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Thermal analysis of heat storage materials

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Abstract

An improved method for testing the thermal performance of encapsulated heat storage materials in large nonstirred samples is presented. The method consists of measuring and comparing the energy loads of two identical thermostatted baths. Water, silicone oil or polyethylene glycol may be used as the working liquids in the baths, depending on the operating temperature. One of the baths operates with the sample of the encapsulated heat storage materials and the second operates with the working liquid alone under similar experimental conditions. Temperatures of the working liquids and the sample can be measured, and compared in the range 0–200°C. Differential measurements of this type provide valuable information on the thermal behaviour of the sample without the need to take into account the heat loss effects which are mainly difficult to determine. The test measurements for paraffin and high density polyethylene are discussed.

INTRODUCTION

Storage of thermal energy in the form of sensible and latent heat has become an important aspect of energy management with the emphasis on efficient use and conservation of the waste heat and solar energy in industry and buildings. Suitable phase changing materials, in sealed containers, with melting points in the range 5–120°C have already been identified and evaluated [1]. The size and shape of the containers vary depending on the loading, recovery and heat transfer characteristics of the heat storage system. Published data on the behaviour of the heat storage materials have been mainly obtained for small quantities on a laboratory scale using calorimetric methods, such as differential scanning calorimetry (DSC). However the use of DSC has its drawbacks; it fails to provide meaningful information on the degree of supercooling and on the freezing point of the substance, because the supercooling tendencies are maximized due to the small quantity of the samples and the poor nucleation characteristics in the DSC testing pans [1]. For hydrates and solutions, it is

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very difficult to ensure that the very small DSC samples contain exactly the amount of water intended. Also determination of the heat of fusion for mixtures by DSC measurement is intrinsically difficult compared with that of a single salt hydrate [2, 3]. The shape and size of the sample in the DSC measurements, which may be of paramount importance, are different from those envisaged in actual design practices using encapsulation [4]. In such cases the measurements on bulk samples provide useful insight into how the material is likely to behave as a storage medium.

Pellegrini et al. [5] described a method of employing twin water baths for testing the thermal behaviour of latent heat storage materials. This method has been modified and improved in this study. By using the appropriate working liquid, the operating temperature may be varied between 0 and 200°C. A data acquisition and control system was introduced into the method to record the temperature and energy loads of the baths. The method may provide information on the heating and cooling curves, the enthalpy changes due to the sensible and latent heats of the sample, and also the heat transfer characteristics between the sample and the various working liquids. The method also enables one to study the effect of size and geometry of the containers on the thermal behaviour of the heat storage materials in large quantities.

EXPERIMENTAL

Apparatus

Change of temperature and energy loads with time are measured, controlled and recorded for two identical baths using the apparatus shown in Fig. 1. It consists of two well stirred identical baths with Techne TU-16A model thermoregulators. The type of working liquid in the baths varies depending on the operational requirements. The specifications of the bath and type of the working liquids are given in Table 1. Each bath is heated by an electrical resistance heater. Assuming that all the electrical energy delivered to the heating resistor is converted into heat, the energy load is controlled with the adjusted input voltage by a variac. The instantaneous voltage and electric currents are measured and recorded by a data logger in order to determine the power inputs for the individual baths. To cool the baths to ambient temperature, identical finned copper coils with tap water circulating in them are used. For temperatures below ambient, additional heat pump systems may be used. Nine individually calibrated thermistors are used to measure the temperatures of the working liquids and heat storage material. The deviations in the power measurements are 1%, while the temperatures are measured within an accuracy of ±0.5°C. The number of readings in the measurements are

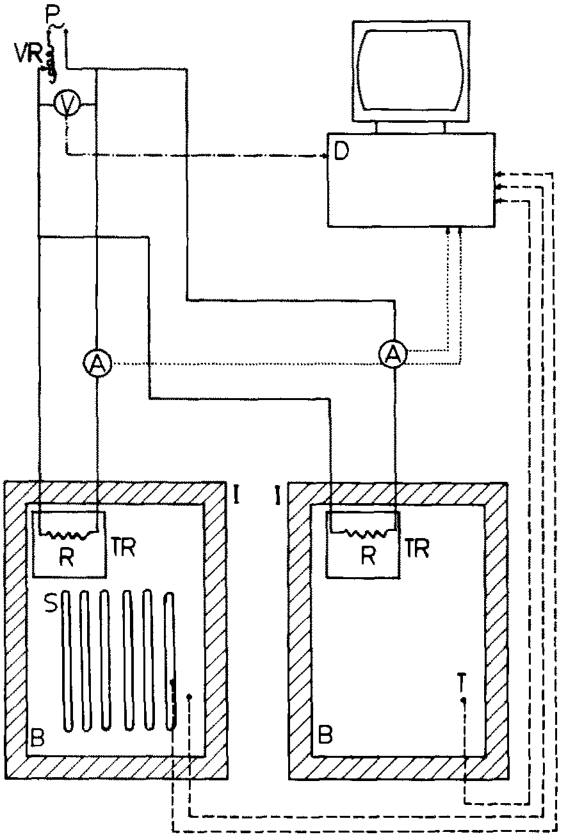

Fig. 1. Test apparatus: B, baths; P, power input; VR, variak; D, data logger; A, ammeter; V, voltmeter; R, resistor; TR, thermoregulator; I, insulation; S, units of encapsulated heat storage materials; T, thermistor; – – –, temperature reading; · · ·, ammeter reading; – · – · –, voltage reading.

adjustable depending on the sample studied and are averaged to achieve a better accuracy.

Procedure

To calibrate the system, the baths are filled with the same amount of working liquids chosen according to the specifications given in Table 1. After that, the change of heat loads of the baths and the temperatures of the working liquids with time are measured and recorded in order to test the baths, with the emphasis on identical behaviour for the heating and cooling modes. A typical temperature change with time for heating and cooling of the working liquids is shown in Fig. 2. After ensuring the identical operating behaviour of the baths, two types of experiment can be carried out: in the first type, two baths are heated simultaneously at a

TABLE 1

Specifications of the bath and the working liquids

Nominal dimensions of the bath	
Length (mm)	560
Width (mm)	330
Working depth (mm)	255 (maximum) 215 (minimum)
Bath capacity (l)	48.5 (maximum) 42.5 (minimum)
Nominal heater power (W)	1800 (240 V) 1700 (220 V) 1500 (120 V) 1250 (100 V)
Maximum watts density (W cm^{-2})	6.2
Circulating pump capacity (l min^{-1})	10 (maximum flow)
Temperature stability (°C)	±0.005
Set point accuracy (°C)	±2
Temperature sensor	Platinum resistance thermometer (PRT)
Working liquids and operating temperatures (°C)	
50% Water + 50% antifreeze	−20–30
Water, preferably deionized with neutral pH	5–95
Silicone oil-200	10–150
Polyethylene glycol-200	40–150
Polyethylene glycol-400	80–200
Silicone oil-550	100–250

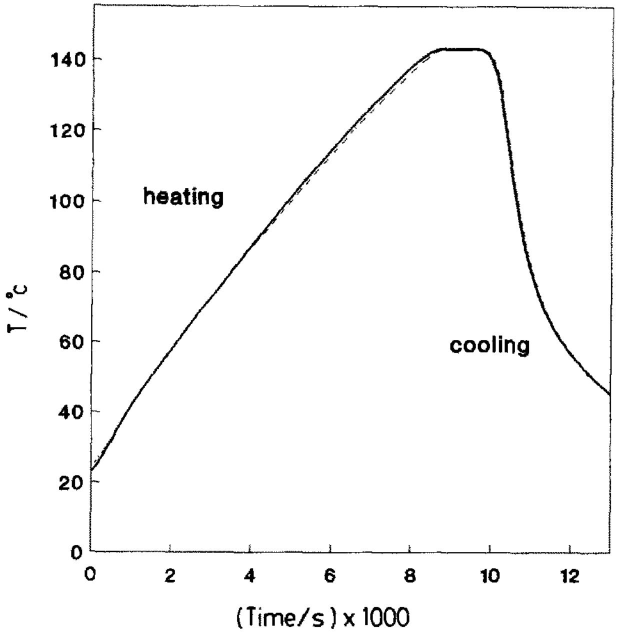

Fig. 2. Calibration curves for the baths: ——, temperature of bath 2; – – –, temperature of bath 1.

constant rate over a fixed temperature interval, when one of the baths contains the sample and the other contains the working liquid alone. Since both baths operate under similar conditions the heat loss to the surroundings Q_L and the heat capacities of the working liquids Q_B are the same and will cancel each other when the energy loads of the baths are compared according to

$$\Delta Q = (Q_B + Q_S + Q_C + Q_L)_{\text{bath},1} - (Q_B + Q_L)_{\text{bath},2} \tag{1}$$

$$\Delta Q = Q_B + Q_C \tag{2}$$

where Q_S denotes the heat absorbed by the sample material and Q_C is the heat capacity of the container. The value of Q_S consists of heat capacities of solid and liquid phases as well as the heat of melting H_m of the sample, which is given for a pure sample by

$$Q_S = M_S[C_{p,S}(T_m - T_0) + H_m + C_{p,l}(T_S - T_m)] \tag{3}$$

$$Q_C = M_C C_{p,C}(T_S - T_0) \tag{4}$$

where M_S is the mass, while $C_{p,s}$ and $C_{p,l}$ are the specific heats of solid and liquid states of the sample respectively. T_0 and T_S are initial and final temperatures of the sample, and T_m is the melting point of the sample. M_C and $C_{p,C}$ are the mass and the specific heat of the container respectively.

In order to determine the heat capacity and phase transition heat of the storage material, a reference material with an identical encapsulation may be used in the second bath, hence the value of Q_S may be calculated from the comparison of the energy loads of the baths

$$\Delta Q = (Q_B + Q_S + Q_C + Q_L)_{\text{bath},1} - (Q_B + Q_R + Q_C + Q_L)_{\text{bath},2} \tag{5}$$

$$Q_S = \Delta Q + Q_R \tag{6}$$

$$Q_R = M_R C_{p,R}(T_S - T_0) \tag{7}$$

where M_R and $C_{p,R}$ are the mass and specific heat, respectively, of the reference material. Materials with known calorimetric properties may be used as the reference. For cooling, tap water and a heat pump may be used depending on the cooling level.

In the second type of experiment, the sample may be introduced into one of the preheated baths at the set temperature, when the other bath contains only the working liquid. Hence the compensation energy required by the bath with the sample may be measured and recorded until the set temperature of the baths are restored. The comparison of the heat loads of the baths will give the summation of heats absorbed by the sample and the container.

$$\Delta Q = (Q_S + Q_C + Q_L)_{\text{bath},1} - (Q_L)_{\text{bath},2} \tag{8}$$

$$\Delta Q = Q_S + Q_C \tag{9}$$

This type of differential measurement as well as the heating and cooling curves will supply valuable information on the thermal behaviour of the heat storage material encapsulated in the required size and shape considering the economy and heat transfer characteristics of the actual system to be designed.

RESULTS AND DISCUSSION

Paraffin and high density polyethylene (HDPE) were tested as samples of heat storage materials. As the working liquid, polyethylene glycol-400 was used. The samples were encapsulated using 43 sealed pyrex tubes of 20 mm diameter and 300 mm height. The total masses of paraffin and HDPE were 2.2 and 1.2 kg respectively.

Before we perform the tests, the calibration curves of the baths for heating and cooling modes were obtained. These curves, as can be seen in Fig. 2, show identical heating and cooling rates for the baths. Besides these, the readings of voltage, two amperages and nine temperatures were also calibrated individually. These readings were connected to a data logger and acquisition system and in every 20 s period 160 readings were taken, averaged and recorded.

The heating and cooling curves of paraffin and HDPE are shown in Figs. 3 and 4, respectively. These figures also show the change of temperature

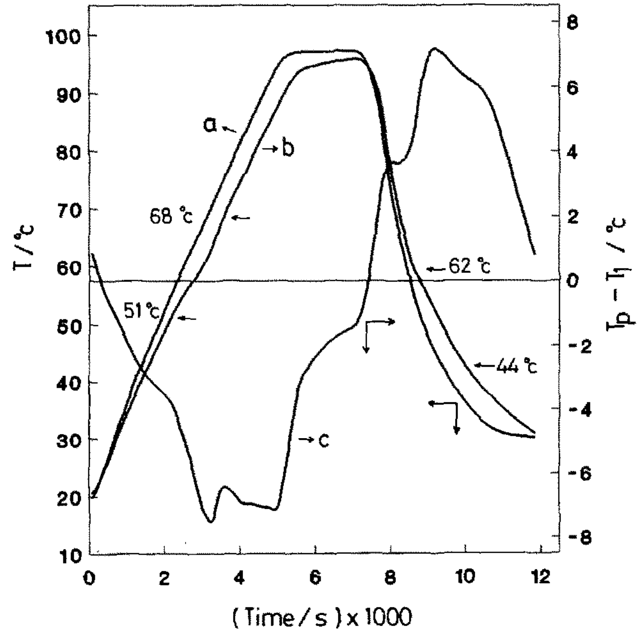

Fig. 3. Heating and cooling curve for the sample of paraffin: (a) temperature of bath 1; (b) temperature of bath 2; (c) temperature difference between the sample of paraffin (T_P) and bath 1 (T_1).

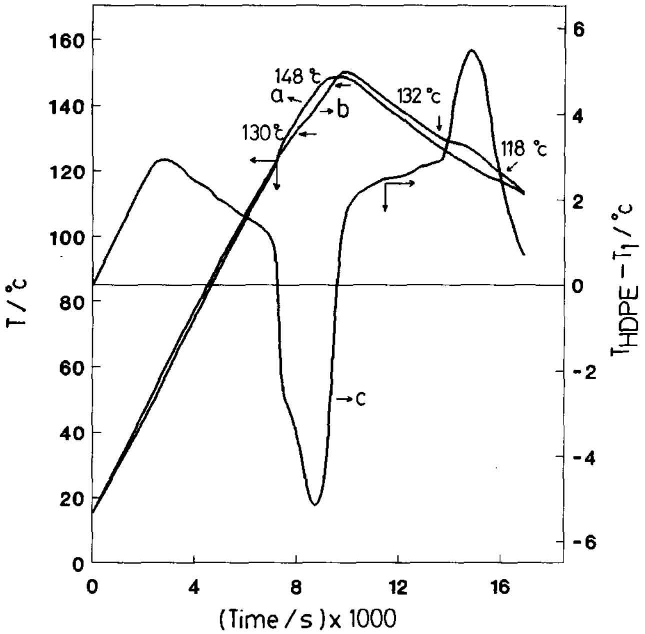

Fig. 4. Heating and cooling curve for the sample of high density polyethylene (HDPE): (a) temperature of bath 1; (b) temperature of the bath 2; (c) temperature difference between the sample of HDPE (T_{HDPE}) and bath 1 (T_1).

difference between the sample and bath with time, which resembles the differential thermal analysis (DTA) measurements. The heights of the peaks occurring in the melting and freezing regions are related to melting and freezing heats, respectively. The measured values of temperature regions for the melting and freezing are 51–68°C and 62–44°C respectively for the sample of paraffin, and 130–148°C and 132–118°C respectively for the sample of HDPE.

The total heat Q_T stored by the encapsulated samples of paraffin and HDPE may be measured by comparing the power loads of the baths obtained from both types of experiments explained above. The total heat consists of heat capacities of the sample in solid and liquid states as well as the heat capacity of the container, and the latent heat of the sample which is given in eqn. (2).

$$Q_T = Q_S + Q_C \tag{10}$$

The measurements of the Q_T obtained from the second type of experiment are shown in Figs. 5 and 6, in which the differences of power loads of the baths are plotted versus the time in seconds. Hence the area under the peaks will give the total heat Q_T.

The test measurements for the samples of paraffin and HDPE are given in Table 2. The agreement between the measured and calculated values of

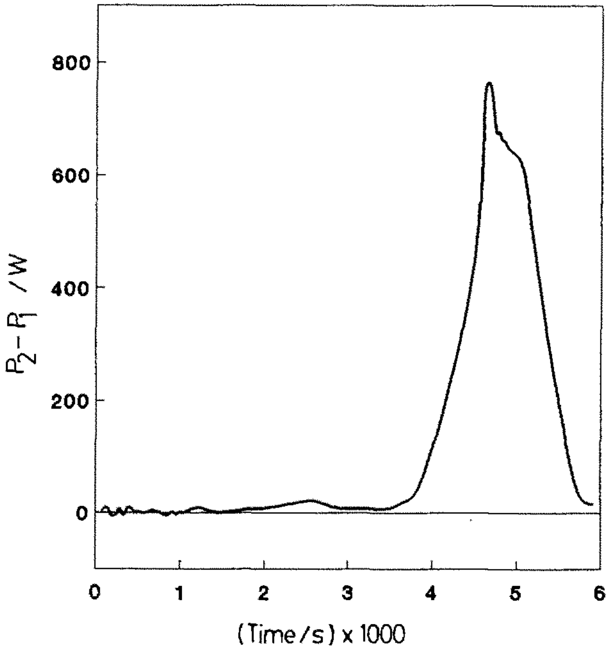

Fig. 5. Difference between the power loads of bath 2 (P_2) containing the sample of paraffin and bath 1 (P_1).

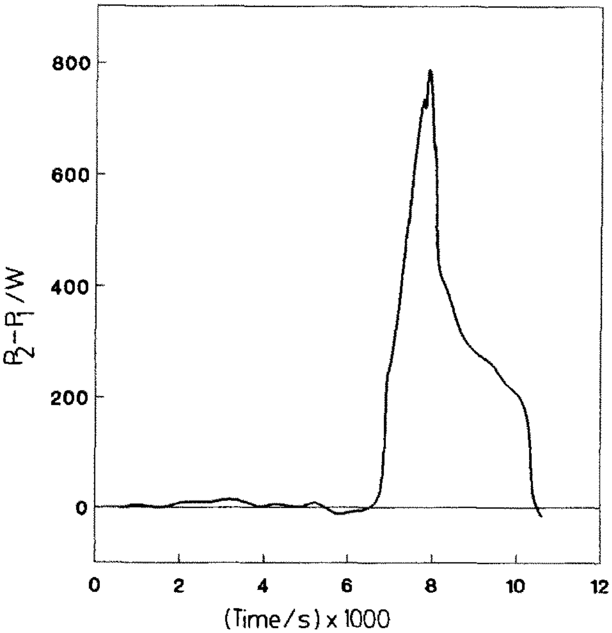

Fig. 6. Difference between the power loads of the bath 2 (P_2) containing the sample of high density polyethylene and bath 1 (P_1).

TABLE 2

Test measurements for the samples of paraffin and high density polyethylene (HDPE)

Type of experiment and samples	Heating		Cooling		Total heat Q_T (kJ)	
	Temp. range (°C)	Time (s)	Temp. range (°C)	Time (s)	Measured	Calculated
Calibration	25–142	9652	142–40	5203		
Type I						
Paraffin	21–96	7382	96–30	4493	915.2	939.7
HDPE	32–150	12064	150–117	7032	1018.2	1013.3
Type II						
Paraffin	22–90	6149	90–37	2905	873.3	896.6
HDPE	20–150	11702			1042.8	1073.1

the Q_T are satisfactory as can be seen from Table 2. The calorimetric data for the samples were taken from refs. 6–8 for the calculated values of Q_T. The measurements of energy and phase transition regions are also consistent with the DSC thermograms of paraffin and HDPE shown in Figs. 7 and 8 respectively. The thermograms were obtained from the Model Dupont 910 DSC module.

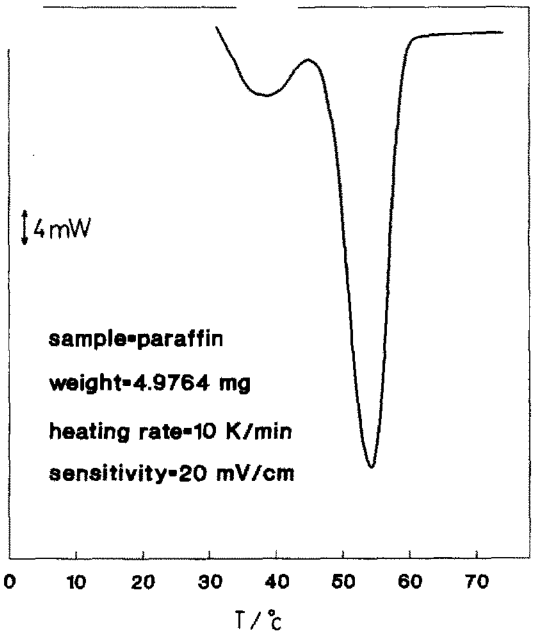

Fig. 7. DSC thermogram for the sample of paraffin.

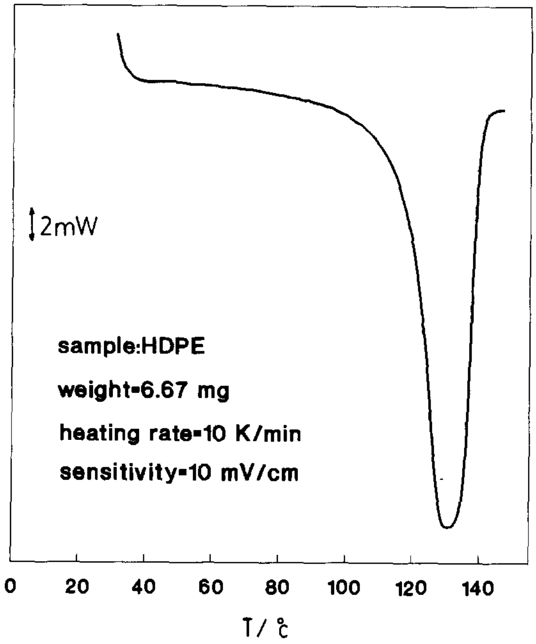

Fig. 8. DSC thermogram for the sample of high density polyethylene.

CONCLUSIONS

An improved method using a twin bath system provides an efficient and simple way for testing the thermal behaviour of the encapsulated heat storage materials in the range of 0–200°C. Using this method, the heat capacities and the phase transition heats of the samples, that are either pure or a mixture, may be measured. The effect of size and shape of the encapsulation on the thermal behaviour of the sample and heat transfer characteristics between the working liquid and sample can also be studied by the method. The thermal analysis measurements of the two heat storage materials of paraffin and high density polyethylene are consistent with the calculated results and DSC thermograms.

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REFERENCES

1 A. Abhat, Sol. Energy, 30 (1982) 313.
2 E.A. Dancy, Sol. Energy, 33 (1984) 41.

3 H. Kimura and J. Kai, Energy Convers. Manage., 28 (1988) 197.
4 H. Feilchenfeld, J. Fuchs and S. Sarig, Sol. Energy, 32 (1984) 779.
5 G. Pellegrini, J. Mignot and S. Sacco, 2nd BHRA Fluid Eng. Int. Conf. on Energy Storage, Stradford upon Avon, UK, May 24–26, 1983.
6 M. Kamimoto, Y. Abe, S. Sawata, T. Tani and T. Ozawa, J. Chem. Eng. Jpn., 19 (1986) 287.
7 A. Haji-Sheikh, J. Eftekhar and D.Y.S. Lou, Spacecraft Thermal Control Design and Operation, 86 (1983) 241.
8 B. Kilkiş and S. Kakac, Energy Storage Systems, Nato ASI Series, Ser. E, Applied Sciences, Vol. 167, Kluwer, Dordrecht, 1989.