Thermochimica Acta, 226 (1993) 163–168
Elsevier Science Publishers B.V., Amsterdam

DSC studies of new energy storage materials. Part 2. New materials and bulk studies [1]

M.W. Babich *, S. Hwang and R.D. Mounts
Chemistry Department, Florida Institute of Technology, Melbourne, FL (USA)
(Received 6 August 1992; accepted 19 April 1993)

Abstract

Energy storage materials (ESMs) have shown some utility in passive supplemental heating applications. This investigation was undertaken to ascertain the value in passive cooling applications of some known and some new ESMs using differential scanning calorimetry. The method works extremely well in all cases tested, both for single heating and cooling runs and for continuous heating and cooling cycles. The scale-up full-room tests give the same results as DSC further validating this method. Though the materials studied all have some desirable properties, none was deemed of general use. From this investigation, the necessary parameters for the discovery of new ESMs have become clear, and study of this is underway.

INTRODUCTION

There has been considerable interest in recent years in the conservation of fossil fuels, alternative energy sources and the reduction of energy costs. This has been particularly true in the construction industry. The focus of our research in this area has been the application of energy storage materials (ESMs) for passive cooling in conjunction with air conditioning systems, an area of great importance in Florida. This interest was spurred by earlier efforts to use low melting fatty acids incorporated in wallboard for supplemental heating [1–3]. We have also been interested in desiccant cooling investigations using TG [4].

In theory, ESMs incorporated into construction materials can function to limit the temperature variation in a structure during a twenty-four hour cycle, especially in off-load periods. This is due to the latent heat of transition associated with a phase change in the material. This heat can be released to a building during cooler periods and be reabsorbed in warmer periods preventing increased warming and thereby levelling power requirements. DSC is especially suited for these studies.

* Corresponding author.
[1] Presented at the 21st Annual NATAS Conference, Atlanta, GA, 13–16 September 1992.

0040-6031/93/$06.00

Ideally these ESMs can be inexpensively integrated into the basic construction materials thereby contributing no additional steps to the actual building process. They should have a phase change with substantial associated latent heat within the normal building temperature range. Therefore, this change must occur at or near the desired ambient room temperature. In this study, the range used was about 20–28°C. In addition to latent heat and temperature range, the following additional factors should be considered: reversibility, toxicity, volatility, aesthetics (including odor, color, etc.), flammability, and ease of incorporation into construction materials.

Using DSC we have reexamined several fatty acids and mixtures of fatty acids with respect to heat evolution or absorption. We have also studied several additional candidates. The results of these studies are shown in Table 1 [5]. Although useful in some applications, these materials were found wanting in several respects, especially in bulk tests [6]. The heat changes were not quite large enough, their odor was not aesthetically appealing, and the results of flammability and smoke tests were unfavorable.

This has led to further studies and the search for new materials [7, 8].

TABLE 1

Thermal results for fatty acids and fatty acid mixtures

Material	mp/°C	ΔH_m/J g^{-1}	fp/°C	$-\Delta H_f$/J g^{-1}
EM625 Coconut acid	25.0	107.1	15.8	110.1
EM626 Coconut acid	25.4	119.1	17.6	119.6
EM627 Coconut acid	30.0	117.2	26.2	147.1
EM659 Capric acid	28.8	147.4	23.2	140.7
EM651 Lauric acid	42.0	132.9	37.9	134.5
EM Methylplamitate	26.8	104.3	20.0	94.1
EK Capric acid	31.0	128.6	27.1	125.8
EK Lauric acid	42.5	126.6	38.1	131.5
EK Methylpalmitate	28.8	163.2	23.3	160.9
EK Methylstearate	37.0	160.7	32.2	159.5
SG Undecylenic acid	24.4	143.5	19.4	144.2
Capric acid/lauric acid ratio				
1/0	28.8	147.4	23.2	140.7
9/1	25.6	71.7	18.2	38.1
7/3	17.7	60.2	13.1	51.1
5/5	19.7	55.5	15.5	40.6
3/7	20.5	123.8	26.9	62.6
1/9	37.4	125.7	33.4	116.9
0/1	42.0	132.9	37.9	134.5

Key: EM, Emery Chemical Co.; EK, Eastman Kodak Chemical Co.; SG, Sigma Chemical Co.

TABLE 2

Thermal results for new enthalpy storage materials (average of three measurements)

Material	mp/°C	ΔH_m/J g^{-1} [b]	fp/°C [a]	$-\Delta H_f$/J g^{-1} [b]
n-Hexadecane [c]	20.0	216	10.4	220
n-Octadecane [d]	28.4	200	17.9	200
1-Dodecanol [c]	23.8	184	17.5	190
n-Heptadecane [c]	22.6	164	19.0	165
Allylpalmitate [e]	22.6	173	16.2	125
Undecylenic Acid [f]	24.6	141	18.1	143
1-Nonadecane [c]	23.2	131	20.1	134
1-Iodohexadecane [c]	22.2	131	8.6	132
n-Octadecylacrylate [g]	25.7	115	22.1	99
Diphenyl ether [c]	27.2	97	−8.2	61
Diphenylmethane [c]	24.4	88	−3.3	75
Chlorobenzothiazole [c]	18.6	65		
3-Iodoaniline [c]	22.5	64		
Polytetrahydrofuran [c]	17.5	59	0.1	76.4
Trimethylcyclohexene [c]	24.1	47		
Phorone [c]	25.8	124	11.2	3.7

[a] Average standard deviation, 0.3°C. [b] Average standard deviation, 4 J g^{-1}. [c] Aldrich Chemical Co. [d] Mainstream Engineering Co. [e] Dajac Laboratories, Inc. [f] Sigma Chemical Co. [g] Scientific Polymer Products, Inc.

New materials studied and their thermal results are shown in Table 2. Several of these had much better thermal properties, as well as more favorable aesthetics and flammability characteristics [9]. These materials have not yet been completely tested with respect to all factors, but they look very promising. In addition, bulk testing needs to be carried out.

This study addresses specific problems and properties of some of these new materials.

EXPERIMENTAL

The DSC curves were obtained using a Perkin-Elmer DSC-7 modified for low-temperature operation using an Intracooler I refrigeration unit. The sample holder is enclosed in a dry box to prevent condensation. This assembly and the data station used have been described elsewhere [5].

DSC runs were carried out on 1–40 mg samples in aluminum sample holders at a heating/cooling rate of 2°C min^{-1} in the temperature range from −10°C to 60°C to establish a good baseline before and after the transition of interest. This same temperature range was used for reversibility studies. The purge gas used was ultra-pure dry nitrogen at a flow rate of 20 ml min^{-1}. Dry nitrogen was also used to purge the dry box assembly. Indium metal and *n*-octadecane were used as standards for calibration. The *n*-octadecane was obtained from the Aldrich Chemical Company and was redistilled at 173.5°C at 10 torr. The sources for all materials investigated are shown in Table 2. These were used as obtained in all cases.

RESULTS AND DISCUSSION

DSC has proven to be a very good method for evaluation of ESM materials. Over forty compounds in seven different chemical classes have been investigated with respect to their thermal properties. Their melting and freezing characteristics are shown in Tables 1 and 2. Several of the new materials have more desirable properties than the fatty acids first investigated with respect to their flammability, odor, size of ΔH and the temperature range of the phase change, but several questions remained unanswered. The reversibility of the change and the overall desirability of the materials were not fully investigated for the new materials.

A recycling study was carried out on undecylenic acid and allyl palmitate. The results of these studies showed extremely good reproducibility and no degradation of material. Recycling studies were also done on the original fatty acid materials absorbed on the wallboard with identical results. Absorbed material behaves in exactly the same fashion as pure material though the peaks are somewhat broadened.

A bulk room test was set up and carried out at the Florida Solar Energy Center, Cape Canaveral, Florida. This test consisted of a sealed room constructed with wallboard impregnated with coconut oil at 20% loading (Emery 626). The rooms are 11 feet × 11 feet in floor area and 8 feet high. A radiant barrier prevents direct solar radiation transfer from exposed walls to make the two rooms function alike in all respects. South walls have a computerized room air conditioner and a window installed. Entrance doors are on the north wall. East and west walls have no penetration. Humidification is also computer controlled. Air temperature and surface temperature were measured at 45 points in the room as well as electricity use (kWh) and power draw (kW). Dew point and dry bulb temperature measurements were made at supply and return locations for the air conditioner. Mass flow rate of infiltration air was measured according to the ASME standard (1984). Heat transfer by conduction was measured by heat flux transducers [6]. The room, shown in Fig. 1, functioned well, but odor was a problem. Odor could be reduced by preliminary baking of small samples. Heat transfer measured in $J\,g^{-1}$ in bulk tests over 24 h cycles correlated reproducibily with our DSC results for Emery coconut oil, within experimental error. For example, a sample of wallboard with 26.1% loading by mass of the coconut oil gave a ΔH_m of 27.6 $J\,g^{-1}$. Dividing ΔH_m by fractional loading gives a value of 106 $J\,g^{-1}$. The value for Emery 625

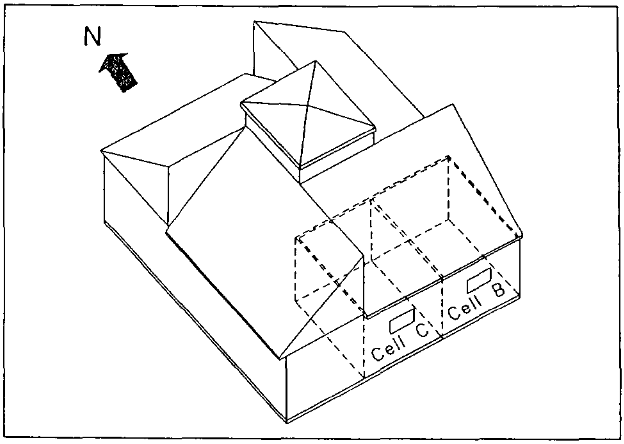

Fig. 1. Schematic drawing of rooms used in the bulk test.

coconut oil from Table 1 is 107.1 J g^{-1}. Similar results were obtained in all cases investigated.

CONCLUSIONS

Some of the new materials exhibit extreme supercooling behavior at the heating rate used in the DSC experiments, as shown in Fig. 2. Studies are

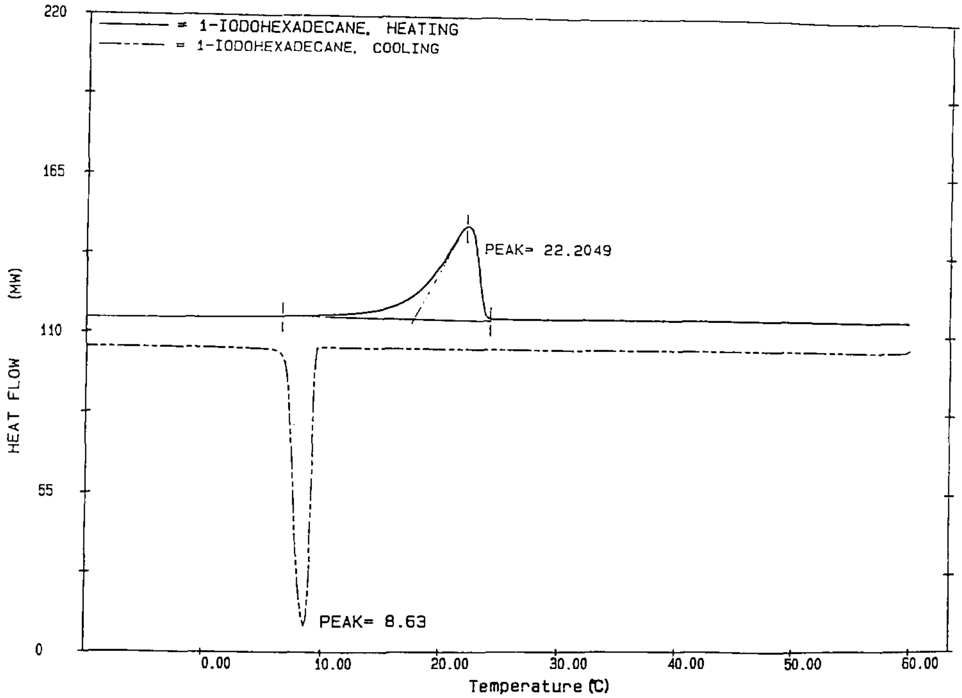

Fig. 2. Differential scanning calorimetry curve for 1-iodohexadecane.

currently underway to see if this is actually a problem during the longer 24 h cycle. The more gradual rate of temperature change in the room may well eliminate any problem associated with this effect. The supercooling effect is not yet well understood for the materials tested. The newer materials must next be evaluated when absorbed on the wallboard, and in flammability and smoke testing experiments. The overall outlook for commercial use of ESMs is very promising.

REFERENCES

1 M. Shapiro, D. Feldman, D. Hawes and D. Bonn, Passive Solar Journal, 4 (1987) 419–438.
2 I.O. Salyer and A.K. Sircar, Thermal Energy Storage Research Activities Review, US Dept. of Energy, New Orleans, Louisiana, 1989.
3 D. Feldman, M.M. Shapiro, D. Bonn and C.J. Fuhs, Solar Energy Materials, 18(3–4) (1989) 201–216.
4 R.D. Mounts, M. Morton and M.W. Babich, Thermochim. Acta, 173 (1990) 81–84.
5 M.W. Babich, S. Hwang and R.D. Mounts, Thermochim. Acta, 210 (1992) 77–82.
6 S. Muthasamy and A. Rudd, Private Communication, Florida Solar Energy Center, Cape Canaveral, Florida, 1992.
7 S. Hwang, M.S. Thesis, Florida Institute of Technology, 1991.
8 M.W. Babich, S. Hwang and R.D. Mounts, Thermochim. Acta, 210 (1992) 83–88.
9 R. Benrashid, Unpublished results, Florida Institute of Technology, 1992.