

ENERGY STORAGE MATERIALS AND COATINGS. DSC AND FLAMMABILITY STUDIES

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Introduction

For many years investigations into the thermal and moisture storage properties of materials undergoing reversible phase changes in the temperature range of interest for that particular application have been conducted. The prototypical material is, of course, water at 0°C or 100°C. The interest in these materials has arisen largely from the need to conserve fossil fuels and cut energy costs. Both reasons are still valid. (1-2)

These materials have been called phase change materials, (PCM's), Energy Storage Materials (ESM's) or enthalpy storage materials in the literature, and these terms are used interchangeably for the most part. They have been incorporated into a wide variety of components used in construction and fabrication of everything from buildings to packaging materials to space suits.

Interest has existed in phase change materials for thermal storage since the late 1940's largely due to the pioneering studies of M. Telkes using Glauber's Salt. (3,4) These studies set the tone and path for work to follow even through thermal storage using this salt was never widely commercially successful. The primary disadvantage of Glauber's Salt is phase segregation upon melting. Work prior to the latest ESM materials was reviewed by Lane in 1987. (5) The early work concentrated heavily on melting of salt hydrates and gave quite mixed results. Non-segregating hydrates (those with congruent melting) such as $MgCl_2 \cdot 6H_2O$ at 117° gave the best results, but are not always available for the temperature range of interest. Table 1 shows a selection of these types of materials which have been used commercially and their temperatures of transition.

One of the most novel approaches developed was to use the solid-solid transition in polyalcohols the temperature of which can be somewhat adjusted by blending. These materials include pentaerythritol and neopentyl glycol (6,7). These transitions have been studied from 25° to 140°C. The lower temperature cases have not proven very useful as yet in any actual application.

Our area of primary interest, of course, has been in the application of phase change materials for thermal storage. PCM's have been used supplementally in both passive heating and cooling applications. These PCM's incorporated into construction materials can function to limit the temperature variation in a commercial or residential structure over a twenty four hour cycle by releasing heat during cooler periods and absorbing heat during warmer periods. Energy savings of 30 - 70% have been projected and up to 90% of annual sensible cooling could be shifted to off-peak hours. Further, coupling enthalpy storage with moisture storage has been shown to control humidity as well.

Desired Properties

Lane has listed some of the following properties for phase change materials. (5) This list was modified by Babich and Hwang and is shown in Table 2. (8-9)

How the importance of the properties on this list are weighted depends entirely on the application intended. The optimum set of properties can be determined for each situation. The choice may be economics driven in one case or application driven in another. It is for this reason that we strongly feel no one material is likely to solve every problem. Instead a range of good phase change candidates must be available to fit the very many possible uses for these materials.

Methods of Study

These ESM materials have been evaluated by a wide variety of methods, but the most successfully used thus far is differential scanning calorimetry (DSC). This method works well for both neat and adsorbed materials and for both heating and cooling cycles. It has also been successfully demonstrated that the small sample size used in these studies gives totally reproducible results in large scale tests. (9) An actual DSC curve for undecylenic acid is shown in Figure 1.

From these curves one may readily obtain the heat of fusion or freezing and also the range of melting or freezing. Supercooling, if present, is obvious in these studies and the shape (width) of the transition is easily seen. These factors make this technique the method of choice. Differential Thermal Analysis (DTA) has also been used in some of the earlier work with some success. Actual bulk studies have been carried out utilizing structures ranging from passive test boxes to full scale room testing. These investigations have been described in detail in other work (10) In tests conducted at the Florida Solar Energy Center (FSEC) it has been shown conclusively that bulk tests agree very nicely with DSC studies conducted by Babich et al. (11)

The Current Situation

PCM's have now been developed which can be added to building materials e.g. wallboard, and which will contribute significantly to reduction of heating and cooling costs. There are three schools of thought with overlapping classes of compounds which presently represent the main efforts in low temperature thermal storage via energy storage materials. These areas can be subdivided by the approaches followed into the area of fatty acids and specifically blended mixtures thereof pioneered by Shapiro and coworkers, the long chain hydrocarbons developed by Salyer and coworkers and the more broad based search for new materials or the coating of older ones for specific uses by Babich et al.

Section I: Fatty Acids

Low melting fatty acids and blends of fatty acids have been considered as PCM's for several years. They have good properties in many respects. They are low-volatility, high boiling, low melting, organic materials which are readily imbibed by construction materials like gypsum wallboard. Further, many examples like coconut oil are very inexpensive making them very attractive as PCM's. Research by Shapiro and others has

been largely driven by economic considerations as well as properties (12-14). Some of the fatty acids and fatty acid mixtures studied early on are shown along with their thermal characteristics in table 3. Many of these mixtures are commercially available.

These materials are imbibed well into wallboard at very easily reproduced rates and with readily measured masses as shown in Figure 2. Further, they tend to be reasonably chemically stable and remain strongly absorbed indefinitely through many thermal cycles. They have normally been studied in the range of 20-30% absorption by mass. For these materials supercooling is not a problem at the rate of temperature change in normal structures. Actual room size structures using wallboard imbibed with fatty acid have been constructed and function well thermally.

The real drawbacks to the use these materials lay in two main areas. First they are aesthetically unappealing. They have odors which were not very evident in lab scale testing but become very strong in large scale testing precluding their use in many structures. They also discolor the wallboard slightly which can be overcome by painting. They contribute both to flame spread and smoke production in flammability tests as shown in Tables 3, (15,16). It has been stated that fatty acids may exhibit corrosivity in some applications though this has not been conclusively demonstrated, and also that they may promote mold growth.

Section 2: Long Chain Hydrocarbons

Low melting long chain hydrocarbons (sometimes called hydrocarbon waxes) have also been effectively utilized as PCM's absorbed into wallboard(17-19). They, like the fatty acids, also have good properties in several respects. These are also low volatility, high boiling, low melting organic materials which can be imbibed effectively by wallboard. A group of these materials studied and their thermal characteristics are shown in Table 5. Some of these are also available at very low cost. Witco Chemical Company for example can provide a predominantly n-octadecane (K-18) at ~\$0.50/lb/as apposed to 99% pure n-octadecane at ~\$10.00/lb. These hydrocarbons have also been effectively encapsulated and pelletized. (19)

These are used at approximately the same loading, 20-30% by mass, as the fatty acids and mixtures. The thermal characteristics are similar. These materials are chemically quite stable though some breakdown over extended times has been noticed. (20). Supercooling is also no problem in these materials at normal ambient thermal cycling rates.

Drawbacks, however, in these materials are quite similar to some of the fatty acids. The chief problem is once again flammability and smoke production. Again epoxy coatings can be effective reducing flammability in some cases to that of untreated wallboard. These PCM's do not support mold growth.

Section 3: Other Materials and Integrated Approaches.

Babich et. al. have taken the approach of ESM's tailored to specific purposes and/or controlling the disadvantages of materials discussed in sections 1 and 2. (8, 9, 11, 20) Many materials have been studied including inorganic materials and silicone waxes some of which show great promise. Work in the area of new materials is in its infancy and is just beginning to yield good results. Further coupling of PCM's with moisture storage coatings may be of even greater utility. (21) These workers have reexamined several organic PCM's and investigated several new ones as shown in Table 5. Many of these, especially hexadecane, 1-dodecanol and allyl palmitate work exceeding well. (9) Unfortunately, allyl palmitate is too expensive for routine commercial use unless a newer, less expensive source can be found.

Babich et al have also clearly demonstrated and discussed at length the effectiveness of coatings of epoxy paints with aluminum and magnesium hydroxides for control of flammability. (22,23) Rate of flame spread, rate of heat release and onset of smoke production have been greatly retarded. In many cases the treated material is as good as untreated wallboard. ASTM and NBS approved tests have been used and sample results are shown in Table 4 and Figure 3. In this figure the amount of control the coating yields is most obvious. The incremental cost increase for this method is very small as most commercial wallboard will have to be painted anyway. These coatings could be applied as the primer by wallboard manufacturers or in the structure after construction. Additionally this method may be successfully coupled with any of the materials discussed previously. Also a method has been developed with tremendous potential to couple ESM's with moisture storage systems. (21, 24) This approach, if further developed, could lead to new combinations of materials which will accomplish thermal storage with humidity control and be fire retardant as well. New congruent melting, salt hydrates are also currently under investigation both for ESM use and in coatings combining moisture exchange with ESM properties. Other desiccant materials are also being tested for use in coatings.

Summary

Tremendous potential exists in the area of ESM's for energy storage and in the area of moisture storage materials coupled with the ESM's. The efficacy of ESM materials for energy storage has clearly been demonstrated as has the utility of moisture storage agents for humidity control. The effectiveness of coatings in reduction of rate of flame spread, onset of smoke production and rate of heat release is indisputable. DSC is clearly the method of choice for preliminary studies of these systems.

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Material Examples of Use	Transition Temp. °C	Heat of Fusion (J/g)	
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O} - \text{CaBr}_2 \cdot \text{H}_2\text{O} - \text{KBr}$	15-34°C	121	Heat sink in heat pumps
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	27°	192	Passive solar panels Central solar Heat
Glauber's salt	32°	251	Greenhouse heating
$\text{MgCl}_2 \cdot \text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	58°	134	Hot water heating
$\text{Na}_2\text{C}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$	58°	225	Railway heating
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	89°	163	Dishwashing systems
$\text{NH}_4\text{AlSO}_4 \cdot 12\text{H}_2\text{O}$	95°	267	Water heating
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	114°	167	Absorption AC

Table 1. Examples of Available Phase Change Materials - Salt Hydrates

Class	Specific Property
Thermal	Suitable phase transition temperature
	Reasonable phase transition range
	Large latent heat of transition
	High boiling point
Physical	Favorable type of phase transition
	Low vapor pressure
	High reproducibility
	Little change in volume
Chemical	Compatible with construction material
	Long term stability of materials
	Non-toxic
	Non-corrosive
	No additional fire hazard
	Low smoke production in fires
	No sensory irritation
Good aesthetic qualities	
Kinetic	No supercooling
	Sufficient crystallization rate
Economic	Cost
	Availability in marketplace

Table 2. Desirable Properties for Phase Change Materials

Material	mp (°C)	ΔH_m (J/g)	f_p (°C)	$-\Delta H_f$ (J/g)
EM625 Coconut Acid	25.0	107.1	15.8	110.1
EM626 Coconut Acid	25.4	119.1	17.5	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 Methylpalmitate	26.8	104.3	20.0	94.1
EK Capric Acid	31.0	128.0	27.1	125.8
EK Lauric Acid	42.5	126.0	38.1	131.5
EK Methylpalmitate	28.8	163.2	23.3	180.9
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	40.8
3/7	20.5	123.8	26.9	82.8
1/9	37.4	125.7	33.4	118.9
0/1	42.0	132.9	37.9	134.5

Table 3. Thermal Results for Fatty Acids and Fatty Acid Mixtures

EM = Emery Chemical Co., EK = Eastman Kodak Chemical Co.,
SG = Sigma Chemical Co.

Samples	# of Sample	D90	D240	D475	Dc	Corrected Dm	Dm/Wt G	Weight G	Sample Weight
α -Cellulose	5	5.4	92	158.6	8.9	195	71.5	1.95	2.7
Wallboard	3	1.4	19.5	35.3	0.8	35.4	0.8	6.3	49.2
FR Wallboard	3	0.8	16.2	38.2	0.2	37.8	0.7	6.1	53.7
S1	3	25.9	241.3	505.3	0.6	505.3	8.1	15.1	63.3
S1 Epoxy	3	2.3	101.6	390.5	4.5	477.8	3.0	12.6	70.4
S1 Al(OH) ₃	3	0.7	36.0	60.5	5.7	497.6	7.3	10.5	68.20
S1 Mg(OH) ₂	3	0.4	15.1	38.0	4.4	505	7.2	22.9	70.2

S2	3	27.7	237.8	496.8	31.5	479.7	7.8	13.2	59.7
S2F	3	25.9	219.5	466.2	31.3	463.7	7.5	10	62
S2 Epoxy	3	5.4	26.7	325	32	486.3	8.1	9.8	38.6
S2F Epoxy	3	3.3	24.9	376.8	29	480.7	7.2	10.9	55.4
S2 Al(OH) ₃	3	2.1	17.4	261	55	473.9	8	11.0	59.2
S2 Mg(OH) ₂	3	2.7	23.5	392	75.5	458.6	8	11.8	57.7
S2F Al(OH) ₃	3	3.3	11.5	252.5	31	463.2	7.1	10.9	65.3
S2F Mg(OH) ₂	3	0.9	10.7	248.4	27	390	6.1	12.2	64.3

S3	3	22.4	180.5	435	9.5	494	8.7	10.8	56.9
S3 Epoxy	3	25.8	160	489.5	5.8	496.9	8.1	9.3	61.3
S3 Al(OH) ₃	3	7.4	128.5	418.3	6.9	501.7	8	10.2	62.3
S3 Mg(OH) ₂	3	0.9	113.2	329.7	8.9	467.9	7.9	11.4	63.4

S4	3	10.4	104.6	499	13.3	487.6	8.6	12.1	56.9
S4 Epoxy	3	12.3	59.5	205.7	5	498.3	9.2	12.6	54.2
S4 Al(OH) ₃	3	15.5	59.2	201.5	4.2	494.7	9.3	11.7	53.6
S4 Mg(OH) ₂	3	0.6	13.1	121.1	2.5	427	7.6	10	56.6

S1=Hexadecane
S2=1-Dodecanol
S3=Undecylenic acid
S4=Coc-nut oil

Table 4. Results from Flame Spread Test.

Material	mp °C	ΔH_m (J/g)	f_p °C	ΔH_f (J/g)
n-Hexadecane b	20.0	216	10.4	220
n-Octadecane a	28.4	200	17.9	200
1-Dodecanol b	23.8	184	17.5	190
n-Heptadecane b	22.6	164	19.0	165
Allylpalmitate d	22.6	173	16.2	125
Undecylenic Acid e	24.8	141	18.1	143
1-Nonadecane b	23.2	131	20.1	134
1-Iodoheptadecane b	22.2	131	8.6	132
n-Octadecylacrylate c	25.7	115	22.1	99
Diphenyl ether b	27.2	97	-8.2	81
Diphenylmethane b	24.4	86	-3.3	75
Chlorobenzothiazole b	18.8	65		
3-Iodoaniline b	22.5	64		
Polytetrahydrofuran b	17.5	59	0.1	76.4
Trimethylcyclohexene b	24.1	47		
Phorone	25.8	124	11.2	3.7

Table 5. Thermal Results for New Enthalpy Storage Materials

*Average of three measurements. Average standard deviation for mp and f_p = 0.3°. Average standard deviation for H = 4 J/g. (a) Mainstream Engineering Co., (b) Aldrich Chemical Co., (c) Scientific Polymer Products, Inc., (d) Dajac Laboratories, Inc. (e) Sigma Chemical Co.

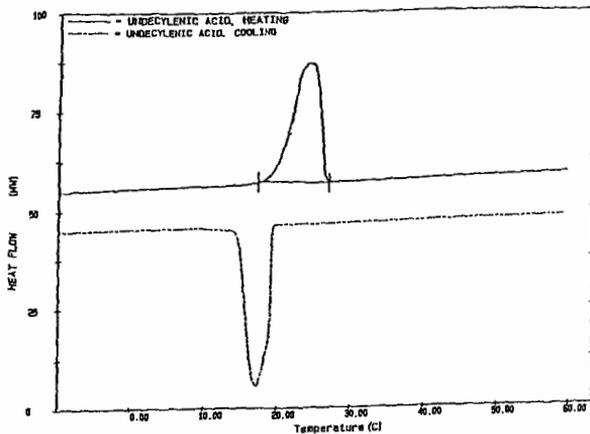


Figure 1. Sample DSC Curve for Undecylenic Acid (Heating and Cooling Curves)

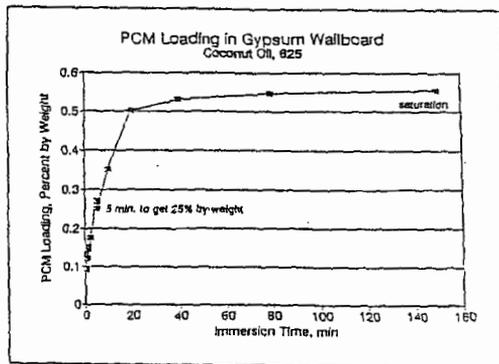


Figure 2. Sample ESM Loading in Gypsum Wallboard

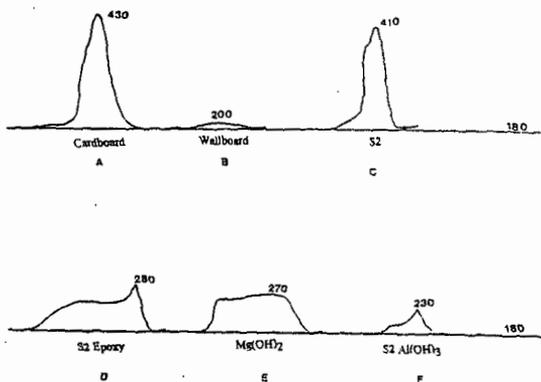


Figure 3. Comparison of maximum temperature in stack NBS Radiant Panel Tests for cardboard (A), wallboard (B) wallboard treated with 1-dodecanol S2 (C), epoxy coated S2 (D), $Mg(OH)_2$ /epoxy coated S2 (E), and $Al(OH)_3$ /epoxy coated S2 (F).