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From concept to application. A new phase change material for thermal protection at -11 °C

Abstract Molecular Alloys as Phase Change Materials (MAPCM) offer opportunities in the fields of energy storage and thermal protection, where the classic Phase Change Materials (PCM) don't exist or they are difficult to find. The MAPCM's are thermo-adjustable materials by means of their composition. The present paper is on the design of a MAPCM to be used for thermal protection at –11 °C. We show how fundamental studies are helpful to choose the right composition that is able to work at the temperature required for an application. Several molecular alloys among n-alkanes were elaborated and characterized. Finally, a multicomponent molecular alloy is proposed and tested in a double wall prototype, for thermal protection of ice cream or other kinds of product around –11 °C. As result, we propose a prototype that it is effective for more than 4 hours and 30 minutes in an external environmental temperature of 20 °C.

Keywords Phase change materials (PCM) · Molecular alloys phase change materials (MAPCM) · n-alkane · Thermal protection · Ice cream

Introduction

In various branches of materials research, mixed crystals play an increasingly important part because they offer the opportunity to optimise properties by means of changes in composition. The mixed crystals, studied by our research groups, as a rule, are from molecular components, and we speak of molecular mixed crystals or molecular alloys. Our interest is in the preparation of mixed crystals, their crystallographic and thermodynamic properties and stability, phase change behaviour, and their use in practical applications [1, 2, 3]. To that end, and rather than studying isolated systems, our research invariably is focused on families of systems, the components of which are members of a chemically coherent group of substances [3, 4]. Generally, the family approach leads to empirical relationships which, apart from their scientific interest, can be used for making predictions to direct experimentation and to reduce experimental efforts, and in particular as a tool in optimising desired properties.

Molecular substances, which combine a relatively high heat of melting with a melting temperature in a range around the ambient temperature, are excellent materials for thermal protection and for storage of thermal energy. Of special interest is the fact that, by making alloys of molecular materials, the range of melting can be adjusted to no matter what temperature. In this respect, Molecular Alloy Phase Change Materials (MAPCM) are superior to the classic Phase Change Materials (PCM). The possible inconvenience that alloys do not melt isothermally, can be overcome: in most of the cases the components of the alloy can be selected such that its thermal window is just one or two degrees. Generally, one can distinguish between two fields of application of MAPCM: the first is thermal protection, and the second storage of thermal energy. In the first case one can think of thermal protection of food [6, 7], of biomedical or pharmaceutical products [8], of electronic or telecommunication devices [9], and so on. In the second case, thermal energy storage applied to, e.g. the heating of buildings [10].

Among the molecular materials, the family of the n-alkanes has a special place, in particular as regards the design of dedicated PCM's. The n-alkanes are ecologi-

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cally harmless and non-toxic, chemically stable and non-corrosive. The n-alkanes have high heats of melting, and, in a number of cases the heat effect of solid-solid transitions can be implied in the performance of the PCM. The n-alkanes, with their great variety of chain lengths, cover a range of applications from –50 to 100 °C. From a theoretical point of view, the n-alkanes have the enormous advantage that all kinds of properties can be correlated in terms of chain length, in terms of number of carbon atoms of the molecules. This aspect is of particular importance, not only for the purpose of optimising temperature and thermal window, but also as a possibility to follow the developments of the oil market, in calculating the cheapest solutions. To date, between the numerous possible combinations, more than 35, binary and ternary, systems have been investigated [11, 12, 13, 14, 15].

This paper is on the design of an n-alkane based MAPCM with a melting temperature at –11 °C and to be used for thermal protection in a domestic setting. A typical application is keeping ice cream at the temperature of below –8 °C, once it has been taken out from a domestic freezer at –18 °C. The idea is that the thermal window with its large latent heat will prevent the ice cream from becoming unfit for consumption as a result of heating by the ambient air. The main steps that have been taken, and reported in this paper, are, first, the search for the "active" material, and, second, the design and testing of a double-wall packaging prototype.

Relation to previous work

Phase change materials (PCMs) can be used for latent heat energy storage and thermal protection [16, 17]. For example, ice has long been used for cold storage. Nowadays chemical companies offer commercial PCMs, and the literature contains references to use of PCMs for heating and cooling buildings [18, 19, 20, 21].

However, PCMs can be used only for very specific applications. There are no PCMs available for many temperature ranges. For a given application, we need to use a PCM in the correct temperature range (application temperature = phase transition temperature) and with the greatest storage capacity.

Here we present the use of Molecular Alloys as Phase Change Materials (MAPCMs), which are thermo-adjustable depending on composition. This new class of materials provides solutions at numerous temperature ranges where classical PCMs are not available. Furthermore, their composition can be modified to provide the material which removes and stores heat at the required temperature. The isomorphism relationship and polymorphism behaviour of the pure components, and analysis of the phase diagram permit us to choose binary and ternary alloys as potential candidates.

Most commercial PCMs are salt hydrates, but organic or fused salts are also used. As a rule, the available salt hydrate PCMs display a variety of phase equilibrium relations, from a material like $Mg(NO_3)_2 \cdot 6H_2O$, which shows completely congruent melting, to $Na_2SO_4 \cdot 10H_2O$, which is not only incongruent, but also shows an inverse temperature-solubility relationship.

In this study MAPCMs are made from n-alkanes. They are non-toxic and chemically stable, and their melting behaviour is congruent. The diversity of n-alkanes MAPCM applications is demonstrated by two patents [1, 2] and a trademark [22]. Within this family, MAPCMs can be developed for applications ranging from –50 to 100 °C.

The authors of this paper are members of the REALM group (*Réseau Européen sur les Alliages Moléculaires*). The REALM group works on mixed molecular crystalline materials pursuing fundamental scientific knowledge and the application of molecular alloys. This European network is member of the "*Xarxa Temàtica dels Alliatges Moleculars*" as well as other European groups and industries from Barcelona (UB, UPC, CSIC, Ducasa), Bordeaux (CNRS, Biotrans), Paris (U. Paris V, U, Paris-Sud), Lannion (France –Telecom), U.Utrecht, U. Ruhr (Bochum), Madrid (Repsol-YPF), Bizkaia (Gaiker, Walter-Pack, Gastronomia Basca) and U. Zaragoza.

The REALM group has studied and developed different kinds of applications using MAPCMs:

1. A radiating floor with energy storage in molecular alloys at night and release during the day (application temperature close to 22 °C); 2. An "active" packaging for protection of cold drinks (application temperature of 8 °C); 3. A device for the dissipation of the heat produced by electronic components (application temperature of 70 °C); 4. Packing for the thermal protection of macromolecules monocrystals and others (application temperature of 6 °C); 5. Packing for blood and other biomedical substances during transport (application temperatures of –18 °C, 6 °C and 22 °C).

The work we present here is innovative in two ways: First, it provides a solution, at –11 °C, at which temperature no other PCM is viable. Second, it is the first time, to our knowledge, that has developed an application that can deal with a difference of 40 °C between the protected material and the external environment.

Search of the "active" material

Generally, the thermodynamic properties of multicomponent systems can be predicted from the properties of the pure components and those of binary subsystems. Therefore, the search for the desired multicomponent alloy invariably starts at the level of pure components and binary systems. The pure components account for the main heat effects and transition temperatures; the binary systems with their phase diagrams are the keys to the thermal windows, and also to the thermodynamic mixing properties. And, last but no least, at every step of the investigation crystallography is needed for the correct characterization of the solid phases.

Table 1 Thermo-energetic and crystallographic properties for the five pure n-alkanes. Tp is a triclinic ordered phase, and R_I is an orthorombic disordered phase

Substance	M (g·mol⁻¹)	δ^{liq} (g/l)	$C_p^{\ liq}$ (298.2 K) (J/g·°C)	T_{fus} (°C)	ΔH_{fus} (J/g)	T_{eb} (°C)	Melting phase	Purity %	Reference
C_{10}	142.28	0.730	2.2	−30.1	194	174.1	T_p	98.86	[23]
C_{11}	156.31	0.740	2.2	−25.5	144	196.0	R_I	99.69	[23]
C_{12}	170.34	0.749	2.2	−10.0	210	216.3	T_p	99.10	[23]
C_{13}	184.36	0.756	2.2	−5.4	157	234.0	R_I	99.80	[23]
C_{14}	198.39	0.763	2.2	5.2	215	253.7	T_p	99.79	[23]

Fig. 1 C_{11}–C_{12}, C_{12}–C_{13}, C_{13}–C_{14} binary phase diagrams[23]; Δn=1. The areas in shading correspond to the zones of the phase diagrams where we have centred the search of the MAPCM
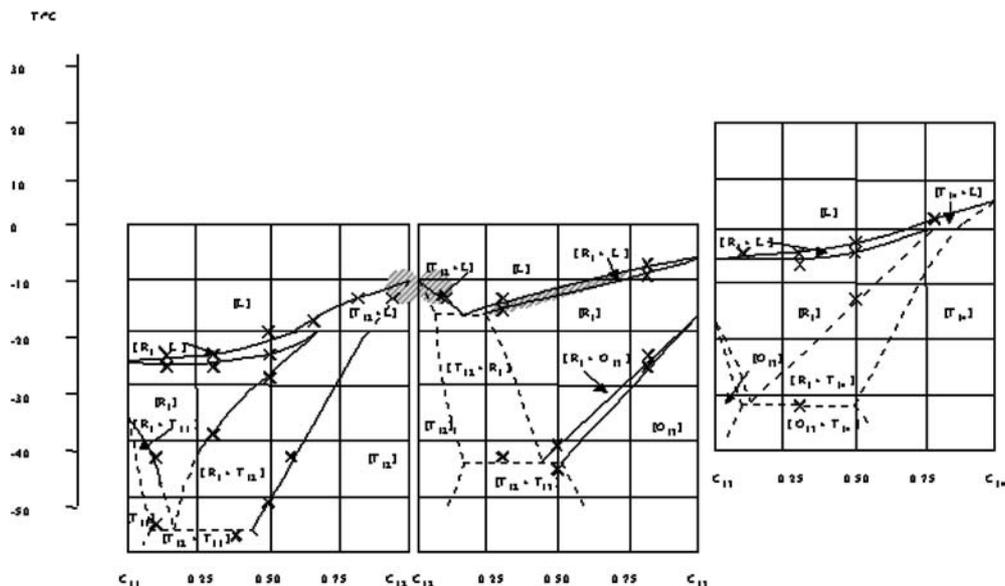
The n-alkane whose melting point is closest to –10 °C is dodecane, $C_{12}H_{24}$, in the following abreviated to C_{12}. Its properties, related to this investigation, are summarized in Table 1, along with the properties of its neighbours, i.e, C_{10}, C_{11}, C_{13} and C_{14}. The polymorphic relationships of the five alkanes are well established [23]. The even alkanes melt from a triclinic, ordered form (Tp), whereas the odd alkanes melt from the rotationally disordered form R_I.

Owing to the polymorphic nature of the alkanes, which, moreover, are different for odd and even alkanes, the temperature vs. composition phase diagram of a binary combination can have a rather complex character. As regards the formation of mixed crystals, it is well know that i) mixed crystals are more readily formed in the disordered rotator form than in the ordered crystalline forms, and that ii) the degree of miscibility in any solid form is higher, the lower the relative difference in chain length, Δn/n, where Δn is the difference in chain length and n the chain length of the smallest chain (for the C_{11} + C_{13}, Δn/n = 2/11). The two aspects, i) and ii), find expression in the phase diagrams shown in Fig. 1 and Fig. 2, for Δn = 1, and Δn = 2, respectively.

Unlike the pure components, the alloys melt over a range of temperature ($T_{liquidus}$ – $T_{solidus}$). For the purpose of practical applications, it is useful to define the effec-

tive thermal window by δ = $T_{liquidus}$ – $T_{95\%}$; it corresponds to temperature interval in which the alloy stores or releases 95% of the total heat effect. For most of the practical applications, the (effective) thermal window should be as small as possible; from Figs. 1 and 2 it follows that many alloys have a window of just one or two degrees.

With regards to the selected temperature of application of –11 °C, it can be observed that there are several alloys that meet this requirement. Candidate alloys are either rich in C_{12}, or have to be found around the equimolar composition in the system C_{12}–C_{13}. In the latter of these cases, it is the rotator form that melts; it implies that the heat effect is smaller than in the case of the alloys rich in C_{12}. The characteristics of six candidate alloys are displayed in Table 2.

Out of the binary systems between nearest neighbours (Δn=1) and next nearest neighbours (Δn=2), two ternary systems can be formed whose components are either nearest or next nearest neighbours (avoiding greater differences in chain length that do not favour alloy formation). These two ternary systems are C_{11}–C_{12}–C_{13} and C_{12}–C_{13}–C_{14}. For theses systems, and concentrating on the rotator R_I to liquid transition, we followed the approach of using pure component and binary thermodynamic mixing data to calculate, to predict the thernary

Fig. 2 C_{10}–C_{12} [23], C_{12}–C_{14} [23], C_{11}–C_{13} [24] binary phase diagrams; $\Delta n=2$. The areas in shading correspond to the zones of the phase diagrams where we have centred the search of the MAPCM
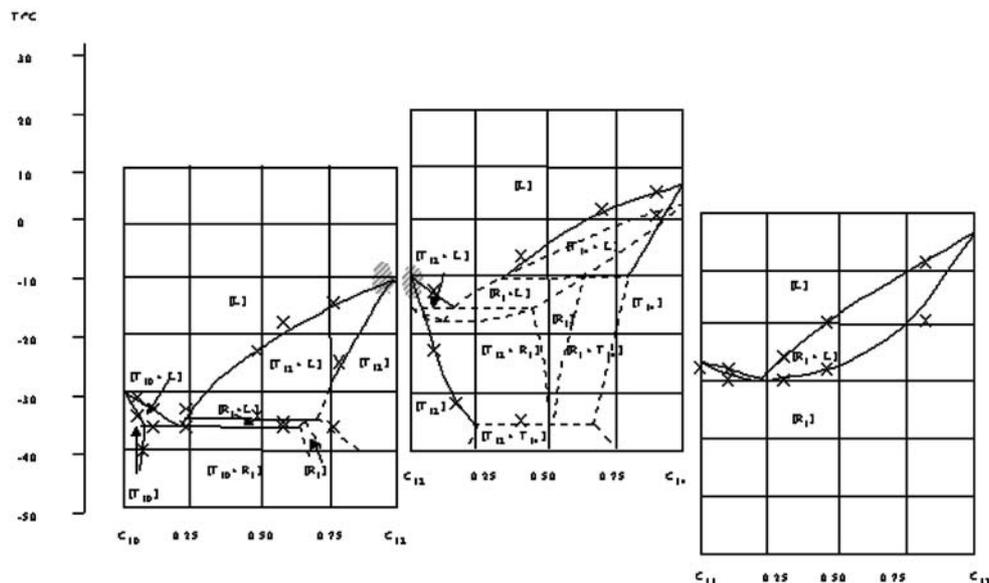

Table 2 Thermo-energetic, crystallographic and economic properties, for some compositions as potential MAPCM

MAPCM	$T_{liquidus}$	$\delta_{95\%}$ (°C)	ΔH_{melt} (J/g)	T_C (°C)	Melting phase	Reference
$0.03C_{10}$–$0.97C_{12}$	–10.8	1.0	190.0	–16.6	T_p	This work
$0.05C_{10}$–$0.95C_{12}$	–11.9	2.1	173.0	–14.4	T_p	This work
$0.98C_{12}$–$0.02C_{14}$	–11.2	1.2	186.3	–15.5	T_p	This work
$0.96C_{12}$–$0.04C_{14}$	–11.2	1.1	184.0	–14.4	T_p	This work
$0.70C_{12}$–$0.30C_{13}$	–14.03	1.8	146.1	–	R_I	[23]
$0.50C_{12}$–$0.50C_{13}$	–11.93	1.5	146.0	–	R_I	[23]
$0.51C_{12}$–$0.40C_{13}$–$0.09C_{14}$	–11.8	1.6	144.1	–12.3	R_I	This work
$0.43C_{12}$–$0.41C_{13}$–$0.16C_{14}$	–11.4	2.3	146.7	–12.0	R_I	This work
$0.03C_{11}$–$0.85C_{12}$–$0.12C_{13}$	–16.1	1.2	141.3	–16.9	R_I	This work
$0.05C_{11}$–$0.63C_{12}$–$0.32C_{13}$	–15.5	1.9	138.2	–16.2	RI	This work
$0.03C_{11}$–$0.55C_{12}$–$0.42C_{13}$	–14.4	2.3	139.2	–15.1	R_I	This work
$0.07C_{11}$–$0.72C_{12}$–$0.21C_{13}$	–17.9	2.6	136.6	–18.8	R_I	This work

equilibrium states. The methodology has been outlined in recent papers on C_{15}–C_{16}–C_{17} [25], and the four systems [26] C_{14}–C_{15}–C_{16}, C_{16}–C_{17}–C_{18}, C_{18}–C_{19}–C_{20} and C_{19}–C_{20}–C_{21}. As regards the pure component data, it may be observed that in the case of C_{12} and C_{14} the transition data are for the vitual transition from rotator to liquid. The results of the computations are shown in Figs. 3 and 4, in the form of isothermal cross-sections of the liquidus surfaces, and together with the thermal windows calculated for a number of compositions. The computational results were verified by DSC experiments. The properties of the selected ternary mixtures are included in Table 2. Obviously, the scientific results displayed in Table 2 have been obtained using pure n-alkanes. Owing to the fact, however, that pure n-alkanes are very expensive, all of the mixtures enumerated in the table are unsuitable for large-scale applications. For economical reasons, as a result, one is dependent on commercially available oil fractions, i.e. on multicomponent mixtures. It implies that Table 2 has the function of being the starting point for a search of the candidate material for the application.

The commercially available material that was selected is a multicomponent mixture containing 97 wt% of C_{12}, 0.04 wt% C_8, 0.6 wt% C_{10}, 0.02 wt% C_{11}, 0.8 wt% C_{13} and 1.54 wt% of a variety of benzene derivatives. X-ray powder diffraction and DSC experiments have shown that its crystallizing and melting behaviour is similar to that of the first mixture in Table 2, i.e. $0.03C_{10}$–$0.97C_{12}$.

The characteristics of the material are:

1. liquidus temperature: –10.8 °C,
2. heat of mealting: 204 J/g,
3. effective thermal window: 0.8 °C.

By DSC experiments, at mg scale, it has been shown that this MAPCM is resistent to repeated cycling: it remained completely unchanged during 45 cycles of heating and cooling.

The prototype

A plastic conical double-wall container was used to test the performance of the proposed system in different situ-
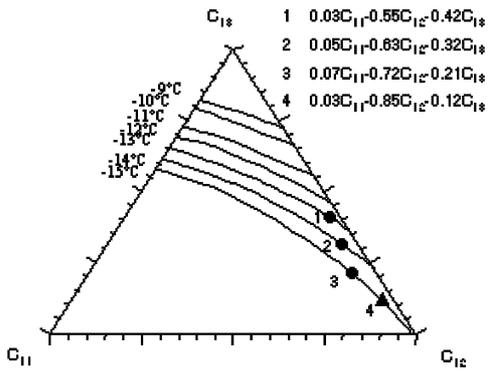
Fig. 3 Ternary compositions as potential MAPCM (see thermo-energetic and crystallographic properties in Table II) of the C_{11}–C_{12}–C_{13} calculated phase diagram. The lines are isotherms and correspond to the liquidus surfaces. ● Thermal window = 2 °C, ▲ thermal window = 1 °C
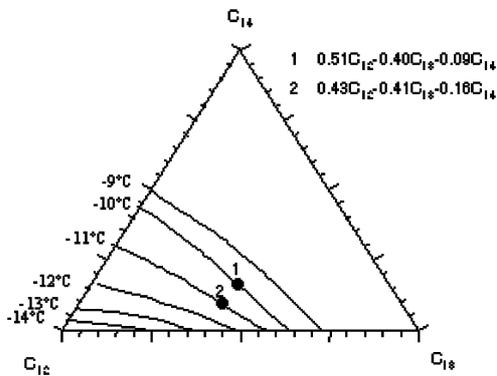

Fig. 4 Ternary compositions as potential MAPCM (see thermo-energetic and crystallographic properties in Table II) of the C_{12}–C_{13}–C_{14} calculated phase diagram. The lines are isotherms and correspond to the liquidus surfaces. ● Thermal window = 2 °C
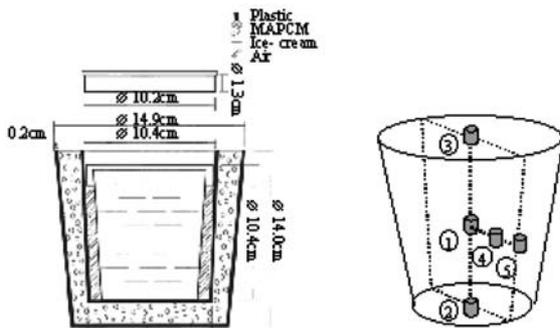

Fig. 5 (a) The prototype. (b) Pt probes distribution in the ice cream

ations (Fig. 5a). It is a commercial container adapted to our experiment. The MAPCM (800 ml) is situated within the double wall with the pasteboard pot with ice cream in the core. A widely commercialised 500 ml strawberry ice cream made from natural products without additives or preservatives (which means that it is not possible to

re-freeze after it melting) was chosen to test the proposed active packaging. This ice cream is commercialised in conical pasteboard containers. The melting temperature where ice cream starts to melt (–8 °C) was determined by DSC and using a Pt probe in the core.

The tests

The temperature inside the ice cream and the external temperature (see Fig. 5b) were measured as a function of time, using several Pt probes. The entire test was carried out within a thermal device in order to control the ambient temperature. From the statistical summer temperature in several European cities, two values were chosen for this ambient temperature: 20 °C and 25 °C.

Different situations have been considered:

1. The conical pasteboard container with a 0.1 mm-thick wall without any thermal protection. This situation corresponds to the most usual case.
2. The conical pasteboard protected by a porexpan box with a 12 mm-thick wall as it is offered in several cases.
3. The conical pasteboard protected by our prototype containing the MAPCM.
4. The conical pasteboard protected by an insulating material which consists of a layer of icolen. The icolen layer thicknes is similar to the MAPCM thickness in the previous case.
5. The conical pasteboard protected by a layer of icolen surrounding the prototype containing the MCPAM.

In each case, the ice cream was first maintained in a freezer at –18 °C until it was moved to a heater at working temperature (20 or 25 °C). The temperature versus time was measured until all the ice cream melted.

Results

As regards the ice cream in the conical pasteboard container with a 0.1 mm-thick wall without any thermal protection, the experiments show that (Fig. 6a):

1. The melting of the ice cream is not homogeneous. It begins at the surface and sides, and finishes at the centre.
2. The ice cream is maintained in an edible state for 35 minutes at an ambient temperature of 20 °C, and for 30 minutes at 25 °C. An edible state means that the melting of the ice cream begins only in its sides according to the manufacturer's recommendations.

To protect the ice cream a porexpan box with a 12 mm-thick wall is offered in several cases. The results (Fig. 6b) show that:

1. As in the former case, the melting of the ice cream is not homogeneous. Nevertheless, in this case the temperatures inside the ice cream are more similar.

Fig. 6 Ice cream evolution in different situations. (a) conical pasteboard, (b) conical pasteboard + porexpan, (c) conical pasteboard + Prototype with MAPCM, (d) conical pasteboard + icolen and (e) conical pasteboard + Prototype with MAPCM + icolen
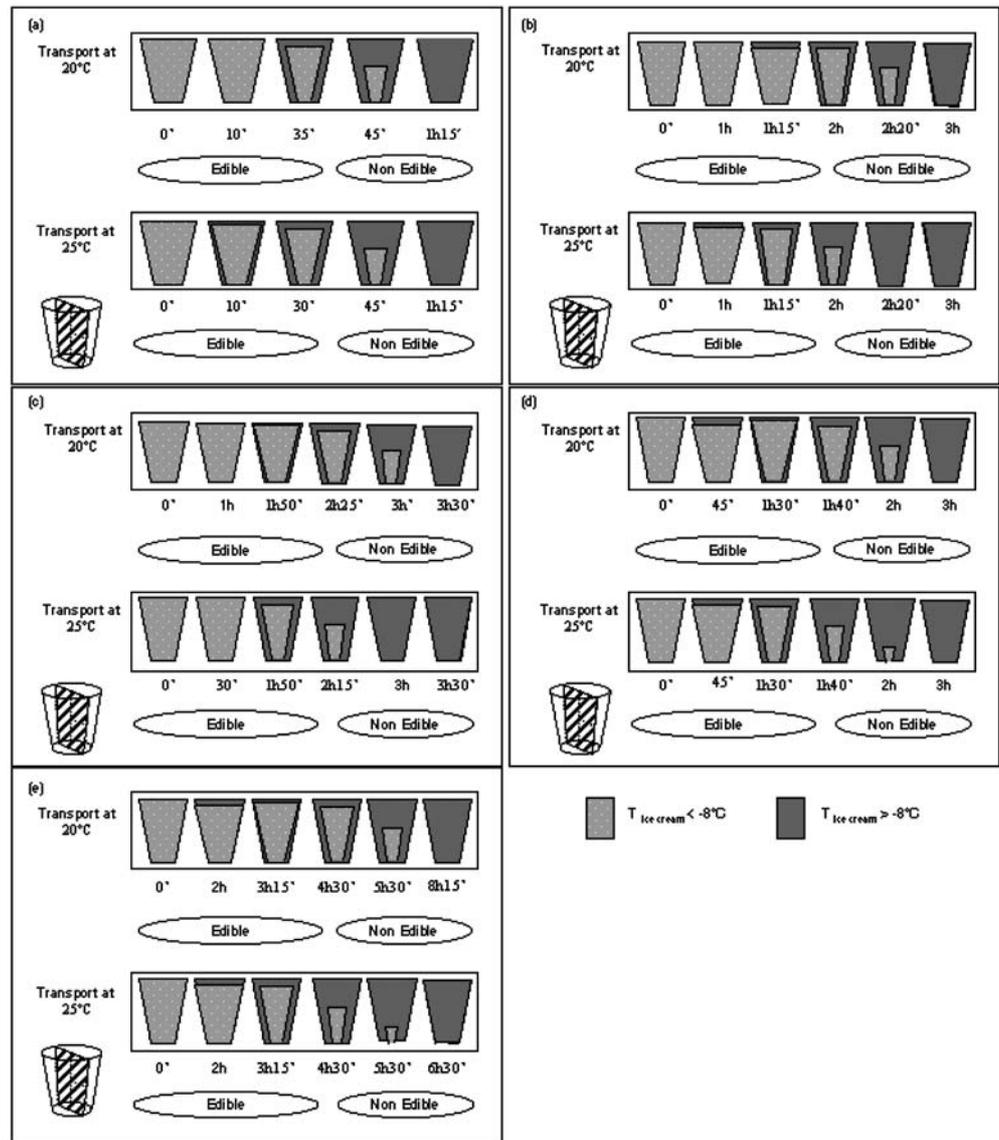
2. The ice cream is maintained in an edible state for 2 hours at an ambient temperature of 20 °C, and for 1 hour and 15 minutes at 25 °C.

If we now use the prototype described previously, with the MAPCM chosen previously within its double walls, and repeat the same experiment, the results are (Fig. 6c):

1. Non-homogeneous melting, as in previous cases. The differences between the temperatures inside the ice cream are lower likely when the porexpan box protects it.
2. A thermal protection time of 2 hours and 25 minutes for an external temperature of 20 °C, and 1 hour and 50 minutes at 25 °C.

In order to evaluate the effect of the MAPCM, the ice cream was protected by an insulating material. A layer of icolen (with similar thickness to the MAPCM) was se-lected due to its good isolation properties and easy feasibility. The results show that (Fig. 6d):

1. The melting of ice cream is not homogeneous, as in previous cases.
2. The ice cream is maintained in an edible state for 1 hour and 40 minutes for an external temperature of 20 °C, and 1 hour and 30 minutes at 25 °C.

Finally, the extraordinary high thermal lag (around 40 °C) between the ice cream temperature and the external one, led us to use an additional layer of 8 mm of icolen in the prototype with the MAPCM. The results are (Fig. 6e):

1. Non-homogeneous melting also here and a temperature distribution in the ice cream similar to the former cases.
2. A thermal protection time of 4 hours and 30 minutes with an external temperature of 20 °C, and 3 hours and 15 minutes at 25 °C.

Conclusions

We have shown that the basic knowledge of the properties of a family of substances (in this case n-alkanes), particularly its capacity to form stable molecular alloys, permits us to conduct the search for a suitable molecular alloy as Phase Change Material for a particular application (in this case the thermal protection of ice cream). A commercial and cheap molecular alloy is proposed for thermal protection of ice cream or other kinds of product around –11 °C.

The results obtained with the prototype proposed show that the effect of the active package is important. This package is able to keep an ice cream at a lower temperature than its melting temperature over 4.5 hours, when kept at an outside temperature of 20 °C. That means a protection 8 times longer than when the ice cream is maintained with only its pasteboard container, and nearly 2 times longer than when the commercially porexpan box is used.

Moreover, any kind of food product or biomedical product can be protected using this double-wall container. Other similar applications in the catering, biomedical, and telecommunication sectors have been studied and are in development.

References

1. Haget Y, Mondieig D, Cuevas-Diarte MA (1999) USA Patent 6: 136–217
2. Haget Y, Mondieig D, Cuevas-Diarte MA (1999) European Patent EP0 548 334 B1
3. Mondieig D, Marbeuf A, Robles L, Espeau P, Poirier B, Haget Y, Calvet T, Cuevas-Diarte MA (1997) High Temperatures-High Pressures 29: 385–388
4. Oonk HAJ, Mondieig D, Haget Y, Cuevas-Diarte MA (1998) J Chem Phys 108[2]: 715–722
5. Mondieig D, Espeau P, Robles L, Haget Y, Oonk HAJ, Cuevas-Diarte MA (1997) J Chem Soc Faraday Trans 93[18]: 3343–3346
6. Espeau P, Mondieig D, Haget Y, Cuevas-Diarte MA (1997) Packaging Technology and Science 10: 253–260
7. Arjona F, Calvet T, Cuevas-Diarte MA, Métivaud V, Mondieig D (2000) Bol Soc Esp CerámVidrio 19[4]: 548–551
8. Rajabalee F, Mondieig D, Métivaud V, Laprie A, Frauca I, Arjona F, Cuevas-Diarte MA (1999) XXV Journées d'Etude des Equilibres entre Phases, Annecy
9. Grignon R, Girardet C, Haget Y (1994) XX Journées d'Etude des Equilibres entre Phases, Bordeaux
10. Cuevas-Diarte MA, Calvet T, Aguilar M, Arjona F, Mondieig D (1999) Technical rapport, Barcelona
11. Métivaud V, Rajabalee F, Cuevas-Diarte MA, Calvet T, Mondieig D, Haget Y (1998) Anales de Química 94: 396–400
12. Métivaud V, Rajabalee F, Mondieig D, Haget Y, Cuevas-Diarte MA (1999) Chem Mater 11: 117–122
13. Robles L, Mondieig D, Haget Y, Cuevas-Diarte MA, Alcobé X (1996) Molecular Crystals and Liquid Crystals 281: 279–290
14. Rajabalee F (1998) European PhD, Université Bordeaux I
15. Métivaud V (1999) European PhD, Université Bordeaux I
16. Lane GA (1983) Solar heat storage Latent heat materials, vol I. CRC Press, Florida
17. Lane GA (1986) Solar heat storage Latent heat materials, vol. II. CRC Press, Florida
18. Kürklü A (1998) Renewable Energy 13: 89–103
19. Telkes M (1947) Heat Vent 44: 68
20. Athienitis AK, Liu C, Hawes D, Banu D, Feldman D (1997) Building and Environment 32: 405–410
21. Turnpenny JR, Etheridge DW, Reay DA (2000) Applied Thermal Engineering 20: 1019–1037
22. Haget Y, Mondieig D, Cuevas-Diarte MA (1993) Dépot de marque ALCAL, Centre National de la Recherche Scientifique (France)
23. Espeau P (1995) European PhD, Université Bordeaux I
24. Rajabalee F, Mondieig D (1999) Technical rapport, Bordeaux
25. Stolk R, Rajabalee F, Jacobs MHG, Espeau P, Mondieig D, Oonk HAJ, Haget Y (1997) Calphad Comput Coupling Phase Diagrams Thermochem 21: 401
26. Métivaud V, Rajabalee F, Oonk HAJ, Mondieig D, Haget Y (1999) Can J Chem 77: 1–4