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The thermal analysis of energy storage materials by differential scanning calorimetry

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Abstract

Energy storage materials (ESM) 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 new ESM 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 ESM have become clear, and this study is underway.

INTRODUCTION

Recent interest in energy storage materials (ESM) for passive cooling applications related to energy conservation has been spurred by earlier proposals to use these materials in supplemental heating [1–3]. Differential scanning calorimetry is a technique ideally suited to determination of both the temperature range of the phase change of interest and the latent heat involved. Both heating and cooling studies are necessary because the application will require continuous cycling. This work is related to our moisture adsorption/desorption studies [4].

In the context of a building heating/cooling system, an energy storage material is a substance which undergoes a reversible phase change during building heating/cooling cycles. The heat of transition associated with the phase change can limit the temperature variation in the building. Energy stored in an ESM can be released to a building during cooler periods. Conversely, in air conditioning applications a precooled ESM can absorb heat during a warm period, preventing excessive warming of the structure.

Energy storage materials can be incorporated into the construction

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materials themselves. In addition to their thermal properties, other properties of ESM such as flammability, toxicity, cost and esthetics (color, odor, etc.) must be considered in the final design of an ESM based building heating/cooling system.

This study was undertaken to see if proposed materials containing fatty acids would be feasible in these applications and to optimize conditions so that the best new materials could be obtained. It is also of considerable interest to determine what chemical properties of materials or mixtures make them effective ESM.

Fatty acids and their low polarity derivatives have specific heats that are comparable to those of hydrocarbons of the same chain length. Heats of crystallization are also comparable and increase with molecular mass. Mixtures of fatty acids have been used to tailor thermal properties for intermediate temperature ranges [5]. These materials also are readily absorbed into building materials such as wallboard, and are not easily leachable out of the material.

EXPERIMENTAL

Differential scanning calorimetry

The DSC curves were obtained using a Perkin-Elmer Delta DSC-7. The instrument has been modified for low temperature operation using an Intracooler I refrigeration unit. The sample holder is housed in a Perkin-Elmer dry box assembly to prevent moisture condensation during low temperature operation. Data collection and analysis was performed on a Perkin-Elmer Model 3700 Data Station.

TABLE 1

Energy storage materials investigated

Emery 625 coconut acid [a,f]	Emery 2216 methyl palmitate [a,k]
Emery 626 coconut acid [a,g]	Kodak methyl palmitate [b]
Emery 627 coconut acid [a,h]	Methyl stearate [b]
Emery 659 capric acid [a,i]	Undecylenic acid [c]
Kodak capric acid [b]	Allyl palmitate [d]
Emery 651 lauric acid [a,j]	Phorone [e]
Kodak lauric acid [b]	

[a] Emery Chemical Co. [b] Eastmann Kodak Co. [c] Sigma Chemical Co. [d] Monomer–polymer and Dajac Laboratories, Inc. [e] Aldrich Chemical Co. [f] 49% lauric acid, 19% myristic acid, 9% palmitic acid, 7% stearic acid, 6.5% octanoic acid, etc. [g] 51% lauric acid, 18% myristic acid, 10% palmitic acid, 7% stearic acid, 7% octanoic acid, etc. [h] 55% lauric acid, 22% myristic acid, 11% palmitic acid, 10% stearic acid, 1% decanoic acid. [i] 97% capric acid, 2% lauric acid, 1% oleic acid. [j] 96% lauric acid, 3% myristic acid, 1% decanoic acid. [k] 95% oleate, 3% linoleate, 2% palmitate.

All DSC runs were carried out on 1–8 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. The purge gas used was ultra-pure dry nitrogen at a flow rate of 20 ml min^{-1}. Dry nitrogen was used to purge the dry box assembly as well. Indium metal and *n*-octadecane were used as standards for calibration. The *n*-octadecane was obtained form the Aldrich Chemical Company and redistilled at 173.5°C at 10 Torr. The sources for all materials investigated as potential ESM are shown in Table 1. These were used as obtained in all cases. The coconut oils are naturally occurring materials containing mixtures of the other fatty acids tested in this investigation.

RESULTS AND DISCUSSION

To be a good candidate for an ESM, a material must have a phase change in the range of ambient room temperature, approximately 20–28°C. This change should have as large a latent heat as possible and be easily reversible. The material should be chemically stable for long periods of time.

Initial studies were undertaken to compare values on known materials previously studied to test our method [5]. The results are shown in Table 2. The materials are all industrial/technical grade. This grade was chosen since it is closest to what will be used in the actual application. The peaks,

TABLE 2

Thermal properties of energy storage materials investigated

Material	Literature m.p. (°C)	Heating cycle		Cooling cycle	
		m.p. (°C)	ΔH_m (J g^{-1})	f.p. (°C)	$-\Delta H_f$ (J g^{-1})
Emery 625 coconut acid	23–25	25.0	107.1	15.8	110.1
Emery 626 coconut acid	23–26	25.4	119.2	17.6	119.6
Emery 627 coconut acid	28–32	30.0	117.2	26.2	147.1
Emery 659 capric acid	31.4	28.8	147.4	23.2	140.7
Kodak capric acid	31.4	31.0	128.6	27.1	125.8
Emery 651 lauric acid	44	42.0	132.9	37.9	134.5
Kodak lauric acid	44	42.5	126.6	38.1	131.5
Emery methyl palmitate	27	26.8	104.3	20.0	94.1
Kodak methyl palmitate	27	28.8	163.2	23.3	160.9
Methyl stearate	38–39	37.0	160.7	32.2	159.5
Undecylenic acid	24.5	24.4	143.5	19.4	144.2
Allyl palmitate	25–26	22.4	166.5	16.0	152.1
Phorone	27	25.8	123.5	11.2	3.7

Heating cycle: initial temperature −10°C; final temperature 60°C. Cooling cycle: initial temperature 60°C; final temperature −10°C. Scanning rate: 2°C min^{-1}.

TABLE 3

Thermal properties of mixtures of capric and lauric acids

Weight ratio (capric acid: lauric acid)	Heating cycle		Cooling cycle	
	m.p. (°C)	ΔH_m (J g^{-1})	f.p. (°C)	$-\Delta H_f$ (J g^{-1})
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[a]	123.8	26.9	62.6
1:9	37.4	125.7	33.4	116.9
0:1	42.0	123.9	37.9	134.5

[a] This sample exhibited a broad melting range from 13.9 to 35.7°C.

Heating cycle: initial temperature 5°C; final temperature 50°C. Cooling cycle: initial temperature 50°C; final temperature 5°C. Scanning rate: 2°C $\min^{-1}$.

therefore, are broadened and the melting points are very slightly lower than literature values for the same pure materials as shown in Table 2. Results for mixtures of materials are shown in Table 3. The mixtures were used to tailor the thermal properties of interest to the specifications required. The ether and ketone were included to see what effect the change in chemical functionality would produce in the thermal characteristics. They were chosen on the basis of appropriate melting points [6].

The coconut oils contain mixtures of fatty acids. All of the materials tested loosely fit our guidelines for ESM with the exception of capric and lauric acids which have higher melting points. These two were chosen so that mixtures could be prepared since the melting point would then be lowered. Most of the substances had very good melting and freezing characteristics as exhibited in Fig. 1. Supercooling was minimal in most of these cases. Since the rate of temperature change in most buildings is much slower than the rate used in the experiment, we expect even less of a problem with supercooling under actual construction test conditions.

Though methyl palmitate and methyl stearate have the highest heats of transition their melting points are out of the range of interest. Of the pure materials, undecylenic acid has about the best overall properties and a favorable energy change of 143.5 J g^{-1}. Emery 626 coconut acid has very good properties as well and is readily available. It should be remembered that a maximum of about 20% fatty acid loading in actual wallboard is reasonable for several reasons and, therefore, only about 20% of the heat per gram of pure substance will be available per gram of wallboard.

The study with mixtures of capric and lauric acid was successful in verifying the ability to tailor thermal properties. Unfortunately from a

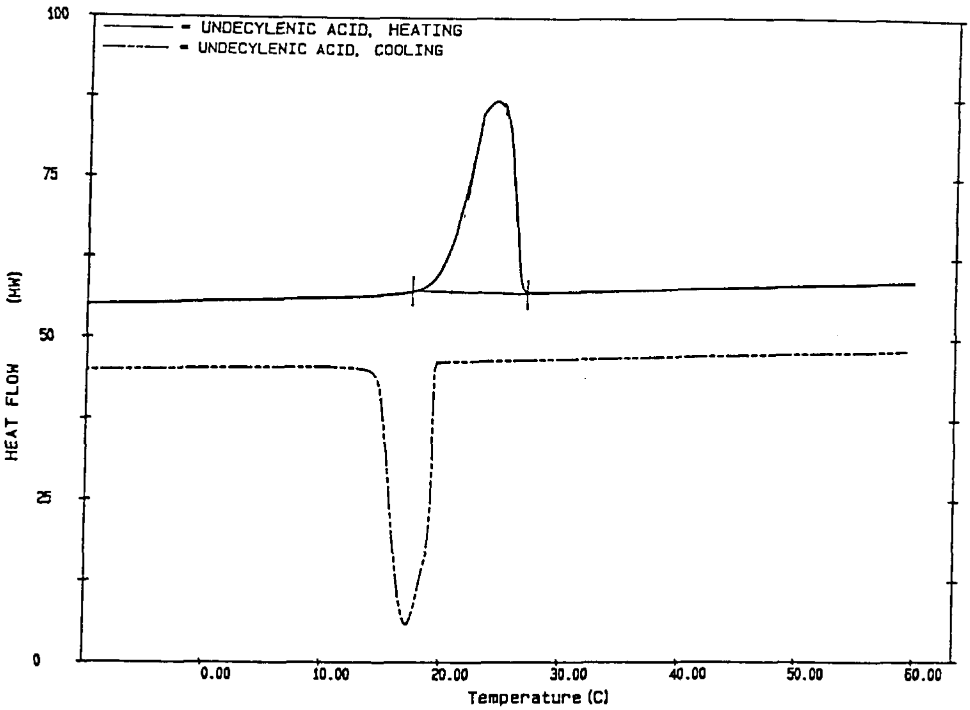

Fig. 1. The DSC curves for heating and cooling of undecylenic acid.

practical point of view the latent heat drops more than originally expected or most mixtures. The 3:7 capric to lauric acid mixture seems about optimum.

Interestingly, in preliminary bulk tests at the Florida Solar Energy Center in a room constructed using wallboard loaded with 20% Emery 626 coconut oil, the overall results of several weeks' tests agree perfectly with the DSC results [7]. DSC is a very good method for evaluation of these materials.

Unfortunately the odor of the fatty acids becomes a problem in bulk. This odor is negligible in small samples. Coatings might control this odor. From these tests it is clear that the materials absorbed in the gypsum wallboard behave much like the pure substances.

SUMMARY

The thermal properties of the fatty acids studied approach what is desirable in ESM, and they should be usable in some applications. The latent heat is a little low and the esthetics leave something to be desired. In addition preliminary flammability tests show excessive smoke formation [8]. Many materials of different chemical functionality are available in the temperature range of interest. Studies of thermal properties of these materials are already underway and several candidates appear to successfully avoid some of these problems.

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