Improvement of the T-history Method to Measure Heat of Fusion for Phase Change Materials

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ABSTRACT: Though conventional calorimetry methods such as differential scanning calorimetry and differential thermal analysis are used generally in measuring heat of fusion, T-history method has advantages of a simple experimental apparatus and no requirements of sampling process, which is particularly useful for measuring thermophyical properties of inhomogeneous phase change materials in sealed tubes. However, the degree of supercooling used in selecting a range of latent heat release and neglecting sensible heat during the phase change process can cause significant errors in determining the heat of fusion. In the present study, it was shown that a 40% discrepancy exists between the original T-history and the present methods when analyzing the same experimental data. As a result, a reasonable modification to the original T-history method is proposed.

Nomenclature

A_c : heat transfer area [m²]
Bi : Biot number, hR/k
C_p : specific heat at constant pressure [kJ/(kg · K)]
h : natural convective heat transfer coefficient [W/(m² · K)]
H_m : heat of fusion [kJ/kg]
k : thermal conductivity [W/(m · K)]
m : mass [kg]
T : temperature [℃]
t : time [sec]

Superscripts

$'$: pure water

Subscripts

0 : initial state
a : atmosphere
f : final state
i : point of inflection
l : liquid state
m : melting point
p : phase change material
s : solid state
t : tube
w : wate

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1. Introduction

Latent heat storage methods have an important role for many applications such as solar thermal systems and an midnight electric power storage devices. Suitable phase change materials (PCM) for the latent heat storage have been used in these fields and developed to stabilize thermophysical properties without thermal degeneration. In the process developing the superior PCM, measurement of the thermophysical properties is necessary and important for assessing its performance.[1-3]

In methods available for determining the heat of fusion and the specific heat, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) methods are popular in spite of their shortcomings. The properties of PCMs including various additives like thickening and nucleating agents should be carefully measured with using the DSC and DTA methods. These methods are, in general, accurate in measuring the heat of fusion, but the thermophysical properties of the sample PCM, only 1~10 mg, might be different from those of the bulk materials with heterogeneous mixture. In addition, the DSC is difficult to use and needs a high cost.[4]

As another method for measuring thermophysical properties of PCM, Zhang et al. proposed a T-history method to be able to overcome the limitation of DSC. Because this method does not take a little sample, it is very convenient when a repeat test can be performed with sealed tubes containing new developed PCMs. Nevertheless, the original T-history method has a limitation on accuracy of thermophysical properties for PCM owing to invalid physical assumptions.

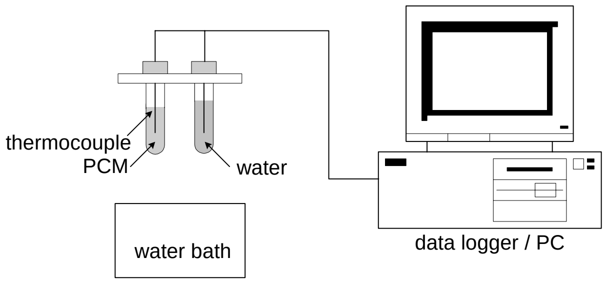

Fig. 1 Schematic diagram of experimental apparatus.

In the present study, we analyzed principles of the original T-history method and proposed a modified alternative to enhance the accuracy.

2. Principle and problems of T-history method

As shown in Fig. 1, test tubes are containing respectively the PCM and reference material (pure water is used generally) whose temperatures must be identical and greater than the melting temperature. Also, this experiment must be performed on the condition of $Bi < 0.1$ that the lumped capacitance method can be applied. The temperature measurement is started by data acquisition equipment when the test tubes are suddenly exposed to an atmosphere. Timewise temperature curves, which Zhang et al. called

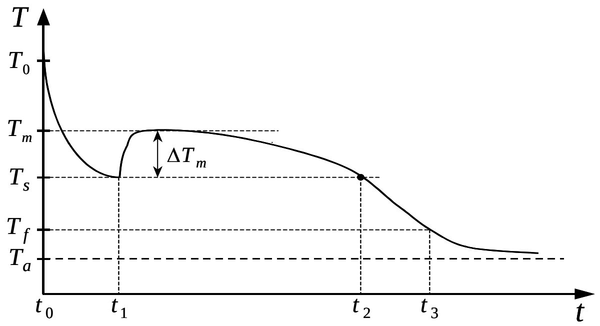

Fig. 2 A typical T-history curve for PCM during a cooling process.

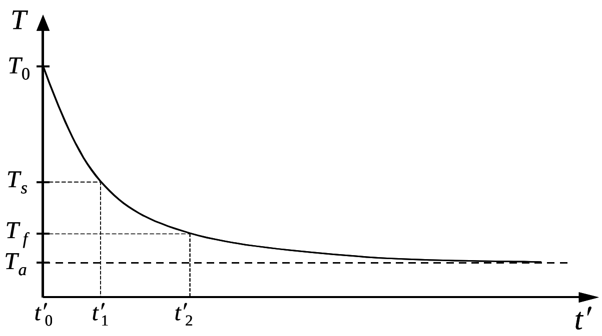

Fig. 3 A typical T-history curve for pure water during a cooling process.

T-history curves, is obtained for PCMs and reference material (Figs. 2 and 3). Then, the heat of fusion and specific heat are calculated from two T-history curves very simply.

The latent heat range must be first determined from the T-history curve for PCM to calculate the heat of fusion. If T-history curve maintains at a constant temperature in the latent heat range, the selection of range is very easy. Unfortunately, most of T-history curves for PCM show a typical pattern as the curve in Fig. 2. Such a situation, the end t_2 of latent heat range cannot be determined intuitively. From this difficulty, the original T-history method used the release temperature of supercooling T_s as the boundary between latent heat and solid sensible heat range. That is, the method uses $t_0 \sim t_1$ for the sensible heat range of liquid, and $t_1 \sim t_2$ for latent heat as shown in Fig. 2.

In fact, the release temperature of supercooling is not related with the end of latent heat range physically. In addition, the degree of supercooling is not a themophysical property, which varies according to the volume, purity, cooling speed, condition of tube surface and agitation. Also, in the original T-history method, it was considered that only the effect of the latent heat is included in the range $t_1 \sim t_2$. As shown in Fig. 2, the sensible heat is not negligible because the temperature difference exists in $t_1 \sim t_2$. In addition, the masses of tube contacting with PCM and pure water must be used in the expression of the thermophysical properties instead of the total mass of tube.

3. Modified T-history method

3.1 Principle of measurement and analysis

The modified T-history method proposed in this study is similar to the original in principles, but it is different in measurement and detailed analysis.

The tubes containing the PCM and pure water were heated in water bath until the temperature of the tubes and materials in tubes was uniform above the melting point of PCMs. After then, as shown in Fig. 1, the tubes were exposed into the atmosphere and their temperatures were measured as a function of time. Figs. 4 and 5 are the T-history curves yielded from the measured data.

When the Biot number, Bi ($= hR/k$, where R is the radius of a tube, k the thermal conductivity of PCM and h the natural convective heat transfer coefficient outside a tube) is less than 0.1, the temperature distribution inside a tube can be regarded as uniform and the lumped capacitance method can be applied.[5]

If the PCM has supercooling process, the boundary between liquid sensible heat and latent heat range can be regarded as the release point t_1 of supercooling. Hence, we can obtain

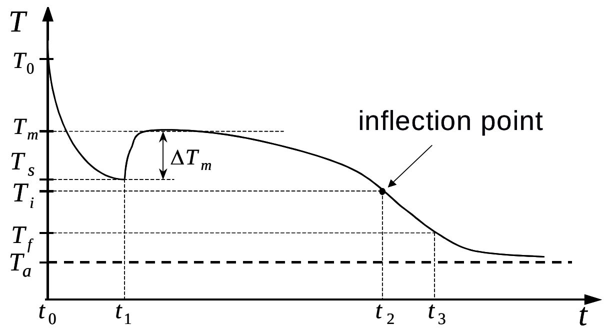

Fig. 4 A typical modified T-history curve for PCM during a cooling process.

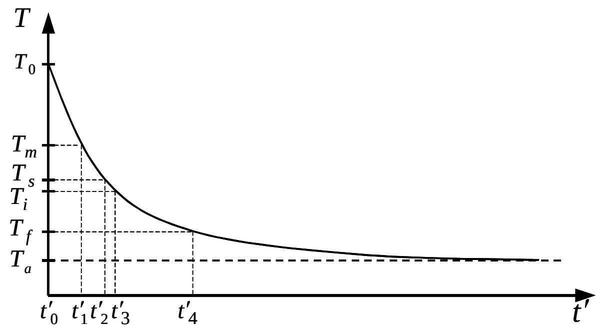

Fig. 5 A typical modified T-history curve for pure water during a cooling process.

Eq. (1) for the liquid sensible heat range ($t_0 \leq t \leq t_1$).

$$(m_{t,p}C_{p,t}+m_pC_{p,l})(T_0-T_s)=hA_cA_1 \quad (1)$$

where m_p and $m_{t,p}$ are the masses of the PCM and tube, respectively, $C_{p,l}$ and $C_{p,t}$ are the mean specific heats of the liquid PCM and of the tube itself, respectively, and A_c is the convective heat transfer area of the tube contacting with the PCM, and A_1 is defined as $\int_{t_0}^{t_1}(T_p-T_a)dt$. Also, T_p and T_a is the temperatures of the PCM and of the circumstance outside a tube, respectively. Of course, though the water bath can be used as the outside of tube, the atmosphere was used to reduce the Biot number.

In the modified T-history method, the boundary t_2 between latent heat and solid sensible heat range was chosen as the inflection point of T-history curve for the PCM where the first derivative of the curve has the minimum value. Because the temperature of the PCM was decrease by $e^{-t/\tau}$ in the sensible heat range but by different trend in the latent heat range, to take the inflection point as the boundary has a physical meaning.

Finally, we obtained the following equation about the heat of fusion H_m in the latent heat range ($t_1 \leq t \leq t_2$). Here, the specific heat of latent heat range was assumed as the average value of those of solid and liquid state. Also, we included the sensible heat of PCM and tube in the latent heat range that was not considered in the original T-history method (the first term of Eq. (2)).

$$\left(m_{t,p}C_{p,t}+m_p\frac{C_{p,l}+C_{p,s}}{2}\right)(T_m-T_i)+m_pH_m=hA_cA_2 \quad (2)$$

where A_2 is defined as $\int_{t_1}^{t_2}(T_p-T_a)dt$.

In similar way, we obtained Eq. (3) for the solid sensible heat range ($t_2 \leq t \leq t_3$).

$$(m_{t,p}C_{p,t}+m_pC_{p,s})(T_i-T_f)=hA_cA_3 \quad (3)$$

where $C_{p,s}$ is the specific heat for the solid PCM, and T_f is the final temperature which can be chosen arbitrarily in $T_a < T_f < T_i$.

Similarly, the following equations from the T-history curve for the pure water can be induced, which has only the sensible heat in considering temperature range.

$$(m_{t,w}C_{p,t}+m_wC_{p,w})(T_0-T_s)=hA_c'A_1' \quad (4)$$

$$(m_{t,w}C_{p,t}+m_wC_{p,w})(T_m-T_i)=hA_c'A_2' \quad (5)$$

$$(m_{t,w}C_{p,t}+m_wC_{p,w})(T_i-T_f)=hA_c'A_3' \quad (6)$$

where m_w and $C_{p,w}$ are the mass and mean specific heat of pure water, respectively, and $m_{t,w}$ is the mass of tube contacting with the pure water, and A_c' is the heat transfer area of a tube contacting with pure water. Also, we define: $A_1'=\int_{t_0'}^{t_1'}(T_w-T_a)dt$, $A_2'=\int_{t_1'}^{t_2'}(T_w-T_a)dt$, $A_3'=\int_{t_2'}^{t_3'}(T_w-T_a)dt$.

From Eqs. (1)~(6), we obtained finally the following equations for the latent heat and specific heats.

$$C_{p,l}=\frac{m_{t,w}C_{p,t}+m_wC_{p,w}}{m_p}\frac{A_c}{A_c'}\frac{A_1}{A_1'}-\frac{m_{t,p}}{m_p}C_{p,t} \quad (7)$$

$$C_{p,s}=\frac{m_{t,w}C_{p,t}+m_wC_{p,w}}{m_p}\frac{A_c}{A_c'}\frac{A_3}{A_3'}-\frac{m_{t,p}}{m_p}C_{p,t} \quad (8)$$

$$H_m=-\left(\frac{m_{t,p}}{m_p}C_{p,t}+\frac{C_{p,l}+C_{p,s}}{2}\right)(T_m-T_i)+\frac{m_{t,w}C_{p,t}+m_wC_{p,w}}{m_p}\frac{A_c}{A_c'}\frac{A_2}{A_2'}(T_m-T_i) \quad (9)$$

Table 1 Summary of the factors considered in the modified T-history method

No.	Factors	Analysis
I	Including sensible heat in the latent heat range	I
II	Using the inflection point istead of the release temperature of supercooling as the final point of latent heat range	II
III	Including the sensible heat of tube in the latent heat range	
IV	Using tube mass contacting with the PCM or water instead of total tube mass	

The factors considered in inducing Eqs. (7)~(9) are summarized in Table 1.

3.2 Measurement and results

To test the equations for the modified T-history method, the sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$) as a main specimen was chosen. The melting point of sodium acetate trihydrate is 58℃. It almost has a constant degree of supercooling and its phase separation is less serious than other salt hydrates during cycle tests. Before test, we confirmed that the temperature of the sample along the tube's longitudinal direction was almost the same and then measured the timewise temperature variation by thermocouple which was placed at the center of tube.

The thermal conductivity of solid state of sodium acetate trihydrate is 0.6 W/(m · K) and the natural convective heat transfer coefficient is about 4 W/(m^2 · K) on the tube outer surface which is placed in the air vertically. To satisfy the condition of Bi < 0.1 in the air, the test tubes of radius 0.5 cm and thermal conductivity 1.4 W/(m · K) were used. Also, to reduce an end effect of tube, the 20 cm length of test tube which is 10 times of the tube diameter is chosen. The test was set under room temperature and a velocity of air less than 0.1 m/s. Figs. 6 and 7 show the T-history curves obtained from the measurement according to the above test and Fig. 8 shows the first derivatives of the T-history curve for the PCM. In Fig. 8, we found easily the point of inflection which is the boundary t_2 between latent heat

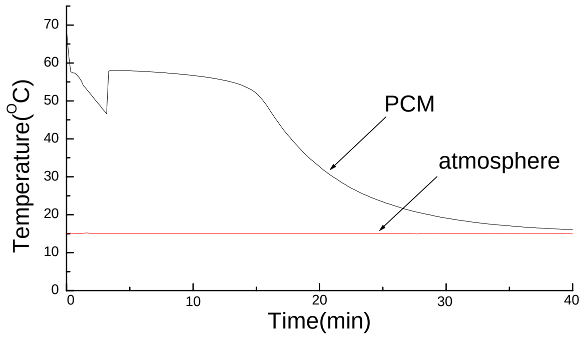

Fig. 6 T-history curve for PCM using CH_3-$COONa \cdot 3H_2O$ as sample.

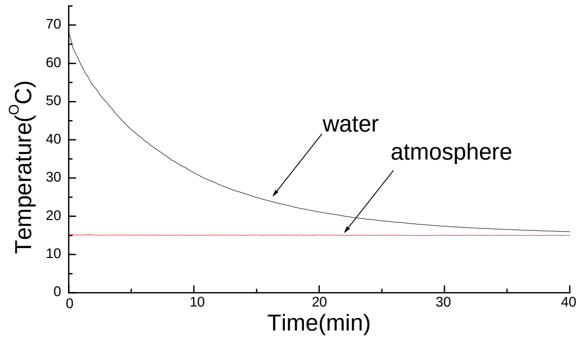

Fig. 7 T-history curve for pure water as reference material.

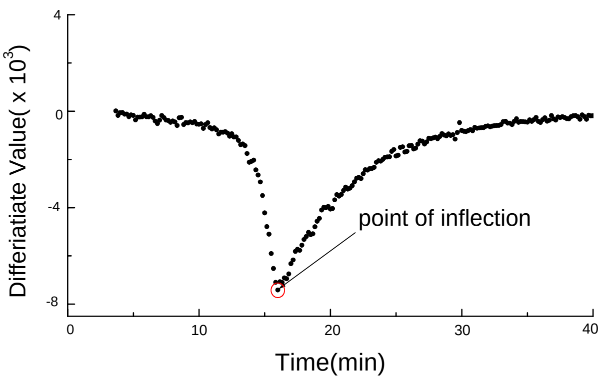

Fig. 8 First derivative curve of Fig. 6 to search a point of inflection.

Table 2 Comparison of results according to analysis methods ($CH_3COONa \cdot 3H_2O$)

	$C_{p,l}$ [kJ/kg℃]	$C_{p,s}$ [kJ/kg℃]	H_m [kJ/kg]
Original T-history	3.41±0.59	1.98±0.45	408±27
Modified T-history	3.77±0.57	2.25±0.24	245±9
Analysis Ⅰ	3.74±0.60	2.35±0.20	236±11
Analysis Ⅱ	3.40±0.60	1.53±0.44	423±33
Reference (6)	3.05	-	226
Reference (7)	3.68	2.11	263
DSC			253

Analysis Ⅰ: Including the effect of sensible heat in the range of latent heat release
Analysis Ⅱ: Using an inflection point in orginal T-history method to determine the range of latent heat release

and solid sensible heat range.

Table 2 represents very different results according to applied analysis methods for the same measurement data. As mentioned in the prior section, the major factors caused this difference may be the neglect of the effect of sensible heat in the latent heat range (factor I in Table 1) and the use of the release temperature of supercooling as the final point of latent heat range (factor II). Analysis I in Table 2 included the effect of sensible heat of PCM in the latent heat range and Analysis II used the inflection point of the T-history curve for the PCM as the boundary between latent heat and solid sensible heat range. Of course, in analyzing the modified T-history, all factors are included. The results in Table 2 were averaged from six experimental data and the confidence interval of 95% were also presented. Comparing the heat of fusion H_m of the original with the modified T-history method, there was about 40% difference. Also, from those of DSC (253 kJ/kg) and literatures (226[6] ~ 263[7] kJ/kg), it is obvious that the results of the original T-history method are not good in accuracy.

3.3 Discussion

As shown in Figs. 4 and 6, the temperature in the latent heat range of the PCMs gradually decreased as increasing time and there is no constant temperature range in most cases. This trend might be the intrinsic characteristics of the PCM or by the effects induced by the temperature difference between the tube center and surface. The original T-history method was expanded under the assumption that temperature is almost constant in the latent heat range, but the temperature drop was obviously observed from the measurements using the sodium sulfate decahydrate and sodium acetate trihydrate, and so on. Therefore, in the case of large temperature drop, this effect must be included in analysis process. We observed that the value of the heat of fusion obtained by considering this effect was very different from that neglecting it. From the results, the difference between the original T-history method and Analysis I considering the sensible heat in latent heat range is about 40% in the heat of fusion. Therefore, the major error of the original method is due to ignorance of the sensible heat in latent heat range for sodium acetate trihydrate. Moreover, the effect of sensible heat in latent heat range will increase as the temperature drop ($T_m - T_i$, shown in Table 3) between melting point and final temperature of latent heat range becomes larger.

During a cooling process, the temperature decreases with the shape of $T \sim e^{-t/\tau}$ for the sensible heat range other than that for the latent heat. Hence, it is sufficiently reasonable that the inflection point can be used as the boundary between latent heat and solid sen-

Table 3 Comparison of T_m, T_s, T_i and their differences (℃)

No.	T_m	T_s	T_i	$T_m - T_i$	$T_s - T_i$
1	58.1	46.6	43.8	14.3	2.8
2	57.8	48.2	46.8	11.0	1.4
3	58.1	48.3	42.5	15.6	5.8
4	58.0	48.3	41.1	16.9	7.2
5	57.9	47.2	44.4	13.5	2.8
6	58.1	45.3	45.7	12.4	−0.4
Average	58.0±0.1	47.3±1.3	44.1±2.2	14.0±2.2	3.3±2.9

sible heat range. As shown in Table 2, the difference of the heat of fusion between the original and modified T-history method using the inflection point as the boundary of solid and latent heat, is only 4% which is unexpectedly small because the $T_s - T_i$ is very small fortunately in sodium acetate trihydrate. Since there is a possibility that the temperature difference $T_s - T_i$ becomes much greater according to the kind of PCM, the inflection point should be used instead of the release temperature of supercooling which has no physical meaning, in order to improve the accuracy. For an extreme verification, Laulic acid whose degree of supercooling is only 1.5 K was tested, but the heat of fusion cannot be obtained by the original method at all. The modified method provided 186 kJ/kg in heat of fusion, which is in good agreement with 179 kJ/kg by DSC.

Furthermore, the original T-history method needs the heat transfer area of the tube for the PCM equals to that for the pure water in an experiment and analysis. To satisfy this condition in a real experiment is somewhat difficult. If the difference of area are treated adequately in the analyzing equations, there is no problem in analysis. Indeed, if the PCM has a volumetric variation during the phase change, the heat transfer area for the PCM become different with that of pure water. So, we developed the modified T-history method takes the heat transfer area arbitrarily. Finally, the effect for the sensible heat of the tube itself was compensated during the latent heat range, which affects the heat of fusion by 6%.

4. Conclusions

In this study, we developed the modified T-history method which overcame the shortcomings of the original in order to measure the thermal properties of PCMs such as the heat of fusion and the specific heats more accurately and easily. As a result, by experimenting for sodium acetate trihydrate as a main specimen, the modified T-history method yields much better results which are consistent with those by DSC and other literatures.

(1) Analysis I including only the effect the sensible heat of PCM in latent heat range differs from the original method by about 40% in the heat of fusion. This means that the large temperature drop in the range influences greatly the result. As most of PCMs have a temperature drop in phase change, this effect should be considered in the analysis.

(2) The effect considering the sensible heat of tube in the latent heat range results in 6% difference, which cannot be also neglected.

(3) There is no physical meaning that the release temperature of supercooling was used as the boundary between latent heat and solid sensible heat range in the original method. The inflection point was taken as the alternative boundary in the new method. In sodium ace-

tate trihydrate, since the temperature difference between the release of supercooling and the inflection point is somewhat small, this effect does not appear apparently. But for Laulic acid whose degree of supercooling is as small as 1.5 K, the original method provides no valid value, which can be by no means applied to paraffin without supercooling.

(4) By taking the heat transfer area arbitrarily, the test becomes much easier in an experiment and analysis.

In conclusion, it was verified that the original T-history method has a merit in methodology, but a serious defect in precision; the presented method improved the accuracy of measurement maintaining its feasibility.

Acknowledgement

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