

DSC studies of new energy storage materials. Part 3. Thermal and flammability studies[☆]

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Abstract

Investigations of the thermal properties of fatty acids as energy storage materials (ESMs) have been proceeding for some time. Several of these, when incorporated into building materials such as wallboard, have proved efficacious for absorbing and releasing heat as ambient temperature rises and falls. This makes them potentially useful for supplemental cooling and heating applications. Unfortunately other properties of these materials such as flammability, odor and smoke production make them undesirable for construction use. This study using DSC and flammability testing describes some new candidates for ESMs which avoid some of these inherent problems; in addition to providing greater energy storage capacity.

Keywords: DSC; ESM; Flammability; Heat storage; Testing

1. Introduction

For many years studies have continued on energy storage materials (ESMs) incorporated into construction materials which, in theory, can function to limit temperature variation in a structure over a twenty-four-hour cycle. This effect is due to the latent heat associated with a phase transition in the material occurring over

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the temperature range of interest. Specifically, for construction applications, this is the ambient temperature range of the structure. Excess heat could be absorbed by the material during warmer periods and released to the surroundings during cooler periods which would then prevent large temperature fluctuations. The first materials investigated were low melting fatty acids and were discussed in several reports [1–5].

Though these fatty acids proved effective in heat release and adsorption, they were unacceptable for many applications owing to the following reasons: aesthetics (odor, color, etc.); smoke production enhancement; and flammability properties. Bulk tests at the Florida Solar Energy Center, Cape Canaveral, Florida, resulted in small rooms smelling like coconut oil.

A search has been initiated for new materials, with some success. In addition to overcoming the above stated problems, the improved properties being sought are higher latent heats, low toxicity, good thermal reversibility characteristics and easy permanent incorporation into construction materials. We have investigated several candidates with very good results [6]. DSC has been especially useful in the studies of these materials, obviating the bulk tests run previously. These will only be necessary for actual final application testing. It has been shown that the DSC results and the previous bulk test results agree in all cases within experimental error [7,8].

Investigation has also begun in the Florida Tech Polymer Flammability Labs with respect to smoke production and flammability of these materials. Preliminary studies have been run and systematic testing has recently started, providing very interesting results [9,10].

2. Experimental

The DSC curves were obtained using a Perkin-Elmer DSC-7 which has been modified for low temperature operation using an Intracooler I refrigeration unit. The sample holder is enclosed in a dry box to prevent condensation. This set up has been described elsewhere [5].

DSC runs were conducted on 1–40 mg samples in aluminum sample holders at a heating/cooling rate of $2^{\circ}\text{C min}^{-1}$ in the range -10°C to 60°C to allow establishment of a good baseline. This same temperature range was used for reversibility studies. Ultrapure dry nitrogen was used as the purge gas both for the sample chamber and the dry box. Indium metal and *n*-octadecane were used as calibration standards. The *n*-octadecane was obtained from the Aldrich Chemical Company and redistilled at 173.5°C at 10 torr. The sources for all materials examined are shown in Table 1. These were all used as obtained.

Commercially available, flame-retardant-grade gypsum wallboard samples were obtained from Goldbond Building Products, and magnesium and aluminum hydroxides were supplied by Huber Chemical. Uncoated and epoxy-coated samples were tested for reference. Commercial Epoxy (Klenk's Epoxy Enamel) was used in

Table 1

Thermal results for new enthalpy storage materials; average of three measurements; average standard deviation for mp and fp, 0.3°C; average standard deviation for ΔH , 4 J g⁻¹

Material	mp in °C	ΔH_m in J g ⁻¹	fp in °C	$-\Delta H_f$ in J g ⁻¹
<i>n</i> -Hexadecane	20.0	216	10.4	220
<i>n</i> -Octadecane ^a	28.4	200	17.9	200
1-Dodecanol ^b	23.8	184	17.5	190
<i>n</i> -Heptadecane ^b	22.6	164	19.0	165
Allyl palmitate ^d	22.6	173	16.2	165
Undecylenic acid ^c	24.6	141	18.1	143
1-Nonadecane ^b	23.2	131	20.1	134
1-Iodoheptadecane ^b	22.2	131	8.6	132
<i>n</i> -Octadecylacrylate ^c	25.7	115	22.1	99
Diphenyl ether ^b	27.2	97	-8.2	61
Diphenylmethane ^b	24.4	88	-3.3	75
Polytetrahydrofuran ^b	17.5	59	0.1	76.4

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

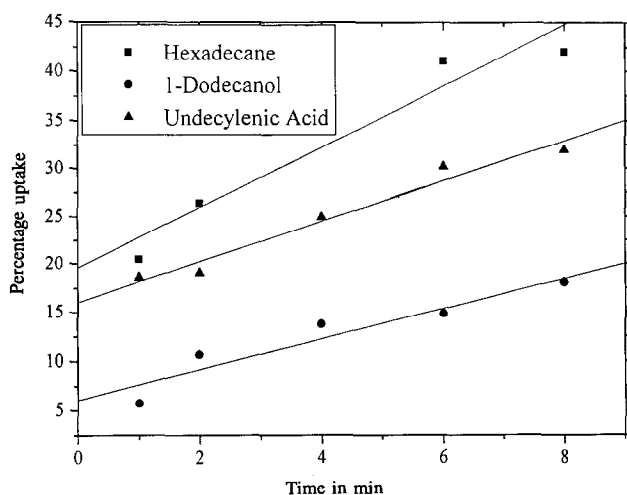


Fig. 1. Effect of time on the adsorption of ESM on wallboard.

all cases. Parts A and B were mixed, the materials added, mixed again and then applied. The coated surface was aged for 4–6 weeks at room temperature prior to testing.

Wallboard samples are prepared by immersion at 70°C for various lengths of time as shown in Fig. 1. They were then allowed to set for two weeks prior to testing to observe whether low molecular mass, volatile materials were evolved.

The flammability of solids may be considered as a function of heat release rate and critical ignition energy of the solid. These properties were measured by the Radiant Panel Test (ASTM E-162). The samples tested were 6 inches \times 18 inches.

Smoke evolution was measured using the NBS smoke chamber (ASTM E-662). Non-flaming samples were tested using the radiant heater alone. A six flamelet burner at the base of the sample was also used for flaming samples. The average is based on three replicates. The wallboard samples used were 3 inches \times 3 inches in area.

Bulk room testing has been previously described [7,8].

3. Results and discussion

DSC is an excellent method for evaluation of the ESMs shown in Table 1. Furthermore, reversibility studies of all these materials proceed satisfactorily, with the exception of those with excessive supercooling at the heating/cooling rate used. Examples of multiple thermal cycles are shown in Table 2. Multiple thermal cycling has been carried out with all test materials. In the one random case tested, there was no appreciable change over fifty cycles. Recycle testing is in progress for several of the better materials absorbed in the gypsum wallboard and which have already been subjected to flammability testing. The code used for identification of these materials in this paper is: S1 hexadecane; S2, 1-dodecanol; S3, undecylenic acid; S4, coconut oil.

Table 2
Example of multiple thermal cycling: temperature range, -10°C to 60°C ; scanning rate, $2^{\circ}\text{C min}^{-1}$

Enthalpy storage material	Melting		Cooling	
	mp in $^{\circ}\text{C}$	ΔH_m in J g^{-1}	fp in $^{\circ}\text{C}$	$-\Delta H_f$ in J g^{-1}
Undecylenic acid (15.8 mg)				
1st run	25.1	142.3	17.0	141.0
2nd run	25.0	141.9	18.7	141.6
3rd run	24.9	144.5	16.6	140.2
4th run	24.8	142.2	17.1	142.3
5th run	24.8	142.1	15.8	141.8
Average	24.9	142.6	17.1	141.4
Standard deviation	0.1	1.0	0.9	0.7
Ally palmitate (5.4 mg)				
1st run	22.4	171.1	16.6	163.8
2nd run	22.4	173.0	16.5	163.6
3rd run	21.7	169.0	16.7	165.5
4th run	21.9	168.7	16.7	163.7
5th run	21.8	171.1	16.7	164.3
Average	22.0	170.7	16.6	164.2
Standard deviation	0.3	1.6	0.1	0.7

Table 3
Flaming NBS smoke chamber results for energy storage materials in wallboard (coated and uncoated)

Sample	No of samples	D90	D240	D475	Dc	Corrected Dm	Dm/Wt	Weight G	Sample Weight
Wallboard	3	2.9	12.1	14.9	0.9	15	0.4	8.5	49.20
FR Wallboard	3	3.9	11.2	17.8	0.6	17.3	0.4	9	55.8
S1	3	1.7	2.8	14	0.9	214	3.5	23.5	60.5
S1 Epoxy	3	11.7	31	36.8	7.5	251	5	26.7	68.6
S1 Al(OH) ₃	3	14.9	37.4	39	4.7	231.7	3.5	27.1	66.5
S1 Mg(OH) ₂	3	13.4	35.3	41.4	5.6	334.2	4.9	27.2	58.7
S2	3	0.7	1.2	17.5	84	44	0.6	21	63.3
S2F	3	0.7	1.6	31.4	85.7	88	0.2	19.9	62.2
S2 Epoxy	3	13.7	14.4	48.3	104.3	64.4	1.1	20.3	60
S2F Epoxy	3	3.2	4.5	66	71.7	88.5	1.4	18.7	65.2
S2 Al(OH) ₃	3	2.9	4.2	27.2	87.6	40.6	0.7	19.4	60.1
S2 Mg(OH) ₂	3	1	1.5	49.6	82.3	79.3	1.3	19.6	57.1
SFS2 Al(OH) ₃	3	1.7	3.8	57.8	80	24.3	1.1	21.0	64.9
SFS2 Mg(OH) ₂	3	1	2.5	38.9	83.4	43.5	0.7	20.2	63.2
S3	3	1.3	21.8	191.3	32.9	467	8.3	21.6	57.2
S3 Epoxy	3	3.4	10.2	229.5	42.6	448.4	7.3	21.6	57.2
S3 Al(OH) ₃	3	1.3	3	196.5	69.5	407	6.9	21	59.9
S3 Mg(OH) ₂	3	0.7	1.8	105.5	29.3	394	6.4	20.5	61.8
S4	3	4.2	52	267	31.3	470.9	8.4	19.5	56.1
S4 Epoxy	3	2.7	32.5	205.4	40.8	458.3	8.3	20.1	55.4
S4 Al(OH) ₃	3	25.2	101.2	397	28.7	484.5	8.8	20.1	55.4
S4 Mg(OH) ₃	3	1.5	9.8	149.7	43.7	397	7.2	18.1	53.4

Allyl palmitate, a material with exceptionally good properties has not yet been tested further due to unavailability of an inexpensive bulk source. Its cost is prohibitive for commercial utility. Synthetic chemists consulted have not yet come up with an inexpensive route to the material.

The supercooling observed with some of the samples in short DSC tests at 2 min⁻¹ heating rate does not seem to be a problem in the much slower changes observed over a twenty-four-hour cycle in the bulk testing.

The results of the smoke and flammability tests on the new samples are most interesting, but their optimum loading and control of loading have not yet been determined. While the amounts of fatty acids absorbed were all about the same for a given amount of time, these new materials vary considerably from each other in absorption properties as shown in Fig. 1. The samples used for flammability testing were all in the range of 20%–30% absorbed materials by mass. All test parameters were as per ASTM specification.

Flaming mode NBS smoke chamber data are shown in Table 3 and show improvement for samples coated with aluminum and magnesium hydroxide, causing delay in smoke production which is important in allowing increased evacuation time in case of fire. However, the overall amount of smoke produced is not reduced.

Table 4
Radiant panel results for energy storage material in wallboard (coated and uncoated)

Samples	No. of samples	F_s	Q	I
Cardboard	3	3.24	52	168.7
Wallboard	2	1.9	3.7	7.3
Fr Wallboard	2	1	6.2	6.2
S1	3	11	58.3	641.5
S1 Epoxy	2	1.8	29.1	67.4
S1 Al(OH) ₃	2	1.5	27	40.6
S1 Mg(OH) ₂	2	1.9	32.8	61.7
S2	2	5.2	46.8	240.3
S2 Epoxy	2	2.6	22	56
S2 Al(OH) ₃	2	1.4	11.5	16
S2 Mg(OH) ₂	2	2.6	21	54.3
S2F	2	4.1	21.3	86.4
S2F Epoxy	2	3.0	21.8	64.5
S2F Al(OH) ₃	2	1.4	13	17.6
S2F Mg(OH) ₂	2	2.2	15.6	34.4
S3	2	4.1	13.6	54.5
S3 Epoxy	2	2.8	19.3	53.1
S3 Al(OH) ₃	2	1.3	8.3	10.9
S3 Mg(OH) ₂	2	1.5	15.6	34.4
S4	2	3.6	16.2	59
S4 Epoxy	2	3.5	20.8	73.6
S4 Al(OH) ₃	2	1.8	13.1	23.4
S4 Mg(OH) ₂	2	1.5	15.2	21.5

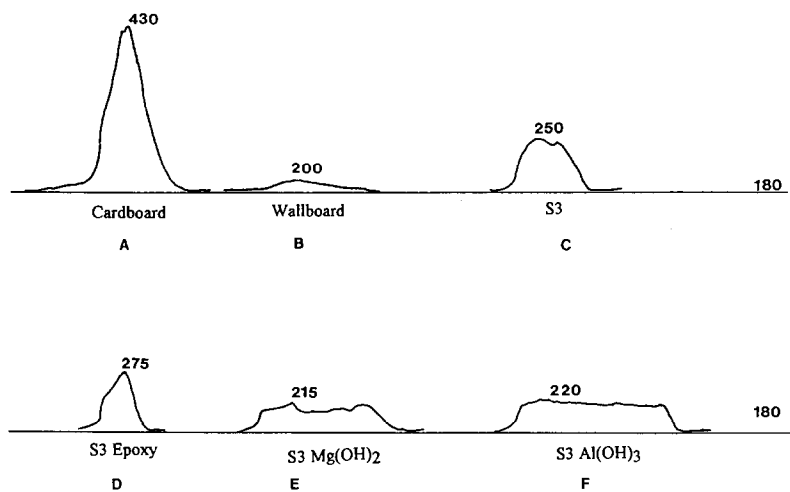


Fig. 2. Comparison of maximum stack temperature in °C (NBS radiant panel heat release test) for materials specified.

Table 5
Thermal results for S1 and S2 on wallboard

Material	Melting		Cooling	
	mp in °C	ΔH_m in J g ⁻¹	fp in °C	$-\Delta H_f$ in J g ⁻¹
S1	19.3	38.29	15.2	37.85
S2	24.2	29.33	19.5	29.61

The radiant panel data given in Table 4 show great improvement in the rate of fire spread and in the heat release, the two important quantitative parameters in measuring flammability of solids. There is a remarkable reduction in stack temperature. The data for S3 are shown graphically in Fig. 2 as an example. In many cases the treated material is as good as plain untreated wallboard and shows excellent flammability characteristics. Therefore, in applications where flammability is a prime consideration, the coated samples can clearly be of great value.

The DSC results for S1, S2, and S3 absorbed in wallboards are still preliminary and also approximate because of the loading problems during absorption described above. Samples used were at about 20% loading by mass. They do, however, follow the same pattern as all materials previously tested as shown in Table 5. Division of ΔH_m by the fractional loading (0.20 ± 0.02) reproduces the ΔH_m value for the appropriate pure material. It appears that a calibration error in the earlier work has resulted in about an 8% decrease in the overall energy measured in Table 1. Some instability in the undecylenic acid samples has been observed after six months. This will be investigated further. This has not appreciably affected the overall results.

4. Summary

The overall outlook for the commercial use of new energy storage materials is very good. Flammability characteristics can be effectively controlled by coating with aluminum and magnesium hydroxide. Further study is required with more accurate determinations of loading of ESM to demonstrate complete compatibility. The rapid and variable uptake of these materials by wallboard is convenient from a commercial standpoint, but more difficult to control in the laboratory. Allyl palmitate, a very good candidate, has not been pursued because of prohibitive cost from a commercial perspective. The instability of absorbed undecylenic acid must also be investigated.

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