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Measurement Methods of Latent Heat for PCM with Low Melting Temperature in Closed Tube

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ABSTRACT: Cycle test for developed phase change material (PCM) is necessary in order to assess the variation of latent heat, which decreases with time by deterioration. T-history method and measurement using heat-flux meter are appropriate for the cycle test in a tube filled with PCM because they do not need an extraction of sample in measuring heat of fusion. In the present study, these methods were applied to a PCM having a melting point below a room temperature, different to the past studies for PCMs melting above a room temperature. As a result of experiment using pure water as specimen, we can obtained reasonable values for heat of fusion.

Nomenclature

A_c : heat transfer area [m^2]
Bi : Biot number, hR/k
C_p : specific heat at constant pressure [kJ/(kg·K)]
ΔE : electromotive force of heat flux meter [mV]
H_m : latent heat [kJ/kg]
m : mass [kg]
q'' : heat flux [W/m^2]
T : temperature [℃]
t : time [sec]

Superscripts

$'$: reference material

Subscripts

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

1. Introduction

The latent heat of phase change material (PCM) used as regenerative materials is very important factor for appraisal of their performance. Numerous research groups have interests in measurement of that by using differential scanning calorimetry (DSC), differential thermal analysis (DTA) and T-history method.(1)

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Among them, the T-history method is reasonable to observe the degradation of latent heat for the PCM preserved in sealed tube under cycle test without extra sampling steps.(2) Further, the modified T-history method improved by the procedure of analysis can be applied to obtain an analysis data having improved accuracy and expanded measuring range.(1,3)

Using the heat-flux meter, Saito et al. calculated the latent heat from calories obtained as increasing temperature by 2℃ in long temperature range.(4) This method usually uses simple apparatus and does not need sampling steps, but it is troublesome to obtain data, since it needs the installation of heat-flux meter and uniformed insulation in the system (Hereinafter referred to 'heat-flux meter method'). However, contrary to the DSC, DTA and T-history method that should be used under the premise of lumped capacitance method, its advantage is to get an accurate data even if the temperature in the inner part of sample is not uniform.

In this paper, we have studied newly proposed method, which is based on the modified T-history and heat-flux-meter method, in measuring for the latent heat of low temperature PCM (LT-PCM) whose melting point is lower than room temperature. In other words, the goal of this study is to propose a new method that can easily calculate the precise latent heat of LT-PCM, which is in the sealed tube. The heat-flux meter method makes measurement of latent heat obtain simply because it uses continuous heating-cooling process instead of the stepwise process. Finally, we have compared the results of the T-history method proposed by us with that of heat-flux-meter method.

The proposed method can be applied to measurement of latent heat for PCM, which is used to air conditioning and refrigeration system, as well as ice slurry, which is interesting in its wide usefulness. Especially, in case of ice slurry, it is difficult to evaluate thermal performance because the latent heat of ice slurry by DSC, DTA method is not feasibly measured.

2. Measurement of latent heat by T-history method

2.1 Background of T-history method

As shown in Fig. 1, the test tubes were charged with PCM and reference material (generally, when the melting temperature of PCM is higher than the room temperature, the distilled water is used.), respectively and then set in a controlled temperature bath (higher temperature than the melting point of PCM). After reaching the equilibrium temperature between test tubes and samples, the test tubes were exposed to room temperature and then their temperatures were recorded according to time. The T-history curve (Fig. 2) for PCM and re-

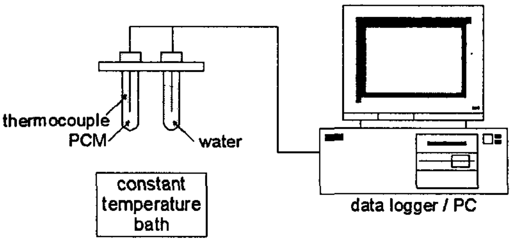


Fig. 1 Schematic diagram of experimental apparatus.

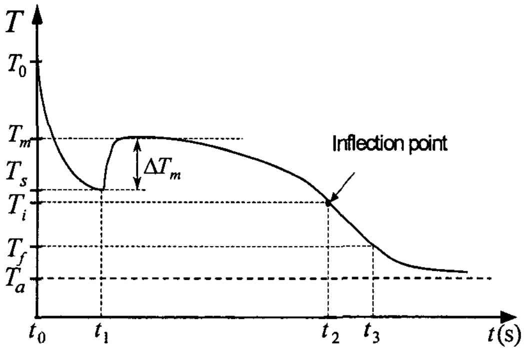
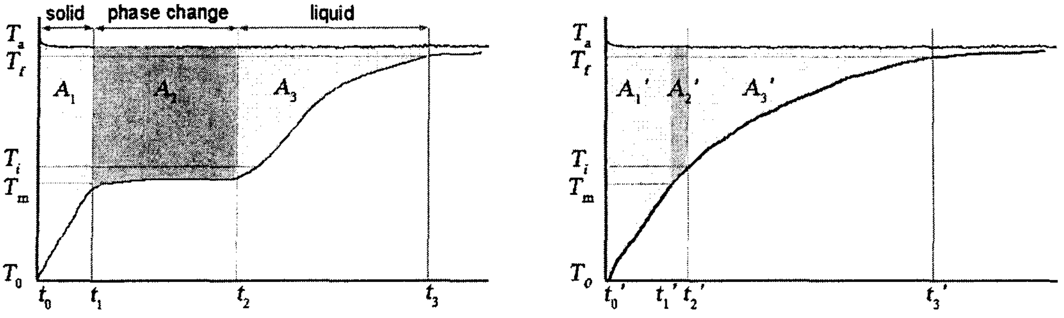


Fig. 2 A typical modified T-history curve for PCM during cooling process.



(a) PCM (b) Reference material

Fig. 3 T-history curves for PCM and reference material during heating process.

Table 1 Areas of interval in Fig. 3

Interval	Temperature range	PCM		Reference material	
		Time range	Area	Time range	Area
Solid	T_0-T_m	$t_0\sim t_1$	A_1	$t_0'\sim t_1'$	A_1'
Phase change	T_m-T_i	$t_1\sim t_2$	A_2	$t_1'\sim t_2'$	A_2'
Liquid	T_i-T_f	$t_2\sim t_3$	A_3	$t_2'\sim t_3'$	A_3'

ference material is obtained from the above experiment. Therefore, the latent heat and specific heats can be calculated from data of T-history curves.

Up to now, the PCM having the melting temperature above room temperature (HT-PCM) have been focused for application of heating system. In this case, the HT-PCM starts to solidify from out-layer of tube when it is taken out to atmosphere. Unfortunately, on the other hand, the LT-PCM starts to melt from the out-layer and the PCM solid should be moved because of natural convection by the different temperature distribution in the tube. This phenomenon should bring about a little error for measurement of latent heat in the solid-liquid mixed phase.

Figure 3 shows a typical T-history curve of LT-PCM and it can be distinguished as three kinds of phases including solid phase, phase change, and liquid phase on the curve. The following equations for latent heat and specific heats can be obtained from the energy equations on each phase.

$$C_{p,s}=\frac{m_{t,r}C_{p,t}+m_rC_{p,r}}{m_p}\,\frac{A_c}{A_c'}\,\frac{A_1}{A_1'}-\frac{m_{t,p}}{m_p}C_{p,t} \tag{1}$$

$$C_{p,l}=\frac{m_{t,r}C_{p,t}+m_rC_{p,r}}{m_p}\,\frac{A_c}{A_c'}\,\frac{A_3}{A_3'}-\frac{m_{t,p}}{m_p}C_{p,t} \tag{2}$$

$$H_m=-\left(\frac{m_{t,p}}{m_p}C_{p,t}+\frac{C_{p,l}+C_{p,s}}{2}\right)(T_i-T_m)+\frac{m_{t,r}C_{p,t}+m_rC_{p,r}}{m_p}\,\frac{A_c}{A_c'}\,\frac{A_2}{A_2'}(T_i-T_m) \tag{3}$$

where, $A_1=\int_{t_0}^{t_1}(T_a-T_p)\,dt$ is the integrated area for solid phase. The areas for each phase are reported in Table 1.

2.2 Measurement of latent heat for LT-PCM

We can apply same method for measurement of latent heat to both HT-PCM and LT-PCM. However, in the LT-PCM, the distilled water cannot be used as reference material because of phase changing of water at 0℃.

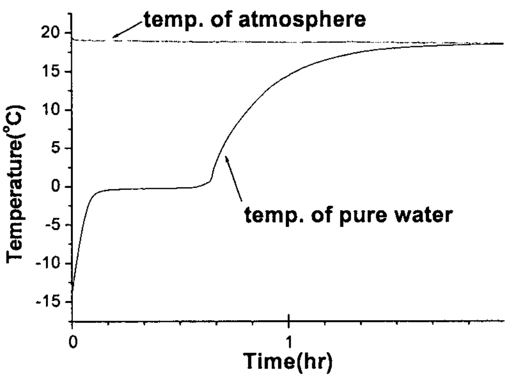


Fig. 4 T-history curve for pure water as test material.

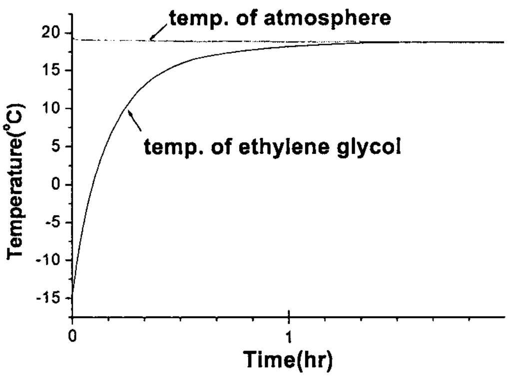


Fig. 5 T-history curve for ethylene glycol as reference material.

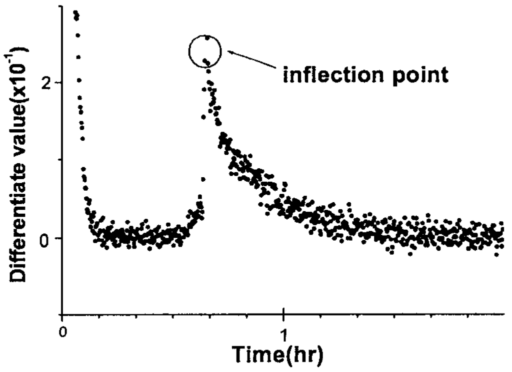


Fig. 6 First derivative curve of Fig. 4 to search point of inflection.

In this work, distilled water was chosen as LT-PCM sample and ethylene glycol (melting point: −11.5℃) as reference material, respectively. After the sample and reference tube were set in 10℃, they were taken out to room temperature. Figures 4 and 5 are T-history curves of distilled water and ethylene glycol, respectively. Figure 6 shows the first derivative curve for T-history curve of distilled water. The inflection points mean the boundary of latent heat range on Fig. 6.

The curve trend on Fig. 4 is shown the opposite direction from that on Fig. 3, but not exactly. In order to define the starting and ending point of latent heat on Fig. 4, the inflection points must be pointed out because there is no supercooling phenomenon as shown in Fig. 2. Especially, in case of water, it is more difficult to measure the precise latent heat because of buoyancy during the melting. Therefore, the stainless wire was installed in the center of test tube to prevent ice floating.

The average temperatures of three thermocouples, which are located at 35 mm, 105 mm, 175 mm from the bottom of test tube (radius: 6 mm, length: 200 mm), were used for the calculation of latent heat. Six times were performed to measure temperature for an identical sample and summarized in Table 2. There is 2.4% deviation from the values of literature.

Table 2 The heat of fusion and specific heat of pure water obtained by T-history method

	$C_{p,s}$	$C_{p,l}$	H_m
1	1.56	4.39	316
2	1.54	3.99	323
3	1.31	4.55	320
4	1.55	4.90	319
5	2.42	4.76	335
6	2.33	4.89	346
Average ±95% confidence limit	1.79±0.49	4.58±0.37	327±12
Reference(6)	2.09	4.18	335

3. Measurement of latent heat by heat-flux meter

3.1 Preparation and correction of heat-flux meter

The heat-flux meter consisted in a series connection of thermocouples is used to measure the heat flux, q'', through the surface of tube and its electromotive force is amplified by a series connection of thermocouples. The length of heat-flux meter is equal to the circumference of polyethylene test tube containing the PCM (Fig. 7). For the measurement of small temperature difference, the serial connected T-type thermocouples were set on the silicon rubber sheet of 1 mm thickness. The number of series connection is 16 times and the each joint was soldered.

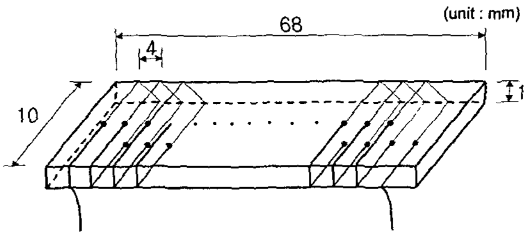


Fig. 7 Heat-flux meter.

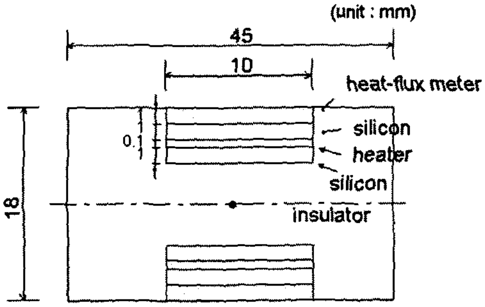


Fig. 8 Calibration device for heat-flux meter.

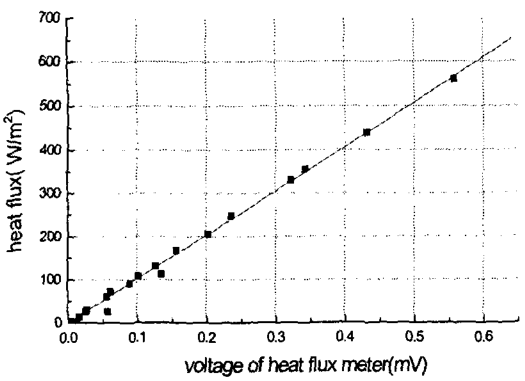


Fig. 9 Calibration graph for heat-flux meter.

The correction rig was built for the correlation curve between electromotive force and heat flux by temperature difference in the heat-flux meter (Fig. 8). In this circuit, a heat occurred from thin nicrome heater should be released to the outside through the heat-flux meter. By thick isopink (insulator), the heat loss could be prevented and the same constructed heater was set on the counter part symmetrically. A silicon rubber sheet was installed between nicrome heater and heat-flux meter as electrical insulator. The upper and lower of silicon rubber were pasted with thermal grease for the reduction of contact resistance.

The output data recording started when the input voltage for heater control was stable. These results were shown in Fig. 9. By the least squares method, the following equation was obtained.

$$q'' = 1014.6\Delta E \qquad (4)$$

3.2 Measurement method of latent heat

The polyethylene tube was filled with the PCM and then thermocouples for measurement of inner temperature and the heat-flux meter were installed in the tube. The test tubes were covered with the silicon rubber sheet in order to obtain uniform temperature distribution by the heat transfer through the tube wall (Fig. 10).

The distilled water was used as the PCM. The test tubes were set in the temperature bath kept at 10℃, which was raised to 20℃ by 0.71℃/min rate. The measurement interval for temperature and the heat flux is 2 seconds.

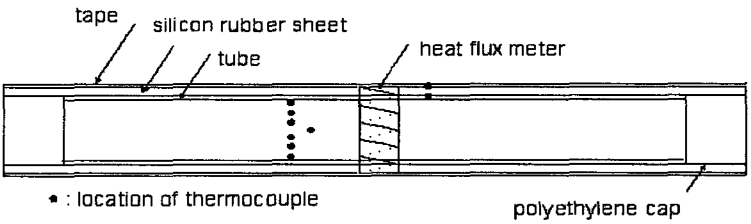


Fig. 10 Section view of test tube with heat-flux meter.

3.3 Results

The temperatures and the heat flux with time were summarized in Fig. 11(a). This consists of the three kinds of phases. The first is the solid phase showing the constant heat flux and the second is the phase change section showing rapid increase of heat flux. Finally, the third is liquid phase showing again the constant heat flux. Figure 11(b) shows the simplified graph for Fig. 11(a); the oblique-line area (A_2) implies the latent heat of the PCM and A_1, A_3, A_4 mean the specific heats corresponding solid-state, phase change, liquid-state, respectively. Therefore, the latent heat and specific heats can be evaluated from the calculated areas.

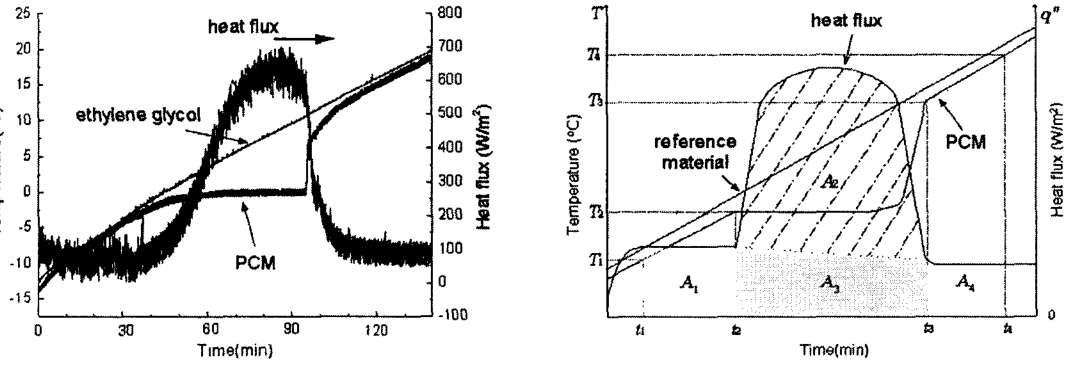
$$C_{p,s} = \frac{AA_1}{m_p(T_2 - T_1)} \tag{5}$$

$$C_{p,l} = \frac{AA_4}{m_p(T_4 - T_3)} \tag{6}$$

$$H_m = \frac{AA_2}{m_p} \tag{7}$$

Table 3 The heat of fusion and specific heat of pure water obtained by heat-flux meter

	$C_{p,s}$	$C_{p,l}$	H_m
1	3.80	7.10	352
2	4.14	6.25	355
3	4.16	5.72	355
4	4.41	6.02	354
5	4.29	5.65	356
6	4.13	5.50	364
Average ±95% confidence limit	4.15±0.22	6.04±0.61	356±4
T-history	1.79±0.49	4.58±0.37	327±12
Reference[(6)]	2.09	4.18	335



(a) Timewise variation of heat flux and temperatures.

(b) Simplified model

Fig. 11 Graph for measuring latent heat-flux meter.

where, A is the area of test tube, m_p is a mass of PCM.

In the above equations, $T_1=-7$℃, $T_2=-2$℃, $T_3=17$℃ and $T_4=19$℃ were applied to the evaluation of the specific heats and the latent heat. The results for the six times experiment were shown in Table 3 with the confidence interval of 95%.

4. Discussion

The latent heat values of LT-PCM obtained by the modified T-history method show a good agreement with that of the literature in only 2.4% difference. Also, the variation of the latent heats for six samples is about 3.7% (327± 12 kJ/kg), which is in a similar level to that of hydrated sodium acetate in the preceding study. In hydrated sodium acetate (melting point: 58℃) as a PCM, because a solid-state is kept in room temperature, the differences of measured temperature in the direction of tube length are very small and the measured latent heats are approximately the same. However, for the distilled water in a melting process, there are a little differences of measuring temperature in the direction of tube length by a natural convection. According to those results, the calculated latent heat was changed within 5%. Especially, the values measured in the upper-side of tube were shown higher than that in the lower-side of tube. The latent heat calculated by average temperature shows closer value to that of literature compared to the latent heat calculated by temperatures obtained at three measuring points (upper, middle and lower point).

On the other hand, the value of the latent heat for LT-PCM is somewhat influenced from the temperature difference caused by different measuring points on the same section. Since this problem can occur in the HT-PCM, the new analytical approach must be needed to obtain the precise results. However, for the verification of latent heat decrease by the cycle test, the existing calculation method is enough to obtain the results.

The heat-flux meter method is easy to measure the latent heat without the extra sampling steps, though it needs to install extra heat-flux meters around the tube. However, there is a difference of 6.2% between the result by this method and that by literatures. This difference would be caused by the precision of the heat-flux meter. It is possible to improve the precision for data by using secondary correction with the standard material whose latent heat is well known instead of using the well-designed heat-flux meter. Particularly, the measuring time by this method is faster than that by the T-history method. It is useful for the measurement of PCM whose melting temperature is near the room temperature, because the bath temperature of test sample can be arbitrarily controlled in this method. This method can be also used to the standard for the result from the T-history method, which has a temperature difference in the direction of length and radius of the test tube. Also, we expect that it can be applied to the measurement of latent heat for ice slurry having irregular state for concentration and melting condition in the sample.

5. Conclusion

We have studied the new measuring method of the latent heat for LT-PCM, whose melting point is lower than the room temperature. The aim of this study has been focused to propose a new measuring method, by which it is possible to measure the variation of latent heat in the multi-components system containing the nucleating agent et. al. through the cycle test. The distilled water was used as PCM and the results were summarized as follows.

(1) The result by the modified T-history method shows a good value about 2.4% lower than that of the literature. However, in the

melting step of PCM, the further detailed analysis will be needed for reducing of the error related with the irregularity of temperature in the direction of radius.

(2) The result by the heat-flux meter method shows a high value about 6.2% compared to that of the literature. This error may be caused from the less precise heat-flux meter made by us.

Acknowledgments

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