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Determination of the PCM melting temperature range using DSC

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ABSTRACT

The melting temperature range is one of the most important parameters for phase change material (PCM), it affects the PCM application areas and the performance of the system integrated with PCM. The melting temperature range of PCM is usually measured by a differential scanning calorimeter (DSC) with the dynamic measurement method. Unfortunately, the measurement results with this method are dependent of the heating rate. Determination of the melting temperature range of PCM means to find the starting melting temperature at which PCM starts melting and the ending melting temperature at which the melting process is finished. In this paper, a new DSC measurement method, which is the partially-melted DSC measurement method, was proposed to determine the ending melting temperature of PCM. With this method, the actual ending melting temperature of the sample PCM was found out and it was independent of the heating rate. Because there was no clear boundary between the non-melted state and the partially-melted state, the actual starting melting temperature of PCM was not able to be determined accurately.

1. Introduction

Compared with sensible heat storage system, latent heat storage system with phase change materials (PCMs) has higher thermal energy storage density while requiring smaller masses and volumes of material [1]. Therefore, PCMs have been used in many fields, such as space heating/cooling [2,3], solar energy storage [4–6], thermal performance improvement of building envelope [7–9], etc.

Given the attempted objectives of PCMs applications, their performances are a cornerstone of the whole system. Therefore, a correct determination of their intrinsic properties is crucial [10]. In theory, the melting process of PCMs is always considered to be isothermal or nearly isothermal. However, actual PCMs have their own melting temperature ranges [11,12]. The melting temperature range is one of the most important parameters for PCM, it affects the PCM application areas and the performance of the system integrated with PCM. The PCM with a narrow melting temperature range is recognized to have better thermal performance because it is easy to absorb or release latent heat. For example, when the PCM was integrated with building walls, the indoor temperature fluctuation was the smallest and the thermal comfort of the room was the best when the PCM melting temperature range was the narrowest [13]. Dumas et al. [14] found that if the DSC measurement result of melting temperature range had bigger "errors", the actual thermal performances of the PCM system would have lower accuracy accordingly.

The melting temperature range of PCM is usually measured by a differential scanning calorimeter (DSC) with the dynamic measurement method. Unfortunately, there is a lack of accuracy in DSC measurements, especially the results are dependent of the heating rate and the mass of the sample [14–19]. The heating rate was larger, the measured melting temperature range was wider (it would be discussed further in Section 2 of this paper). However, the actual melting temperature range of a kind of PCM should be unique. It meant that the actual melting temperature range was not able to be found out with the traditional DSC measurement method [20]. Therefore, to solve this problem, a new DSC measurement method was proposed in this paper, and the main objective of this research was to determine the actual ending melting temperature of PCM with this method.

2. Measured PCM melting temperature range with dynamic DSC measurement method

The sample PCM used in this research was RT27, which is an organic paraffin from Rubitherm Technologies GmbH [21]. RT27 was chosen because it was stable, homogeneous and did

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not have supercooling problem. A DSC, whose model is DSC 8000 from PerkinElmer Company, was used to test the phase change performance of the sample PCM. To ensure the accuracy of the measurement, DSC calibration must be conducted before the actual measurement. The calibration method of this DSC was manual calibration, which contained baseline optimization, sample temperature calibration, furnace calibration, heat flow calibration, and smart scan. Indium and zinc were used in the sample temperature calibration. Nine-point calibration method was used in the furnace calibration, the difference between the furnace temperature and the program temperature was less than 0.05 °C. Indium was used in the heat flow calibration. In addition, a scale with an uncertainty of 0.001 mg was used to measure the weight of the sample. Both of these two devices have very high degree of accuracy and meet the measurement requirements.

The most common measurement method for DSC was dynamic method, which consisted of a heating process and a cooling process, the dynamic DSC curves of sample PCM at different heating/cooling rates are shown in Fig. 1. The values of characteristic parameters in the phase change processes are shown in Table 1. It was observed that the DSC curve was affected by the heating/cooling rate, the melting peak would shift to the higher temperature while the solidifying peak would shift to the lower temperature. These could be explained by the thermal gradient in the sample [22]. In DSC, the temperature sensor monitored the surface temperature of the sample (ignoring the effect of crucible). During the heating process, although the surface temperature of the sample increased, the inner temperature of the sample was still lower than the surface temperature because of the sample thermal resistance, which meant that the sample temperature was overestimated during heating process. The heating rate was higher, the temperature difference between inside and outside of the sample would be larger, the sample would still absorb latent heat even if its surface temperature was already beyond its actual ending melting temperature, so the peak would shift to the higher temperature. On the contrary, during the cooling process, the sample temperature was underestimated, so the peak would shift to the lower temperature. From Table 1, it is also observed that the heat of fusion (H_f) at different heating/cooling rates were almost identical, which meant the heat of fusion was not affected by the heating/cooling rate (it should be noted that this material was conserved in the lab for more than six years, its heat of fusion was lower than the value from the manufacturer).

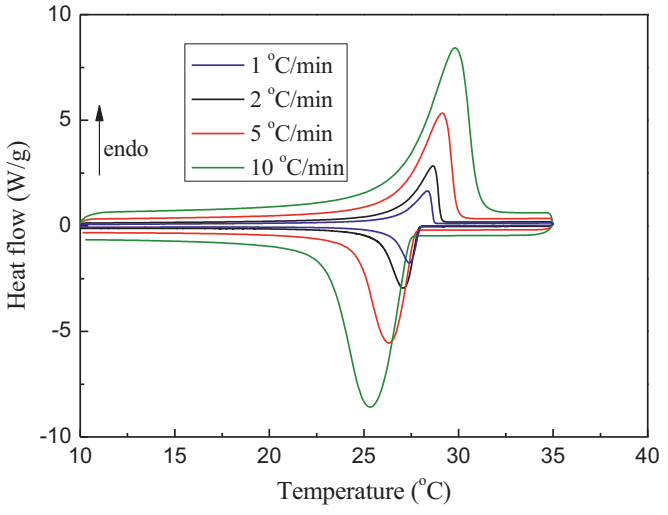

Fig. 1. Dynamic DSC curves of PCM at different heating/cooling rates.

Based on the DSC curves, the measured melting temperature range was usually determined manually. While some researchers recognized the temperature range between the onset temperature (T_{onset}) and the endset temperature (T_{endset}) as the actual melting temperature range. As shown in Fig. 1 and Table 1,T_{endset} were increased with the increase of the heating rate in heating process, while T_{onset} were almost identical, which meant that the measured melting temperature range would change with the heating rate. The heating rate was higher, the measured melting temperature range was wider. However, for a kind of PCM, it should have the sole melting temperature range. It meant that the measured melting temperature range by dynamic DSC measurement was not correct. Therefore, other measurement method should be found to determine the actual melting temperature range, which must be unique and was not affected by the heating rate.

3. Determination of the PCM melting temperature range

Based on the melting temperature range of PCM, three different states of any PCM can be identified as (1) when the PCM temperature is lower than its starting melting temperature, it is deemed to be in the not-melted state; (2) when the PCM temperature is higher than its ending melting temperature, it is deemed to be in the fully-melted state; and (3) when the PCM temperature is between its starting melting temperature and its ending melting temperature, it is deemed to be in the partially-melted state [11,12]. Partially-melted state means PCM absorbs only a part of the latent heat during heating process, and then it is only able to release a part of the latent heat during the following cooling process. While fully-melted state means PCM has absorbed all the latent heat, and then it is able to release all the latent heat during the following cooling process. Determination of the actual melting temperature range of PCM means to find the starting melting temperature at which PCM starts melting and the ending melting temperature at which the melting process is finished. Therefore, the ending melting temperature and the starting melting temperature of PCM are discussed below, respectively.

3.1. Ending melting temperature of PCM

For traditional dynamic DSC measurement method, as shown in Fig. 1, because of the thermal resistance of the sample, the sample temperature was overestimated during heating process, so the measured melting temperature range of PCM was affected by the heating rate. To avoid the temperature overestimation, the effect of the sample thermal resistance must be eliminated.

Here in this research, to find out the actual ending melting temperature of PCM, a new DSC measurement method was proposed, it was referred to as “partially-melted DSC

Table 1
Characteristic phase change values at different heating/cooling rates.

	Cooling/heating rate (°C/min)	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	H_f (J/g)
Melting	1.0	26.86	28.37	28.69	130.80
	2.0	26.88	28.65	29.05	130.58
	5.0	26.74	29.14	29.87	130.19
	10.0	26.85	29.82	30.98	130.05
Solidifying	1.0	27.94	27.38	26.44	129.02
	2.0	27.85	27.09	25.82	130.67
	5.0	27.66	26.32	24.54	131.57
	10.0	27.38	25.34	23.07	134.04

measurement method". The DSC scanning steps were as follows: firstly, the sample was held for 1 min at the starting temperature (minimum heating temperature) on which the PCM was in the non-melted state, then the sample was heated from the starting temperature to the maximum heating temperature (i.e., from the non-melted state to the partially-melted state, the maximum heating temperature was higher than the PCM starting melting temperature but lower than the PCM ending melting temperature), and then the sample was held for several minutes at the maximum heating temperature to ensure the sample reach thermal equilibrium. Finally, the sample was cooled down to the starting temperature (i.e., the initial non-melted state). Taking RT27 as an example, a partially-melted DSC measurement program was: (1) held for 1 min at 20.0 °C, (2) heated from 20.0 °C to 28.0 °C at 5 °C/min, (3) held for 5 min at 28.0 °C, (4) cooled from 28.0 °C to 20.0 °C at 5 °C/min. The 1st and 3rd step were performed to eliminate the effect of the sample thermal resistance, the sample must be held for a period of time in a certain temperature value, so the sample had enough time to keep the thermal equilibrium in this temperature and its temperature would be uniform. After scanning, the absorbed latent heat during heating process and the released latent heat during cooling process were calculated. By changing the maximum heating temperature, a list of partially-melted DSC measurements were conducted, and the absorbed latent heat and the released latent heat during these measurements were also calculated. When the maximum heating temperature was higher than the ending melting temperature of PCM, the absorbed (released) latent heat was equal to its heat of fusion, when the maximum heating temperature was lower than the ending melting temperature of PCM, the absorbed (released) latent heat was lower than its heat of fusion. Therefore, according to the relationship among the absorbed heat, the released heat and the heat of fusion of PCM, the actual ending melting temperature was able to be found out.

As shown in Fig. 1, it was observed that the melting temperature range should be between 25 °C and 32 °C, so the maximum heating temperature in partially-melted DSC measurements were also set to be between 25 °C and 32 °C, and the temperature interval between two measurements was 0.5 °C. Fig. 2 shows the DSC curves of PCM with this method, the heating/cooling rate was 5 °C/min. Fig. 2(a) and (b) is the variations of heat flow with the PCM temperature and the time, respectively.

As shown in Fig. 2(a), although the maximum heating temperatures were different in these measurements, it was found that the variations of heat flow during heating processes were almost identical. If the traditional dynamic DSC measurement method was used to analyze the data, the ending melting temperature was about 30.2 °C. When the maximum heating temperatures were between 25.0 °C and 30.0 °C, because they were lower than 30.2 °C, the PCM melting process did not finish, it should be in the partially-melted state. The absorbed latent heat should be increased with the increase of the maximum heating temperature. When the maximum heating temperatures were 30.5 °C, 31.0 °C and 32.0 °C, because the PCM maximum temperatures were higher than 30.2 °C, it should be in the fully-melted state. However, when the maximum heating temperatures were 28.5 °C, 29.0 °C, 29.5 °C and 30.0 °C, as shown in Fig. 2(a), the solidifying processes of PCM were almost identical with the solidifying processes when the maximum heating temperature were 30.5 °C, 31.0 °C and 32.0 °C, which meant that when the maximum heating temperatures were 28.5 °C, 29.0 °C, 29.5 °C and 30.0 °C, the PCM was able to absorb and release all the latent heat and it should also be in the fully-melted state.

Because the amounts of absorbed latent heat were not able to be observed and compared clearly when the maximum heating

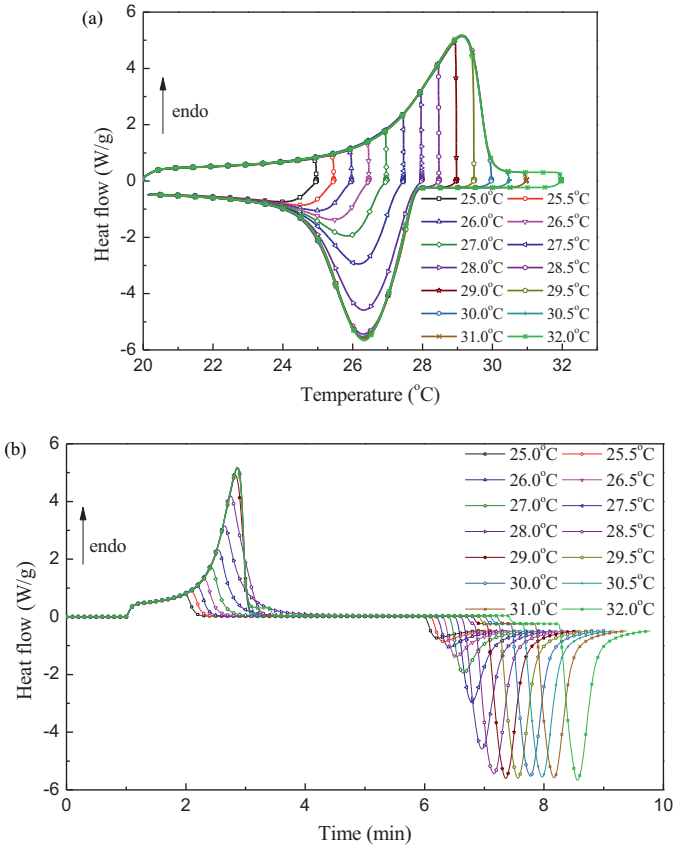

Fig. 2. DSC curves of PCM for different maximum heating temperatures (25.0–32.0 °C) at 5 °C/min (a): heat flow vs. temperature; (b): heat flow vs. time.

temperatures were lower than 30.5 °C in Fig. 2(a), the variations of heat flow with time during DSC measurements are also presented in Fig. 2(b). As shown in this figure, when the maximum heating temperatures were 28.5 °C and 29.0 °C, although the heating curves were different from the heating curves when the maximum heating temperatures were 29.5 °C or higher, the cooling curves were almost identical with the cooling curves when the maximum heating temperatures were 29.5 °C or higher.

The amounts of absorbed and released latent heat during DSC measurements were calculated and shown in Table 2. As shown in Fig. 2(b) and Table 2, when the maximum heating temperatures were lower than 28.5 °C, the PCM was not able to absorb and release all the latent heat, while when the maximum heating temperatures were 28.5 °C or higher, the PCM was able to absorb and release all the latent heat, the amounts of absorbed heat were nearly the same, so were the amounts of released heat. Based on Fig. 2 and Table 2, it is concluded that when the maximum heating temperature was 28.5 °C or higher, the PCM was in the fully-melted state. Therefore, the actual ending melting temperature should be between 28.0 °C and 28.5 °C. It is also observed that when the temperature ranges were 27.0–27.5 °C, 27.5–28.0 °C, and 28.0–28.5 °C, the amounts of absorbed latent heat were more than other temperature ranges. For example, when the maximum heating temperature was increased from 28.0 °C to 28.5 °C, the amount of latent heat absorbed by the PCM was increased by 40 J/g. Therefore, the main melting temperature range of the PCM was 27.0–28.5 °C.

The previous DSC results showed that the actual ending melting temperature was between 28.0 °C and 28.5 °C, in order to find out the exact value of the ending melting temperature, the partially-melted DSC measurements were also conducted for the temperature range 28.0–28.5 °C, and the temperature interval was 0.1 °C.

Table 2
Absorbed and released heat of PCM for different maximum heating temperatures (25.0–32.0 °C) at 5 °C/min

Maximum heating temperature (°C)	Absorbed heat (J/g)	Released heat (J/g)
25.0	7.69	6.99
25.5	11.83	10.81
26.0	17.28	16.43
26.5	24.78	25.27
27.0	37.63	40.18
27.5	57.50	70.70
28.0	90.69	109.45
28.5	130.62	132.93
29.0	128.97	132.93
29.5	131.06	132.71
30.0	131.27	132.80
30.5	130.89	132.92
31.0	130.85	133.02
32.0	130.65	132.91

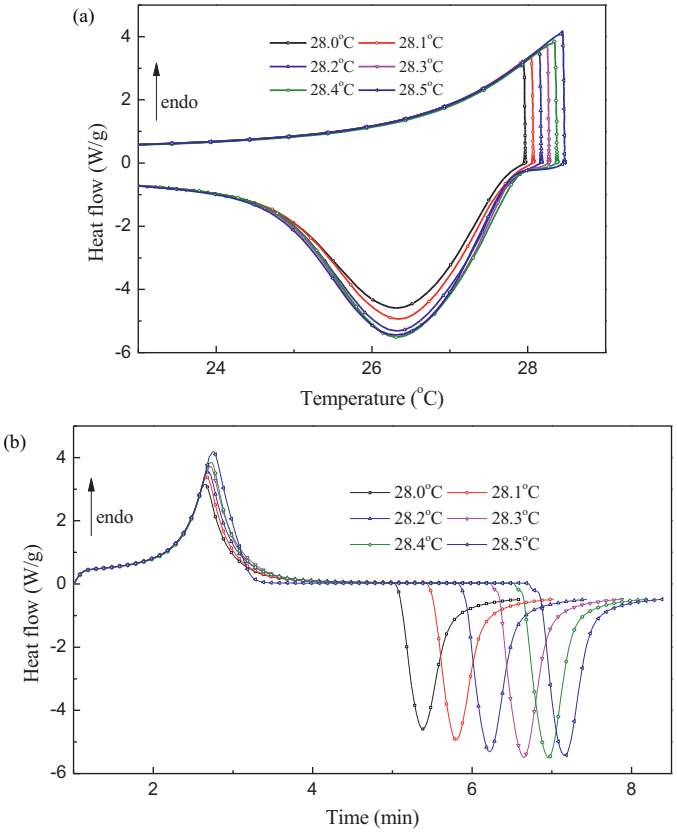

Fig. 3. DSC curves of PCM for different maximum heating temperatures (28.0–28.5 °C) at 5 °C/min (a): heat flow vs. temperature; (b): heat flow vs. time.

The measurement results are shown in Fig. 3 and Table 3. It was found that during these tests, the absorbed heat of PCM was increased with the increase of the maximum heating temperature, when the maximum heating temperature was 28.4 °C or lower, the PCM was not able to absorb all the latent heat. Therefore, it is concluded that the actual ending melting temperature of the PCM was 28.5 °C.

To figure out whether the ending melting temperature (i.e., 28.5 °C) was independent of the heating rate, the partially-melted DSC measurements at 1 °C/min were also conducted, the measurement results were shown in Fig. 4 and Table 4. It was also found that when the maximum heating temperatures were lower than 28.5 °C, the PCM absorbed and released only a part of the latent heat, it was in the partially-melted state. When the maximum heating temperatures were 28.5 °C or higher, the PCM was able to absorb and release all the latent heat, it was in the fully-melted state. These findings were the same as those when the heating rate was 5 °C/min. Therefore, the actual ending melting temperature of the PCM was 28.5 °C, and it was independent of the heating rate.

Table 3
Absorbed and released heat of PCM for different maximum heating temperatures (28.0–28.5 °C) at 5 °C/min

Maximum heating temperature (°C)	Absorbed heat (J/g)	Released heat (J/g)
28.0	90.69	108.79
28.1	98.08	116.07
28.2	106.59	127.23
28.3	114.33	132.80
28.4	115.90	132.62
28.5	130.62	132.93

3.2. Starting melting temperature of PCM

As shown in Fig. 1 and 2, during the heating processes, the heat flow signals increased gradually with the increase of the temperature (time), there was no clear boundary between the non-melted state and the partially-melted state, so the actual starting melting temperature was not able to be found out accurately.

As shown in Table 1, it is found that although the heating rates were different, the onset temperatures (T_{onset}) were almost identical, they were all about 26.8 °C. In addition, the main melting temperature range was 27.0–28.5 °C, which meant the PCM absorbed only a small part of the latent heat when the PCM temperature was 26.8 °C. In a way, the onset temperature might be recognized as the starting melting temperature of the PCM. However, because the melting process had already begun when the PCM temperature was lower than the onset temperature, it should be noted that the onset temperature was not the actual starting melting temperature.

4. Conclusions

The melting temperature range was one of the most important parameters for PCM. In this paper, a new DSC measurement method, which was the partially-melted DSC measurement method, was proposed to determine the actual ending melting temperature of PCM. It was found that when the PCM temperature was lower than 28.5 °C, it was able to absorb and release only a part of the latent heat, it was in the partially-melted state; when the PCM temperature was higher than 28.5 °C, it was able to absorb and release all the latent heat, it was in the fully-melted state. Therefore, it was concluded that the actual ending melting temperature of the PCM was 28.5 °C.

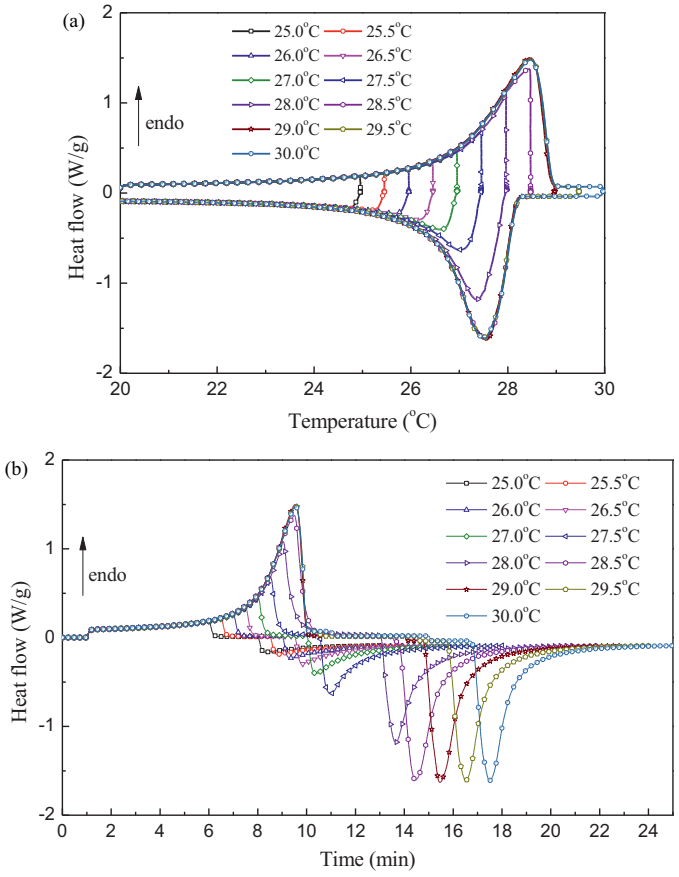

Fig. 4. DSC curves of PCM for different maximum heating temperatures (25.0–30.0 °C) at 1 °C/min (a): heat flow vs. temperature; (b): heat flow vs. time.

Table 4
Absorbed and released heat of PCM for different maximum heating temperatures (25.0–30.0 °C) at 1 °C/min

Maximum heating temperature (°C)	Absorbed heat (J/g)	Released heat (J/g)
25.0	9.04	7.22
25.5	12.67	10.47
26.0	17.52	14.71
26.5	24.25	21.43
27.0	34.23	30.57
27.5	51.56	49.99
28.0	87.79	95.04
28.5	131.28	130.69
29.0	129.58	130.26
29.5	130.74	130.83
30.0	130.81	130.71

Because there was no clear boundary between the non-melted state and the partially-melted state, the actual starting melting temperature of PCM was not able to be determined accurately.

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