Experimental Study on Phase Change Materials and Plastics Compatibility

A. Lázaro, B. Zalba, and M. Bobi
GITSE (Grupo de investigación en Ingeniería Térmica y Sistemas Energéticos), Área de Máquinas y Motores Térmicos, Departamento de Ingeniería Mecánica, Universidad de Zaragoza, Campus Río Ebro, 50018-Zaragoza, Spain

C. Castellón and L. F. Cabeza
GREA (Grupo de Investigación en Energía Aplicada), Área de Máquinas y Motores Térmicos, Departamento d'Informàtica i Eng. Industrial, Universitat de Lleida, Jaume II 69, 25001-Lleida, Spain

DOI 10.1002/aic.10643
Published online September 15, 2005 in Wiley InterScience (www.interscience.wiley.com).

Energy storage is a useful tool to increase energy efficiency and energy savings. Solid-Liquid phase change materials (PCMs) are used in latent heat thermal energy storage systems. Plastics are currently used as encapsulate materials with PCM, but previously a compatibility test should be made to ensure long term stability. It is not possible to find experimental studies of organic PCM migration in plastics in the literature. The main objective of this work is an experimental study of the compatibility of some PCMs typically used for thermal energy storage with a melting temperature around 22°C and some plastic materials currently used as encapsulate materials. The PCMs tested are molecular alloy C16-C18, RT20, RT25, RT26, and TH24, and plastic materials tested are PP, LDPE, HDPE, and PET. As a consequence of the results, the best plastic to be used with each PCM and combinations that should be avoided are chosen. © 2005 American Institute of Chemical Engineers *AIChE J,* 52: 804–808, 2006
Keywords: phase change material, plastic, compatibility, migration

Introduction

Energy storage is a useful tool to increase energy efficiency and energy savings. There are three ways to store energy: chemical energy (reversible reactions), sensible heat, or latent heat.

Latent heat thermal energy storage is the most used technology because the energy stored density is higher if a proper temperature range of phase change is chosen. Liquid-Solid phase change also provides this energy stored with lower volume change compared to any other phase change. Therefore, the design of liquid-solid phase change material heat exchangers is easier.

There are two kinds of liquid-solid phase change materials (PCMs), organics and inorganics. This difference is made because of the different chemical and physical behavior. Paraffins are the most used organic PCMs, and hydrated salts are the most used inorganic PCMs. There are many applications in use or being developed of latent heat thermal energy storage with phase change materials,[1-3] such as free-cooling systems or microencapsulated PCMs embedded in construction elements.

Liquid-Solid phase change materials must be encapsulated. This can be done with microencapsulation or macroencapsulation. When macroencapsulation is desired, the most common encapsulate materials are plastics or metals.[3]

In a latent heat thermal energy system design with phase change materials, as important as heat transfer aspects and correct dimensioning, is to take into account materials aspects, such as thermal properties (PCM enthalpy-temperature curves[4]) and compatibility behavior.

Attending to its nature, it is possible to predict compatibility problems of inorganic PCMs with metals, developed as corro-

Correspondence concerning this article should be addressed to B. Zalba at bzalba@unizar.es.

Table 1. Properties of the Tested Plastics[10]

	PET	PP	PEHD	PELD
%water absorption (24 hours) ASTM D570	0.1	0.01-0.03	<0.01	<0.01
Density (g/cm^3) DIN 5479	1.37	0.90-0.907	0.94-0.96	0.914-0.928
Radiation strength	Good	acceptable	acceptable	acceptable
Specific heat (kJ/kgK)	1.05	2.0	2.1-2.7	2.1-2.5
Coefficient of linear expansion ($K^{-1} \cdot 10^6$)	70	150	200	250
Thermal conductivity (W/m · k)	0.24	0.17-0.22	0.38-0.51	0.32-0.40
Service temp. max/continuous (°C)	100	100	70-80	60-75
Service temp. min/continuous (°C)	−20	0/−30	−50	−50
Resistance to solutions of inorganic salts	resistant	resistant	resistant	resistant
Permeability to CO_2	1	31	—	—
Permeability to O_2	1	23	—	—
Permeability of water	1	0.2	—	—

sion, and organic PCMs migration in plastics. Some studies have been developed on metals corrosion with inorganic PCMs.[5-8] But it is not possible to find experimental studies of organic PCM migration in plastics in the literature. Some behavior predictions can be found in Lane.[9] General tables describing compatibility of plastics with other materials where paraffins are included could be found, but they are not quantitative and not specific.

In thermal energy storage systems, costs are a very important factor of viability. Therefore, even though paraffin interactions with plastics are known by industry, plastics are proposed as encapsulate materials with PCMs for many applications, for example, free-cooling.[2]

The main objective of this work is an experimental study of the compatibility of some PCMs typically used for thermal energy storage with a melting temperature around 22°C, and some plastic materials currently used as encapsulate materials. For our research and the development of PCM application, it was also important to obtain information about the PCMs' behavior in plastic encapsulates. The plastics used in this paper are elementary composition, but after these tests some plastic additives could be studied to improve the compatibility behavior.

Experimental

Standards

No international standards on PCM migration in plastics tests were found. Therefore, the standard ISO 175:1999 Plastics, Methods of Test Determination of the Effects of Immersion in Liquid Chemicals, was chosen to perform experiments because its objective is very similar to the one of this work.

Table 2. Properties of the Tested PCMs

Substance	Melting Point (°C)	Manufacturer
Molecular alloy 34%C_{16}–66%C_{18}	19.5-22.2	Own manufactured
RT20 alkanes	20	Rubitherm
RT26 alkanes	26	Rubitherm
RT25 alkanes	25	Rubitherm
TH24 salt hydrated	24	TEAP

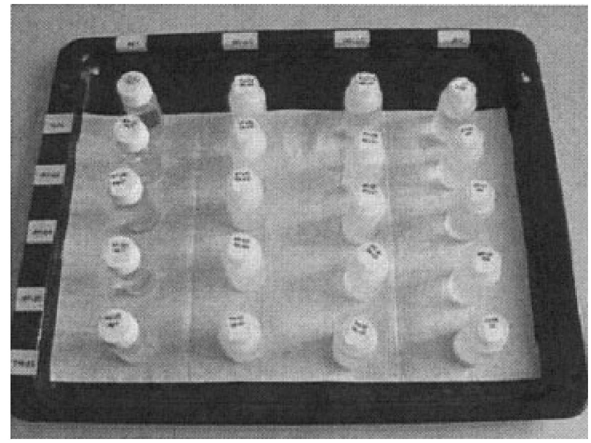

Figure 1. The bottles containing PCMs used in the tests.

Materials

Plastics typically used in the industry were chosen: high density polyethylene (HDPE), low density polyethylene (LDPE), polyethylene terephthalate (PET), and polypropylene (PP). Their properties are detailed in Table 1.

In the experiments, plastic bottles were used to contain the tested PCMs. The thickness of the bottles was 0.3 mm when HDPE, LDPE, and PP were used, and 0.1 mm when PET was used.

In this work, five common PCMs, four organics and one salt hydrate, with similar melting points were tested. The organic PCMs were: a molecular alloy of C_{16}-C_{18} developed by the authors,[2,10] RT20, RT26, and RT25. The inorganic PCM was TH24. Their properties are shown in Table 2.

Methodology

As far as possible, the standard ISO 175:1999 was used to perform the experiments.

The PCM was melted and stirred in order to have a homogeneous sample. Then, a 30 mL volume sample was introduced into each different plastic bottle. A furnace was used to cycle the bottles thermally so that melting and solidification processes could take place. Figure 1 shows the bottles containing PCMs used in the tests. The experiment consists of repeated melting and solidification cycles during the length of the test.

The liquid phase will be the most unfavorable state because

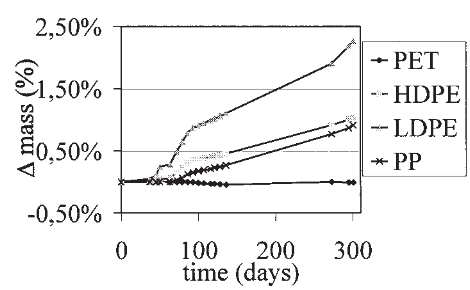

Figure 2. Δ Mass (%) evolution of molecular alloy.

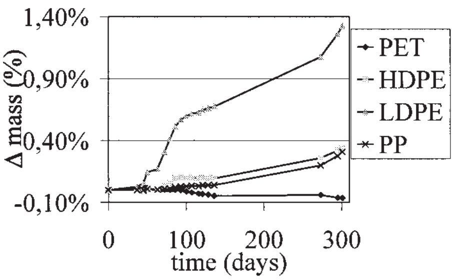

Figure 3. Δ Mass (%) evolution of RT26.

in this state the migration processes are favored. This was why repeated melting and solidification cycles were performed. The furnace was switched on with low power during the melting process until the temperature rose to 35°C. This temperature was kept during about 1 hour. For the solidification process, it was enough to switch off the furnace and open the door to let the bottles reach room temperature.

The bottles were visually inspected periodically in order to see plastic deformations or other physical state change phenomena.

A gravimetric analysis of the bottles containing PCM prior to and following the compatibility test provides mass variation. A Mettler-Toledo 0.01 mg (<31 g) /0.1 mg (>31 g) precision balance was used in this gravimetric analysis. Mass loss is calculated with:

$$\Delta m = m(t_0) - m(t)$$

$$\Delta m(\%) = \frac{m(t_0) - m(t)}{m(t_0)}$$

where $m(t_0)$ is total mass (bottle and PCM) prior to the compatibility test, and m(t) total mass at the moment the test is made.

The measurements were made when the bottles were at room temperature in order to diminish deviation due to variations of temperature. Once the bottles were at room temperature, an adsorbent paper was used to remove the PCM outside the bottles and the dust particles deposited in the walls. Then the total mass of each bottle with each PCM was measured with the precision balance.

Results

Test duration was about ten months, giving at least 150 thermal cycles. The results are presented in Figures 2 to 7.

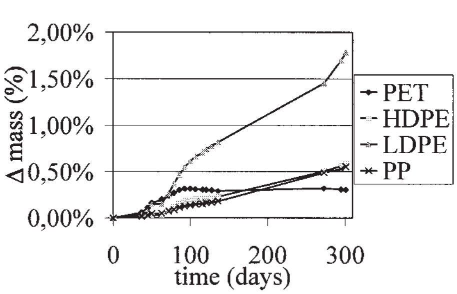

Figure 4. Δ Mass (%) evolution of RT25.

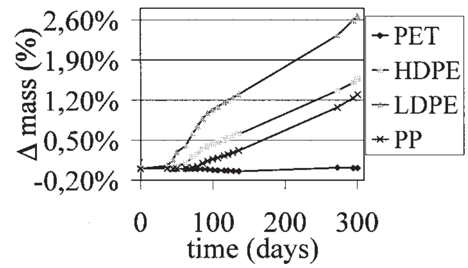

Figure 5. Δ Mass (%) evolution of RT20.

At the beginning of the test, the measurements were made almost weekly. Later, a long period of time without measuring was left. The measurements made after this period showed that the mass variations continued with the tendency shown at the beginning.

Taking into account uncertainty propagation for gravimetric measurements and expressing mass variations as mass rate, the different plastics behavior for each PCM could be compared (Table 3).

Discussion

Attending to mass measurements, a lower mass variation means a better encapsulate material. Therefore, a suitable plastic encapsulate material for each PCM could be chosen. These results are shown in Table 4.

It should be highlighted that PET wall thickness was one-third of the rest of the plastics.

With organic PCMs, LDPE bottles show big deformations. As shown in Figure 8, these deformations could be appreciated after a few days.

The tests demonstrate, as expected, that LDPE is not a suitable encapsulate material for any PCM. Also, the best

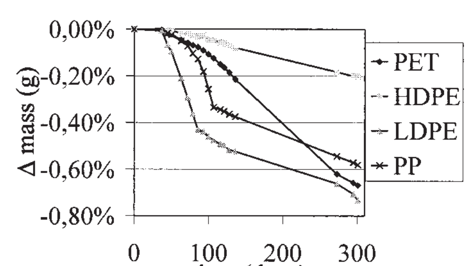

Figure 6. Δ mass (%) evolution of TH24.

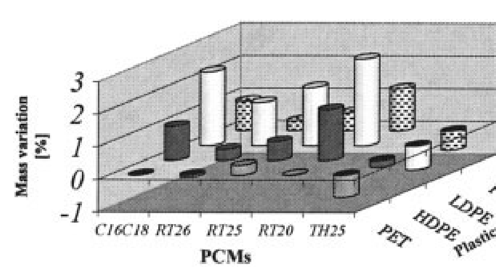

Figure 7. Mass variation (%) of all PCMs tested after ten months.

Table 3. Results of Mass Variation After the Duration of Experiments

	LDPE	HDPE	PET	PP
Molecular alloy	2.2593% ± 0.0003%	1.04569% ± 0.00005%	−0.00926% ± −0.00005%	0.91137% ± 0.00005%
RT26	1.32191% ± 0.00005%	0.33552% ± 0.00005%	−0.0641% ± −0.0005%	0.30952% ± 0.00005%
RT25	1.78076% ± 0.00005%	0.58008% ± 0.00005%	0.3069% ± 0.0004%	0.55466% ± 0.00005%
RT20	2.6688% ± 0.0003%	1.56741% ± 0.00005%	0.01327% ± 0.00005%	1.29649% ± 0.00005%
TH24	−0.7320% ± −0.0003%	−0.2034% ± −0.0003%	−0.6690% ± −0.0003%	−0.5808% ± −0.0003%

encapsulate material should be chosen for each PCM separately.

The mass increase found in some samples was surprising because when the tests were designed, only migration effects were expected. Moisture sorption is proposed as an explanation for this mass increase. The high water permeability of PET compared to the other plastic materials tested (Table 1) and the fact that the inorganic PCM mass increased with all materials corroborate this proposal. The water sorption of PCM and migration in plastics are described by Lane.[9] For inorganic PCMs it is even more predictable because they are hydrated salts. There is no migration of inorganic PCMs in plastics. The inorganic PCM tested only shows increase of mass. This fact agrees with the prediction if only water sorption is considered. In any case, for applications of PCM, water sorption is not the most important problem, whereas migration of PCM in plastic causes efficiency losses and security problems. The decrease of mass proves the PCM migration in plastics.

Mass variations, due to migration effects and water sorption, in ten months are non-negligible and demonstrate that plastic and PCM interaction exists. PET bottles containing organic PCMs had lower mass variations; but analyzing mass evolution, it could be seen that the initial mass losses are greater than the following, so it is likely that the water sorption compensates the PCM migration (Figures 2 to 6). A thermal energy system lifetime could be about 20 years,[9] so during this time the maintenance of properties cannot be guaranteed if these pairs were used.

The demonstrated interaction between plastics and PCMs is important because of:

Table 4. Suitable and Not Suitable Pairs of PCM and Plastic Material

	Best Plastic Encapsulate Material	Not Recommended Plastic Encapsulate Material
Molecular alloy	PET	LDPE
RT26	PET	LDPE
RT25	PET	LDPE
RT20	PET	LDPE
TH24	HDPE	LDPE

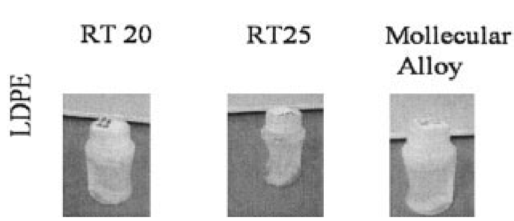

Figure 8. Deformations in LDPE bottles.

- Health security: it depends on applications, but paraffins in air or water could injure people.
- Performance security: PCM could alter plastics, losing their resistance properties.
- System efficiency: PCM losses decrease energy storage density.

Conclusions

A compatibility test between four organic PCM (molecular alloy C16-C18, RT20, RT26, RT25) and one inorganic PCM (TH24) and four plastics (LDPE, HDPE, PET, and PP) has been made. Visual inspection and gravimetric analysis were made during ten months, the duration of the experiments. Two effects have been detected, organic PCM migration in plastics and moisture sorption.

LDPE bottles had the highest mass variation and big deformations. Therefore, LDPE was discarded as encapsulate material.

Attending to the results of the tests, when a molecular alloy is used as PCM in plastic encapsulate as thermal energy storage, or in any other application used as molten paraffin, the best encapsulate material is PET.

When RT20, RT25, and RT26 are used, the recommended plastic encapsulate material is also PET. If moisture sorption is taken into account, PP could also be recommended.

When TH24 is used as molten salt and water sorption is not desired, PEHD should be chosen. PP, PET, and PELD showed big mass increase. Therefore, they are not recommended as encapsulate material when moisture sorption can entail problems.

The plastics used in this article are elementary composition PP, PET, HDPE, and LDPE, but after these tests some plastic additives could be studied to improve the compatibility behavior.

Acknowledgments

This work was partially sponsored by the Spanish project DPI2002–04082-C02–02 (Plan Nacional de Investigación Científica, Desarrollo e Innovación Tecnológica 2000–2003). The authors would like to acknowledge Rubitherm and TEAP for providing the PCM samples.

Literature Cited

1. Dincer I, Rosen MA. *Thermal Energy Storage. Systems and Applications*. New York: Wiley; 2002.
2. Zalba B, Marín JM, Cabeza LF, Mehling H. Free-cooling of buildings with phase change materials. *International Journal of Refrigeration.* 2004;27:839-849.
3. Zalba B, Marín JM, Cabeza LF, Mehling H. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Applied Thermal Engineering.* 2003;23:251-283.
4. Marín JM, Zalba B, Cabeza LF, Mehling H. Determination of en-

thalpy-temperature curves of phase change materials with the T-history method—improvement to temperature dependent properties. *Measurement Science & Technology.* 2003;14(2):184-189.
5. Cabeza LF, Illa J, Badía F, Mehling H, Hiebler S, Ziegler F. Immersion tests on metal-salt hydrate pairs used for latent heat storage in the 32 to 36°C temperature range. *Materials and Corrosion.* 2001;52:140-146.
6. Cabeza LF, Illa J, Badía F, Mehling H, Hiebler S, Ziegler F. Middle term immersion tests on metal-salt hydrate pairs used for latent heat storage in the 32 to 36°C temperature range. *Materials and Corrosion.* 2001;52:748-754.
7. Cabeza LF, Roca J, Nogués M, Mehling H, Hiebler S. Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 48 to 58°C temperature range. *Materials and Corrosion.* 2002; 53:902-907.
8. Cabeza LF, Roca J, Nogués M, Mehling H, Hiebler S. Long term immersion corrosion tests on metal-PCM pairs used for latent heat storage in the 24 to 29°C temperature range. *Materials and Corrosion.* 2005;56(1):33-38.
9. Lane GA. *Solar Heat Storage: Latent Heat Material. Volume II: Technology*. Boca Raton, FL: CRC Press; 1986.
10. Cuevas-Diarte MA, Calvet-Pallas T, Tamarit JL, Oonk HAJ, Mondieig D, Haget Y. *Nuevos Materiales Termoajustables*. Mundo Científico; 2000. (In Spanish.)

Manuscript received Dec. 29, 2004, and revision received Jun. 22, 2005.