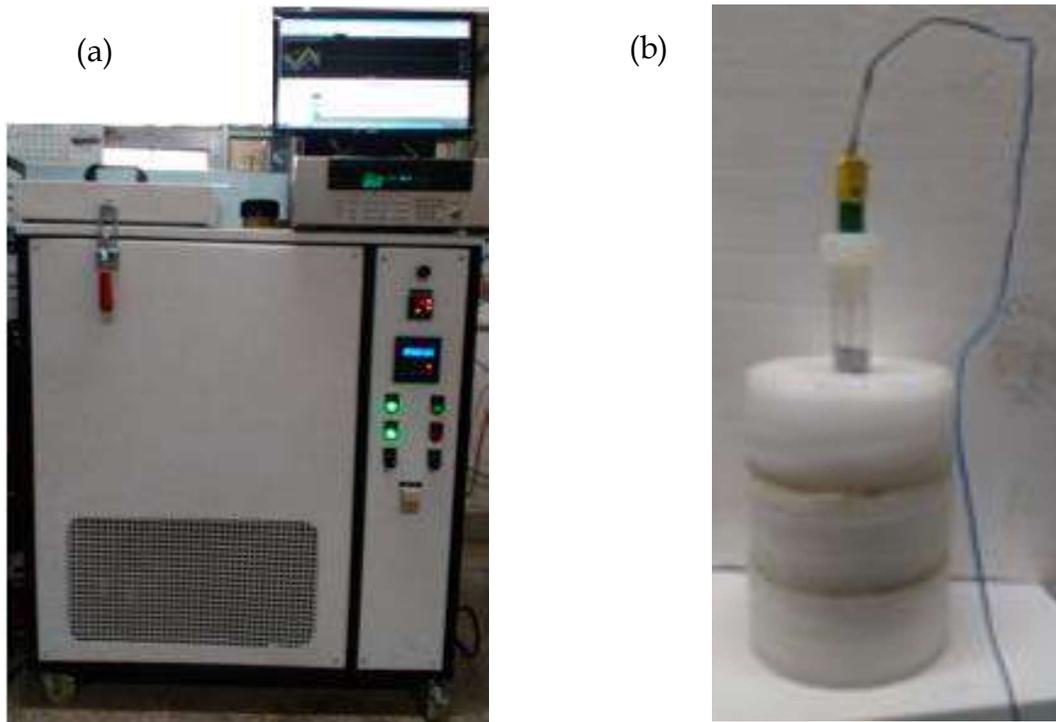


Figure 4.1: Actual photograph of (a) T-history installation and (b) glass test tube with EPP insulation and K type thermocouple used for T-history measurements

4.3 EXPERIMENTAL DETAILS

We used Sandnes approach to determine enthalpy of PCMs as a function of temperature. The enthalpy versus temperature curve provides important information such as useful temperature range for operation, increase in temperature during crystallization, available enthalpy at different supercooling temperatures, thermal energy lost in supercooling process, and specific heat of PCM in solid and liquid phases. The deionized water is used as a reference sample because of its well-known heat capacity. The weight of each sample is kept constant (~ 50 g) for T-history measurements. The test tubes with deionized water and PCM samples are placed in size 28 cm (Length) X 15 cm (Diameter) cylindrical insulation, made of expanded poly propylene. Temperature sensor is placed at the center of glass test tubes. The test tubes are placed inside controlled air chamber of T- history set up, shown in Figure 4.2.

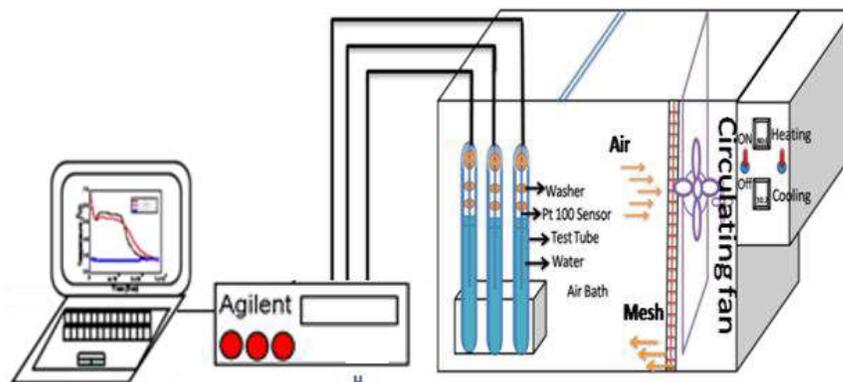


Figure 4.2: Schematic structure of T-history measuring setup assembled at IITJ

Initially, the water and PCM samples are heated above melting temperature of PCMs inside the air chamber and then cooled to the ambient temperature below melting temperature of PCM to record T-history data. The ambient temperature is also recorded simultaneously. The temperature history of all samples are recorded at every 10 seconds time interval using data logger and stored in computer. These recorded T-history data of water sample are used for calculating rate of heat loss from deionized water sample using the following Eq. (4.1):

$$\dot{q}_{w,i} = (m_w c_{p,w} + m_t c_{p,t}) \frac{\Delta T_{w,i}}{\Delta t_i} \quad (4.1)$$

Where $\dot{q}_{w,i}$ is the rate of heat loss from water test tube, m_w mass of water, $c_{p,w}$ constant pressure specific heat capacity of water (4.18kJ kg⁻¹ K⁻¹), m_t mass of glass test tube, $c_{p,t}$ constant pressure specific heat capacity of test tube (0.84 kJ kg⁻¹ K⁻¹), $\Delta T_{w,i} = T_{w,i+1} - T_{w,i}$ temperature difference between two consecutive measurements of water and $\Delta t_i = t_{i+1} - t_i$ is time interval between two consecutive measurements, which is 10 second for these measurements.

The calculated rate of heat loss from deionized water sample versus temperature difference between deionized water and ambient ($T_w - T_{amb}$) is plotted. A second order polynomial has been fitted to these heat loss data, as shown by red solid line and used to estimate the heat loss coefficients k_0 , k_1 , and k_2 , as described in following Eq. (4.2):

$$\dot{q}_{(T_w - T_{amb})} = k_0 + k_1(T_w - T_{amb}) + k_2(T_w - T_{amb})^2 \quad (4.2)$$

The temperature versus time measurements of PCM samples in conjunction with the calculated heat loss coefficients k_0 , k_1 and k_2 for deionized water are used to calculate the combined rate of heat loss from PCM and test tubes containing PCM samples, using following equation:

$$\dot{q}_{PCM+test\ tube,i} = k_0 + k_1(T_{PCM,i} - T_{amb,i}) + k_2(T_{PCM,i} - T_{amb,i})^2 \quad (4.3)$$

The rate of heat loss from PCM is calculated using following equation:

$$\dot{q}_{PCM,i} = \dot{q}_{PCM+test\ tube,i} + (m_t c_{pt}) \frac{(T_{PCM,i+1} - T_{PCM,i})}{(t_{i+1} - t_i)} \quad (4.4)$$

Where $\dot{q}_{PCM+testtube,i}$ and $\dot{q}_{PCM,i}$ are the rate of heat loss from PCM and test tube and the rate of heat loss from PCM at ith time interval, m_t mass of test tube, $c_{p,t}$ constant pressure specific heat capacity of test tube (0.84 kJ kg⁻¹ K⁻¹), $T_{PCM,i+1} - T_{PCM,i}$ temperature difference between two consecutive measurements of PCM and $t_{i+1} - t_i$ is time interval between two consecutive measurements, which is 10 seconds for these measurements. The calculated rate of heat loss from PCM using Eq. (4.4) is used to calculate the change in enthalpy ($\Delta H_{PCM,i}$) of PCM for ith time interval using following Eq. (4.5):

$$\Delta H_{PCM,i}(T_{PCM,i}) = \frac{\dot{q}_{PCM,i} \Delta t_i}{m_{PCM}} \quad (4.5)$$

The calculated $\Delta H_{PCM,i}$ are summed to calculate the cumulative enthalpy of PCM samples with respect to the temperature using Eq.(4.6):

$$H_{PCM}(T_{PCM}) = H_0 + \sum_{i=1}^{i=N} \Delta H_i \quad (4.6)$$

Were, H_0 is an arbitrary reference value, we used $H_0=0$

4.4 RESULTS AND DISCUSSION

4.4.1 Temperature Uniformity inside T-History Air Chamber

The spatial temperature uniformity inside the air chamber was examined by recording T-history measurements for de-ionized water. Initially, 50g water was taken in four glass test tubes and then heated in air chamber up to 70 °C at different spatial configurations. The cooling response of samples was recorded at time interval of 10 seconds. The results are plotted in Figure 4.3.

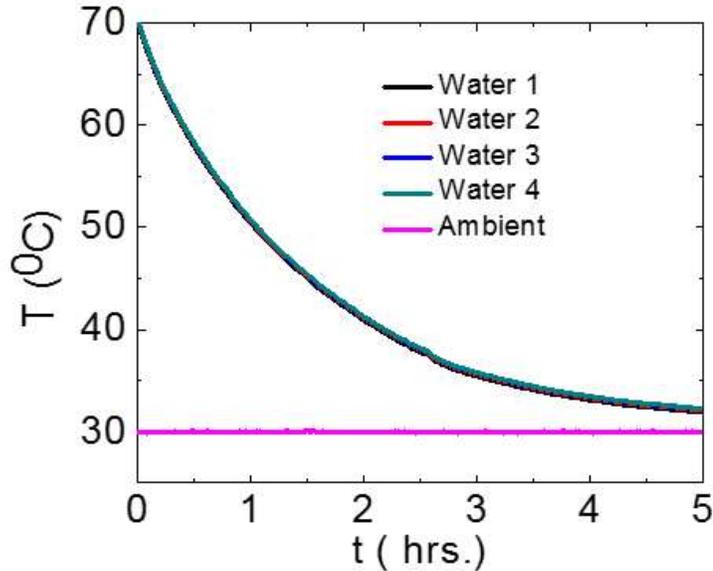


Figure 4.3: Cooling thermal response of four deionized water test tubes placed at different locations of air chamber

All cooling curves of water samples overlapped each other, Figure 4.3. These measurements substantiate the spatial uniformity of temperature within the test chamber. Thus, the present setup can be used for measuring T-history response for various materials simultaneously inside the single chamber.

4.4.2 Validation of T-History Results

We carried out measurements on organic (palmitic acid) and inorganic material (sodium acetate trihydrate) phase change materials and used to determine the enthalpy verses temperature data for these materials to validate the method and to ensure proper operation of T-history setup for phase change materials, used in the present thesis work. These materials are considered because of their known thermophysical properties. Further, results are compared with DSC measurements on these samples and found fair agreement in the results.

4.4.2.1 T-History Measurements of Palmitic Acid

In this experiment, 50 g of palmitic acid (PA) and deionized water samples were taken in two identical glass tubes test tubes and heated up to 80 °C inside air camber to ensure the complete

melting of PCM sample. After complete melting and stabilization of PCM and water samples, the temperature of air chamber was reduced at 25 °C. The cooling response of PA and water samples was recorded from 75 °C at every 10 seconds time interval, and measurements are shown in Figure 4.4 (a). The nucleation in PA starts at 59.5 °C and then it increases up to 59.8 °C. The temperature of PA remains constant at ~ 59.8 °C, because of the releasing the stored latent heat of fusion during solidification. The first order derivative of the temperature - time response (dT/dt) is also plotted in Figure 4.4 (a) to find out complete liquid to solid phase transition point, which is named as inflection point. Thus, complete thermal response curve of PCM can be divided into three different regions, liquid phase region (75-59.5 °C) liquid-solid mixed phase region (phase change region) (59.8.-51.5 °C) and solid phase region (< 51.5), as explained in Figure 4.4 (a).

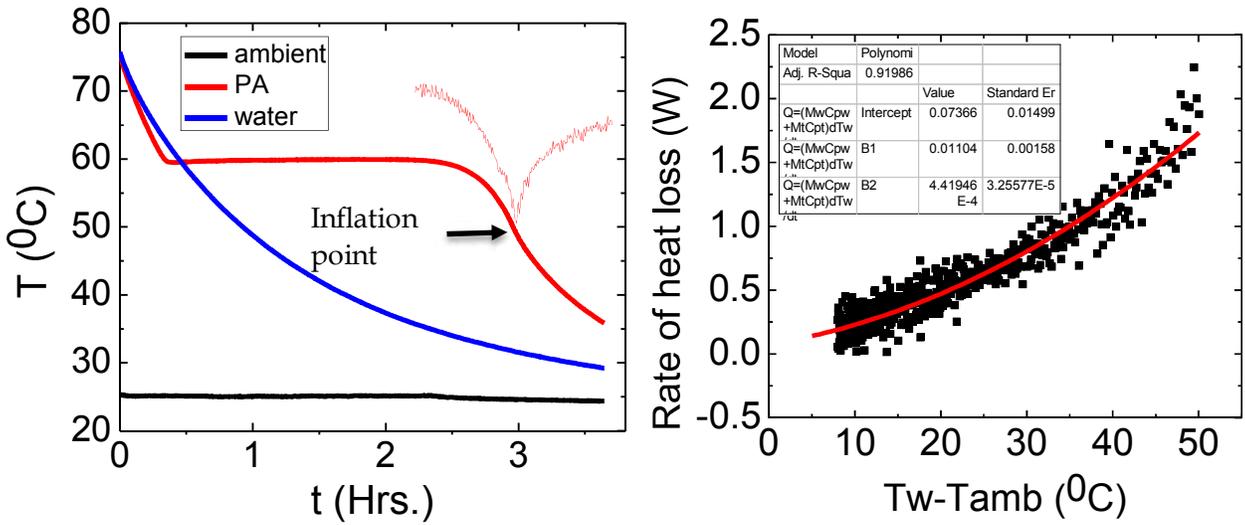


Figure 4.4: (a) The recorded cooling curve of palmitic acid (red color), water (blue color) in conjunction with environmental temperature of chamber (black color) and (b) rate of heat transfer from water test tube as a function of temperature difference between water and ambient temperature ($T_w - T_{amb}$) with fitting of second order polynomial.

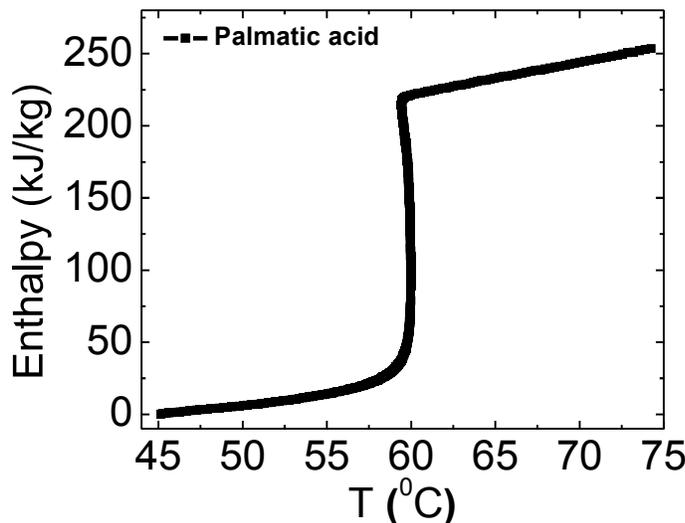


Figure 4.5: Enthalpy versus temperature curve for palmitic acid derived from T-history data

4.4.2.2 Differential Scanning Calorimetric Measurements of Palmitic Acid

The melting temperature and latent heat of fusion of PA are also determined using differential scanning calorimeter (DSC), model Q10 (TA Instruments, USA make). The pristine PA sample is ground using mortar and pestle to prepare the powder samples for DSC measurements. A small ~3-5 mg quantity of PA is weighed using digital microbalance, model CX65S (Citizen make) within ± 0.01 mg accuracy limits. The weighed sample is filled in Al pan and crimped by crimping machine from TA instruments. An identical empty crimped Al pan is used as a reference sample to nullify the effect of Al pan in the measurements and analysis. The measurements are carried out under continuous purging of 50 ml min^{-1} N_2 inert gas. The low heating and cooling rates (1K min^{-1}) are used to ensure the thermal equilibrium within sample during DSC measurements. The DSC is calibrated with indium reference sample before carrying out any measurements on sample. The melting dynamics of these materials are shown as endothermic (down) peaks in DSC thermograph, Figure 4.6. The melting temperature of materials is determined by extrapolating the onset temperature of DSC peaks, as marked by the slopes in the respective Figure. The latent heat of fusion is determined by calculating the area of the melting peak from the measured DSC thermograph, Figure 4.6. The estimated thermophysical properties using DSC are listed in Table 4.1.

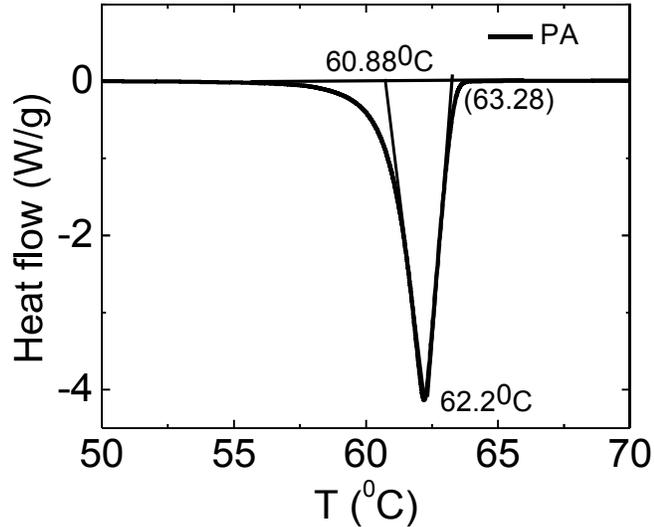


Figure 4.6: DSC thermograph of palmitic acid

Table 4.1: Comparison of T-history and DSC results for palmitic acid

	Melting point (T_m) ($^{\circ}\text{C}$)	Latent heat of fusion (L) (kJ/kg)	Specific heat of liquid ($c_{p,l}$) ($\text{kJ/kg } ^{\circ}\text{K}$)	Specific heat of solid ($c_{p,s}$) ($\text{kJ/kg } ^{\circ}\text{K}$)
T-History	59.8	208.6	2.24	1.19
DSC	60.88	199.1	2.18#	NA
Absolute error	1.08	9.5	0.06	
Relative error	1.77%	4.8%	2.75%	
# Data taken from literature (source Cedeno et al., 2000)				

The melting point and latent heat of fusion, and specific heat in liquid phase of PA measured with T-history setup are in good agreement of DSC results, Table 4.1. Hence, designed T-history setup can be used to measure thermophysical properties of heterogeneous samples.

4.4.3 Study of Supercooling

Hydrated salts are popular PCMs for thermal energy storage applications due to their high latent heat of fusion, high density and low cost. These PCMs are prone to show supercooling, which is not desired for common TES applications as this may reduce the performance LHTESS. Nevertheless, this property provides an opportunity to store thermal energy for longer durations, while keeping the supercooled liquid PCM at ambient temperatures. The stored thermal energy can be withdrawn at the time of requirement by seeding the crystallization in supercooled liquid PCM. Thus, accurate measurement of supercooling temperature is important for designing efficient TESS as per requirements. We measured supercooling temperature for sodium acetate trihydrate (SAT) using T-history and DSC methods, and results are shown in Figure 4.7.

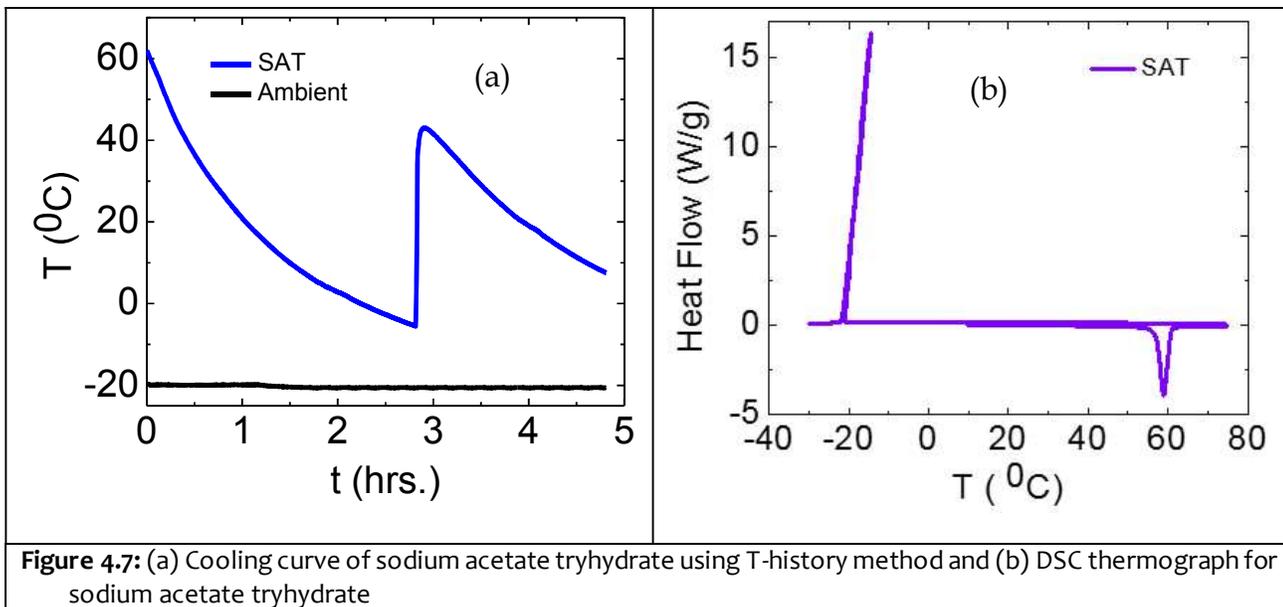


Figure 4.7: (a) Cooling curve of sodium acetate trihydrate using T-history method and (b) DSC thermograph for sodium acetate trihydrate

The supercooling temperatures for SAT measured with T-history (Figure 4.7(a)) and DSC methods (Figure 4.7(b)), are ~ -7 °C and ~ -21 °C respectively. The values of self-nucleating temperatures measured with DSC are lower, as compared to that from T-history measurements. The difference between these results is attributed to the variation in the amount of samples used for respective measurements. In the case of DSC measurements, 5.19 mg of sample is used, which reduces the probability of nucleation as compared to voluminous sample (50 g), used in T-history measurements. The detailed thermophysical properties of SAT are discussed chapter 6.

4.5 CONCLUDING REMARKS

A simple and economic T-history setup with heating and cooling temperature range -0 to 100 °C is designed and fabricated to measure thermophysical properties of PCMs. Special attention has been paid to design temperature controlled air bath to obtain constant and uniform temperature

distribution inside air chamber. Both heating and cooling experiments are carried out in the same chamber to minimize the experimental errors associated with sample handling, such as movement of test samples from one chamber to another and indoor air humidity fluctuations. The temperature dependent enthalpy of palmitic acid was determined using T-history set up and thermophysical properties such as melting point, melting temperature range, latent heat of fusion, specific heat of solid and liquid phase of PA were extracted and results are in agreement within 5% of DSC results. Further, degree of supercooling for SAT measured from DSC is higher as compared to that of T-history measurements, as explained in section 4.4.3. Since, the bulk quantity of PCM is used in TESS, therefore T-history results for supercooling in PCMs are more reliable as compared to DSC results.

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