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Protection of temperature sensitive biomedical products using molecular alloys as phase change material

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Abstract

In this paper we present an example of the application of molecular alloys for thermal protection of biomedical products during transport or storage. Particularly, thermal protection of blood elements have been considered at different temperatures. All steps from basic research to marketing have been addressed. The high latent heat of fusion of the components allows us to propose molecular alloys as materials for thermal energy storage and also for thermal protection over a large range of temperatures, which can be used in many industrial sectors.

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1. New materials for energy storage and thermal protection

The use of phase change materials (PCMs) for thermal energy storage is well known [1]. We have shown that if the components are chosen judiciously, one can generate molecular alloys phase change materials (MAPCM) suitable for thermal energy storage and thermal protection [2]. This new class of materials is interesting for various reasons, the main reason being that they provide solutions over a range of temperatures where classical PCMs are scarce or even non-existent. Above all, one can modify their composition in order to obtain the material which stores and removes heat at a required temperature. Because their composition can be modified, molecular alloys are thermo-adjustable materials. The diversity of MAPCM applications and their feasibility have been proven. Two patents and a trademark (Alcal®) have been registered, one of which is presently in use [3].

What is original in molecular alloys in comparison to other kinds of alloys, is the notion of "polyatomic entity". The mixed crystal, solid solution, or molecular alloy, $A_{1-x}B_x$ (for a binary alloy) is built from a statistical distribution of molecules of A and B in a crystallographic framework where x is the molar fraction of B.

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Molecular alloys are made on the basis of organic substances. Different families are considered based on various molecule sizes and shapes and different intermolecular interactions. Polymorphism is rich and complex in these types of materials. For each of the alloy components, stable and metastable phases are structurally and thermodynamically characterized. Fundamental work is a necessary basis for a rational choice of potential candidates for energy storage and thermal protection at different application temperatures. Polymorphism behaviour and isomorphism relationships of the pure components, and phase diagram analysis permit us to select binary and ternary alloys as potential candidates for use. Among the different families of substances, the *n*-alkanes give especially interesting MAPCMs. With numerous possible combinations, research into more than 35 (binary and ternary) systems has been carried out. Within this family, it is possible to develop MAPCM for a large domain of applications ranging from −50 to +100 °C. Research into other families like *n*-alkanols, aliphatic acids, and dicarboxylic acids is also being done.

2. Energy storage and thermal protection with MCPAM

The molecular alloys with a high latent heat of transition (usually melting) can be used to store

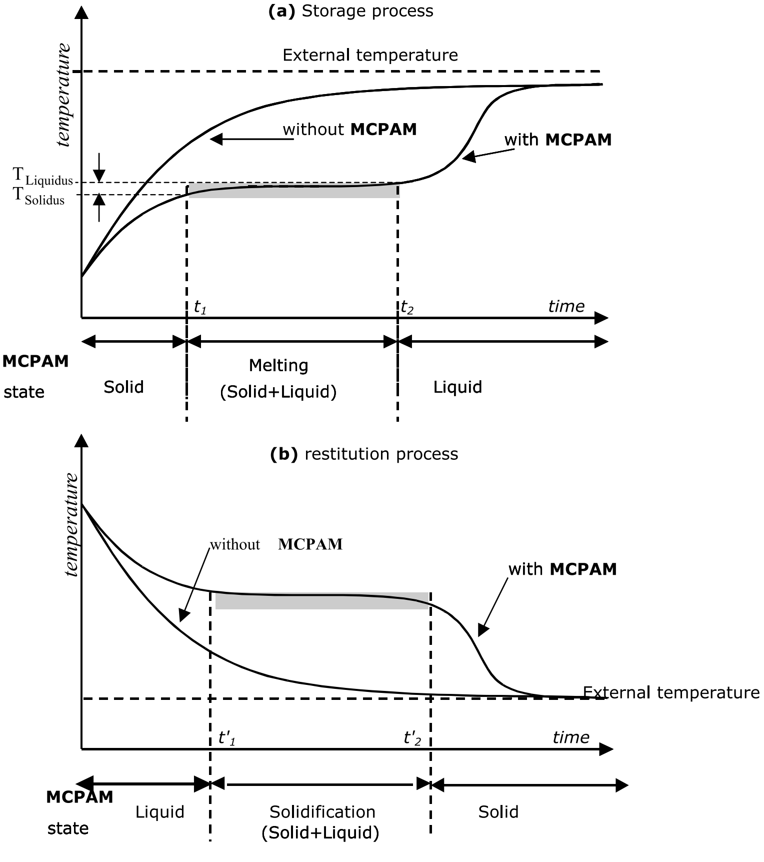

Fig. 1. Evolution of temperature as function of time: schematic representation of storage (a) and restitution (b) processes. T_{solidus} is the solidus temperature (temperature at which the solid starts to melt) and T_{liquidus} is the liquidus temperature (temperature at the last particle of solid melts). $\delta = T_{\text{liquidus}} - T_{\text{solidus}}$ is the thermal window.

energy and provide thermal protection. The alloy melting is, in general, a non-isothermal phenomenon. Melting begins at the solidus temperature, and finishes at the liquidus temperature (Fig. 1). We call the thermal window (δ) the temperature range of melting. During melting, the alloy stores energy. During solidification, it releases the same quantity of energy. Fig. 1 shows this process. When a MAPCM is heated, its temperature rises until melting begins (time t_1). In this step, a quantity of energy is stored by the alloy in a sensible heat form. During melting (between t_1 and t_2) the MAPCM is maintained at a quasi-constant temperature if its thermal window, δ, is narrow, and stores the supplied energy in a latent heat form. When all of the MAPCM is melted, its temperature rises again and a new step of sensible heat storage takes place. If the MAPCM is then cooled, the energy restitution step begins. The temperature decreases until the beginning of solidification (between t'_1 and t'_2) which happens at a quasi-constant temperature, and decreases only when all the alloy is solid. The MAPCM releases the same quantity of energy stored during its heating in the form of sensible and latent heat. If we choose an adequate MAPCM, a cycled process can be performed with energy storage and restitution as a result. Obviously, the process time is a function of the latent heat and the quantity of the MAPCM used.

3. Protection of temperature sensitive biomedical products

As an example, we will describe a device for thermal protection of biomedical products, particularly blood elements (Fig. 2). A double-walled pouch (Fig. 2-②) containing MAPCM is used. This pouch surrounds the blood bag and is held by a carrier bag (Fig. 2-③). Six of these units are transported in a rigid plastic safety device (Fig. 2-①).

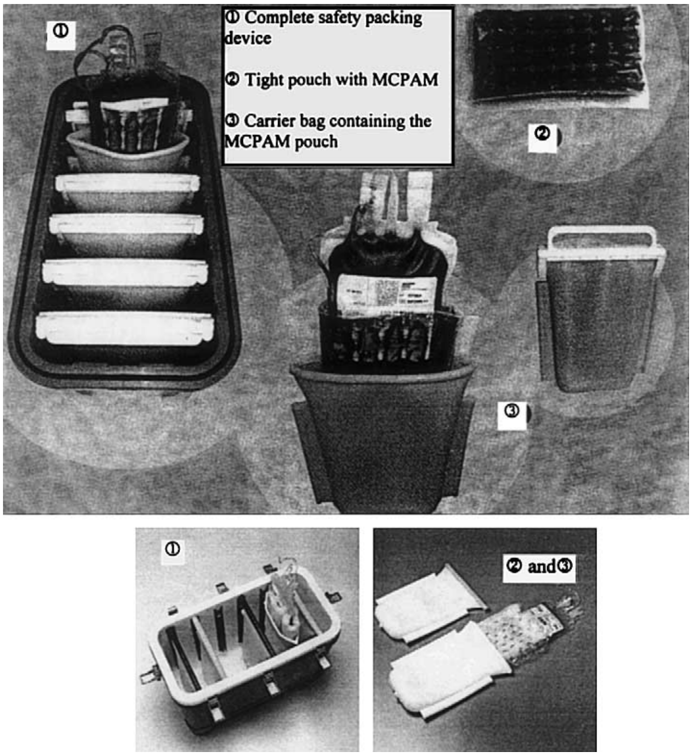

Fig. 2. Packaging for blood thermal protection: ① complete safety packing device; ② tight pouch with MCPAM; ③ carrier bag containing the MCPAM pouch.

The operating principle is simple. The MAPCM pouches are first placed in a freezer to allow MAPCM solidification. When the MCPAM is completely solidified, the MCPAM pouches are displayed as described above (Fig. 2). Then, when the blood is transported with this device at ambient temperature, external calories are stopped by the MAPCM. In the first step, the calories are absorbed by the MAPCM in the solid state, increasing its temperature until the solidus temperature is reached. Thereafter, the calories are used to melt the MAPCM. During MAPCM melting, the device is maintained in a quasi-isothermal situation. The plateau slope is very low due to the very narrow thermal window of the MAPCM. Plateau duration is obviously a function of the conditions of use (external temperature, latent transition heat and quantity of MAPCM involved). As a consequence, the blood inside the container is thermally protected by the MCPAM effect.

Three temperature domains of blood protection have been considered: −30, +4 and +22 °C. Subsequently we will describe a particular application to maintain blood at $(4 \pm 2\ °C)$ during its transport, for example, from a hospital to its final destination.

4. Selection of an appropriate MCPAM

For this purpose, we require a material with a melting and a crystallisation temperature within the $+2\ °C \leqslant T \leqslant +6\ °C$ temperature range. Five pure *n*-alkanes were chosen with a melting temperature adapted to the desired temperature range: C_{12}, C_{13}, C_{14}, C_{15} and C_{16} (C_n denoted a *n*-alkane with *n* carbon atoms in the chain). From a fundamental point of view, the polymorphism of the *n*-alkanes in this range of *n* were previously determined [4]. But pure *n*-alkanes are not the cheapest solutions. Moreover, in numerous cases they cannot be used because their melting temperature is not adapted to the application temperatures. These findings led us to develop binary, ternary or multicomponent materials with *n*-alkanes as components. In the latter case we were able to find a low-priced commercial material with properties close to those previously cited. Among the binary phase diagrams determined in the *n*-alkane family, five could give binary alloys in the required temperature range: C_{12}–C_{14}, C_{13}–C_{14}, C_{13}–C_{15}, C_{14}–C_{15} and C_{14}–C_{16}. Even though some of these binary diagrams are rather complex, in all these cases there is a domain of binary alloys in the form of T_p (triclinic ordered phase) or R_I (orthorhombic rotational disordered phase) which melt with a narrow thermal window at temperatures useful for our application and with a sufficiently high melting entropy. As a result of this analysis, we selected several zones of composition in these systems and we elaborated and tested several molecular alloys as potential MAPCMs.

Five ternary systems involving these binary systems could give potential molecular alloys suitable for thermal protection: C_{12}–C_{13}–C_{14}, C_{13}–C_{14}–C_{15}, C_{14}–C_{15}–C_{16}, C_{12}–C_{14}–C_{16} and C_{12}–C_{14}–C_{16}. We analysed some compositions in several particular zones and calculated their solid–liquid equilibrium regions using the Txy-CALC program [5,6]. The aim was to select the compositions with a liquidus temperature adapted to the application, and a thermal window lower than 2 °C. Examination of both the liquidus and solidus isothermal lines gave us the ternary compositions suitable for the application involved. Several of the selected compositions were elaborated experimentally and tested by differential scanning calorimetry (DSC). Good agreement was obtained with the theoretical results.

From the results obtained for binary and ternary systems, some compositions were selected as potential MAPCM within the temperature range of this study. As molecular alloys elaborated from pure or near pure components are too expensive for commercial application, we were looking for a cheaper molecular alloy. These materials are normally multicomponent. Our objective was to find a multicomponent alloy with similar characteristics to those determined for binary or ternary alloys. One material has been selected. DSC and X-ray powder diffraction analyses have shown that its behaviour is similar to a single phase. Its characteristics are:

- Liquidus temperature (T_{liquidus}): 4.8 °C
- Melting entropy (ΔH): 207 J/g

- Efficient thermal window (δ): 1.5 °C

The thermal behaviour of this MAPCM tested by DSC over cycles of heating and cooling at a milligram scale showed no differences after cycling.

A prototype was used to test the performance of the proposed system in different situations. The MAPCM (330 g) was situated within the double wall of the pouch with the blood bag in the core. Six blood bags each protected by a MAPCM bag (active package) were placed in a closed rigid box (Fig. 2). The blood temperature and the external temperature were measured by several Pt probes as a function of time.

The results obtained with the proposed prototype show that the effect of the active package is important. The box package including the MAPCM is able to maintain a blood bag at a temperature lower than 10 °C over 6 h, when kept at an outside temperature of 22 °C (the time of protection being, of course, longer if the outside temperature is lower or if the rigid box is protected by an insulating material). This achieves a protection eight times longer than when the blood bag is placed in the box without MCPAM.

5. MCPAM applications

Formulations of MCPAM have been also derived for safe transportation packing for effective temperature control at −30 and +22 °C.

A similar methodology has been used to develop:

- A radiant floor with energy storage in molecular alloys (an application temperature close to +22 °C) during the night and restitution during the day, for a heat system, in collaboration with Ducasa [7].
- An "active" packaging for fresh drink protection (application temperature of +10 °C) in collaboration with Sofrigam [8].
- A device for the dissipation of heat produced by electronic components (application temperature of +70 °C), in collaboration with Thomson [9].
- A packaging for the thermal protection of ice-cream during transport (application temperature of −10 °C) [10].
- A packaging for the thermal protection of macromolecule monocrystals and others (application temperature of +6 °C), in collaboration with a research institute from Granada [11].

At present, we are studying:

- A thermal protection device for telecommunication components, in collaboration with France-Telecom.
- A thermal protection system for the catering sector, in collaboration with Gaiker, Walter–Pack, and Gastronomia Basca.

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