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The search for novel energy storage materials using differential scanning calorimetry

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Abstract

The use of energy storage materials (ESM) has been demonstrated for passive heating and some passive cooling applications. As detailed in a previous paper the fatty acid materials investigated were found wanting in several capacities including odor and amount of heat stored. Further, differential scanning calorimetry has been shown to be an excellent method for determining the desired thermal properties. This paper begins a search for new ESM materials which are not organic acids and which have higher latent heats of melting/freezing and more desirable esthetic properties. Six classes of compounds not previously investigated were represented in the study including: hydrocarbons, ethers, alcohols, ketones, halogenated species and polymers.

INTRODUCTION

The energy required for heating and cooling is a major operating cost of a building. Thermal energy storage materials can reduce these costs. Energy storage materials (ESM) are any material that can absorb thermal energy at one time and release it at a later time. The storage of thermal energy can be based on the heat capacity of the material or on the heat associated with a phase transition [1–5].

The application of energy storage materials in building heating systems is well known and has been discussed in the preceding paper [1]. Materials such as water, stone, brick or concrete can be used to store energy on the basis of their heat capacity. Many systems, for example, have been designed which use solar energy to heat such materials during the day and then allow the heat to be released during the cooler night hours.

ESM can also be employed to reduce the costs associated with the cooling of buildings. The use of ESM in air conditioning systems is more complex than in heating systems. The materials are used to reduce the temperature oscillations in the building and to level the cooling power

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requirements. In cooling applications, the ESM is located in the living area and its temperature is restricted to normal indoor building temperatures. The thermal energy storage must occur within this temperature range. Therefore, a material that exhibits a phase transition at or near room temperature can be utilized as a phase transition thermal energy storage material.

Additional factors that are important for ESM in use in an air conditioning environment include high heat of transition, reversibility, high rate of reversibility, toxicity, volatility, odor, flammability, and then ability to be successfully incorporated into construction materials.

In practice the materials are incorporated into building construction materials such as gypsum wallboard. At temperatures below the melting point the ESM exists in its solid form. As the outside temperature increases and the building begins to heat up it will absorb heat by melting. This will slow the rate of temperature rise of the building. Eventually through operation of the air conditioning system the ESM will convert back to its solid form. The overall effect of the ESM is to increase the thermal capacitance of the building and decrease temperature fluctuations.

Although there are no commercial systems that employ phase transition energy storage materials in an air conditioning system, research at the Florida Solar Energy Center in Cape Canaveral, Florida, has demonstrated the feasibility of the concept [6].

A previously reported, the fatty acids coconut acid, capric acid and lauric acid exhibit a melting point near 25°C. They exhibit reversible melting transitions with a heat of transition in the range from 110 to 150 J g^{-1} [1]. Although the fatty acids exhibit satisfactory thermal properties, there are some difficulties which would have to be overcome in order for these materials to be employed commercially. The fatty acids have a slight odor. Although the odor is not highly objectionable, it would probably be necessary to seal the materials behind a barrier to control the odor. This would be an added expense and complication. In addition the fatty acids are flammable; a fire retardant or flame barrier would probably be required in real world applications [1].

Because of the problems associated with the use of fatty acids, we initiated a search for alternative phase transition based ESM. In this paper we describe a study of the thermal properties of alternative ESM.

EXPERIMENTAL

All DSC curves were obtained using a Perkin-Elmer DSC-7 equipped for low temperature operation as previously described [1]. The instrument was calibrated using *n*-octadecane and indium metal. Samples (15–40 mg) were held in aluminum sample cups, and runs were at 2°C min^{-1} under a

TABLE 1

Energy storage materials investigated

Material	m.p. (°C)
Hydrocarbons	
n-Hexadecane [a]	18
n-Heptadecane [b]	22–24
n-Octadecane [a]	28.24
1-Nonadecene [b]	23
Diphenylmethane [b]	22–24
Ethers	
Diphenyl ether [b]	28
Alcohols	
Butanediol [b]	26
1-Dodecanol [b]	24–27
Ketones	
2,6,6-Trimethyl-2-cyclohexene-1,4-dione [b]	25
Phorone [b]	27
Halogenated compounds	
Chlorobenzothiazole [b]	21–23
3-Iodoaniline [b]	25
1-Iodohexadecane [b]	21–23
Polymers	
Poly(tetrahydrofuran) [b]	27
n-Octadecyl acrylate [c]	24
Allyl palmitate [d]	25–26
Additional acids	
Undecylenic acid [e]	25

[a] Mainstream Engineering Co. [b] Aldrich Chemical Co. [c] Scientific Polymer Products, Inc. [d] Dajac Laboratories, Inc. [e] Sigma Chemical Co.

protective nitrogen blanket. The sources for the materials are shown in Table 1. All materials were used as received.

RESULTS AND DISCUSSION

A thorough search of the literature yielded a list of 31 materials with a reported melting point in the range 18–28°C [7]. Exclusion of materials which were highly toxic or reactive resulted in the list in Table 1. It includes 17 compounds in six chemical classes: hydrocarbons, ethers, alcohols, ketones, halogenated compounds and polymers. The literature melting point is given in Table 1.

The results of thermal measurements for the compounds investigated are summarized in Table 2. The desired thermal properties are high

TABLE 2

Thermal results for energy storage materials

	m.p. (°C)	ΔH_m ($J\,g^{-1}$)	f.p. (°C)	ΔH_f ($J\,g^{-1}$)	$\Delta H_m/\Delta H_f$ [b]	m.p. − f.p.
n-Hexadecane [a]	20.0	216	10.4	220	0.98	9.6
n-Octadecane [a]	28.4	200	17.9	200	1.00	10.5
1-Dodecanol [a]	23.8	184	17.5	190	0.97	6.3
n-Heptadecane [a]	22.6	164	19.0	165	0.99	3.6
Allyl palmitate [a]	22.6	173	16.2	125	1.38	6.4
Undecylenic acid [a]	24.6	141	18.1	143	0.99	6.5
1-Nonadecene	23.3	131	20.1	134	0.98	3.2
1-Iodehexadecane	22.2	131	8.6	132	0.99, S	13.6
n-Octadecylacrylate	25.7	115	22.1	99	1.16	2.5
Diphenyl ether	27.2	97	−8.2	61	S	
Diphenylmethane	24.4	88	−3.3	75	S	
Chlorbenzothiazole	18.6	65			S	
3-Iodoaniline	22.5	64			S	
Polytetrahydrofuran	17.5	59	0.1	76.4	S	
Trimethylcyclohexene-1,4-dione	24.1	47			S	
Phorone	25.8	124	11.2	3.7	S	

[a] Average of three measurements. [b] Complete freezing was not achieved in some cases.
S denotes supercooling. Average standard deviations: 0.3°C for m.p. and f.p.; 4 $J\,g^{-1}$ for ΔH.

transition enthalpy, transition range within the ideal limits of 22–28°C, reversible behavior and absence of supercooling or other unusual effects.

Based on the observed enthalpies, the compounds investigated can be divided into three categories: those with enthalpies greater than, approximately equal to, and those observed for the fatty acids. The five compounds at the top of Table 2 gave transition enthalpies in the 160–220 $J\,g^{-1}$ range. This is up to 80% higher than the 110–140 $J\,g^{-1}$ range observed for the previously studied fatty acids. The two compounds in the center of the table gave ΔH values comparable to the three fatty acids; all the others yielded significantly lower ΔH values.

In addition to high transition enthalpy, the temperature range associated with the melting and freezing cycles must fall within the 22–28°C temperature extremes of an air conditioned building. Only one of the compounds, *n*-octadecyl acrylate, met this criterion. All of the other materials exhibited freezing temperatures that extended well below 22°C under the conditions of our tests. The freezing point for *n*-heptadecane, 1-dodecanol, 1-nonadecene, allyl palmitate and undecylenic acid were only slightly below 22°C. The rate of temperature change for a building would typically be far less than the 2°C min^{-1} used in our studies. At a slower rate of change the effective freezing point for these materials may shift to a higher value. In addition each of these materials exhibited a

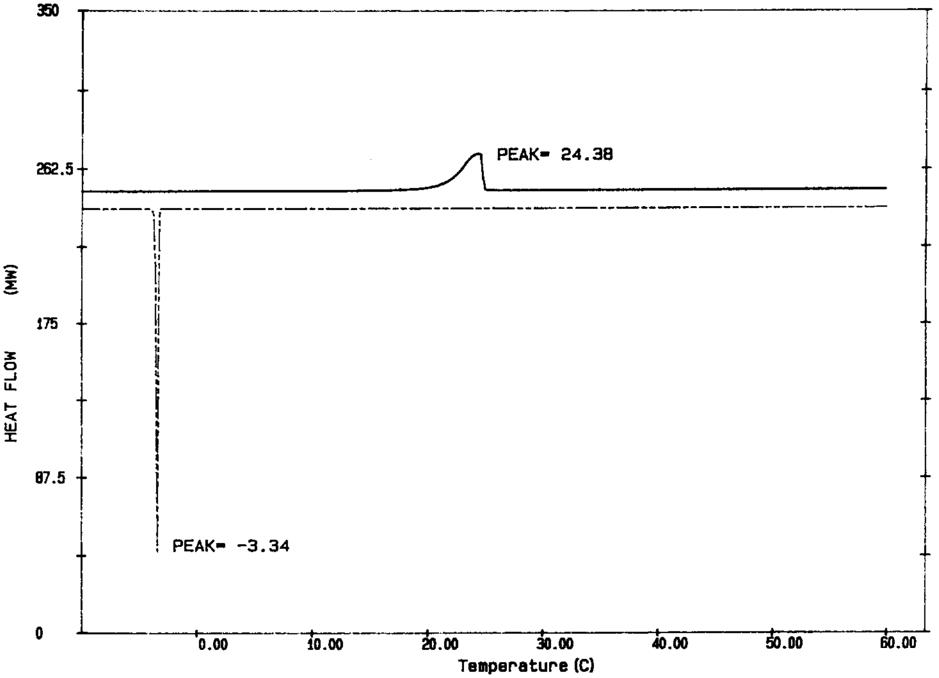

Fig. 1. DSC curve for diphenylmethane showing supercooling. Heating cycle: initial temperature, −10°C; final temperature, 60°C. Cooling cycle: initial temperature, 60°C; final temperature, −10°C. Rate: 2°C min^{-1}.

melting point well below 28°C and a melting/freezing range of less than 7°C. Use of a compound with slightly higher molecular weight may allow the melting/freezing curve to shift closer to the ideal 22–28°C range. The extreme supercooling behavior of some of the samples is best illustrated in the DSC curve for diphenylmethane in Fig. 1. Fortunately, this extreme supercooling is found in only a few cases.

All of the compounds which did not exhibit supercooling exhibited thermal reversibility as indicated by a ratio of forward and reverse enthalpies close to 1. Some of the compounds exhibited significant supercooling. Interestingly, these were all substances with low ΔH values. None of the compounds with high ΔH values exhibited any noticeable supercooling. Unfortunately each of the halogenated compounds showed supercooling. The halogenated compounds are of interest because of their flame retardent properties. 1-Iodohexadecane is the only possible exception: although it clearly exhibited supercooling at a scan rate of 2°C min^{-1}, slower temperature change rates should decrease the amount of supercooling.

SUMMARY

We have identified several alternatives to the use of fatty acids as ESM in air conditioning systems. *n*-Hexadecane, *n*-heptadecane, *n*-octadecane, 1-dodecanol and allyl palmitate all exhibit ΔH values greater than those given by fatty acids. However, under the conditions of our study they exhibited a melting/freezing range that is slightly too broad and that extends below 22°C. Further studies at slower heating rates and with compounds with longer chain length are planned.

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REFERENCES

1 M.W. Babich, S.W. Hwang and R.D. Mounts, Thermochim. Acta, 210 (1992) 77.
2 D. Feldman, M. Shapiro, D. Banu and C.J. Fuhs, Sol. Energy Mater., 18(3–4) (1989) 201–216.
3 M. Shapiro, D. Feldman, D. Hawes and D. Bonn, Passive Sol. J., 4 (1987) 419–438.
4 J.A. Bock, D.P. Gundlach, I.A. Khoury and H.G. Langer, Thermochim. Acta, 121 (1987) 165–179.
5 I.O Salyer and A.K. Sircar, Thermal Energy Storage Research Activities Review, U.S. Department of Energy, New Orleans, LA, 1989.
6 M. Swami and A. Rudd, personal communication, Florida Solar Energy Center, Cape Canaveral, FL, 1991.
7 Z. Rappoport (Ed.), Handbook of Tables for Organic Compound Identification, 3rd edn., Chemical Rubber Company, Cleveland, OH, 1967.