The Advantages & Challenges of Phase Change Materials (PCMs) In Thermal Packaging

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OVERVIEW

Cold Chain Technologies, Inc. (CCT) designs and manufactures temperature-controlled packaging that employs Phase Change Materials (PCMs). PCMs are passive thermal energy storage materials used in the thermal packaging industry to maintain a temperature-sensitive product within the manufacturer's required temperature range during all transportation phases (i.e. from manufacture to end user). Typical temperature requirements for temperature-sensitive products range from -80°C to +40°C, the most common being at a point between 2°C and 8°C. PCMs are commonly used in combination with water-based refrigerants (or by themselves) within insulated shipping containers.

To increase the duration of thermal control within a given temperature range, PCMs are normally selected such that their phase change temperature is <u>within</u> the required temperature range of the product being shipped (i.e. +5°C PCM is used to meet a +2°C to +8°C temperature requirement). As the PCM changes its phase (for example, from solid to liquid, at 5°C) it effectively <u>extends</u> the duration of temperature control by cooling the product via its latent heat. Although liquid water will resist temperature change, it does not undergo a phase change until 0°C. As such, for a 2°C to 8°C shipper, using liquid water (only) to protect the product from getting to hot or too cold is *much less efficient than using a PCM.* Some quick calculations quantify this:

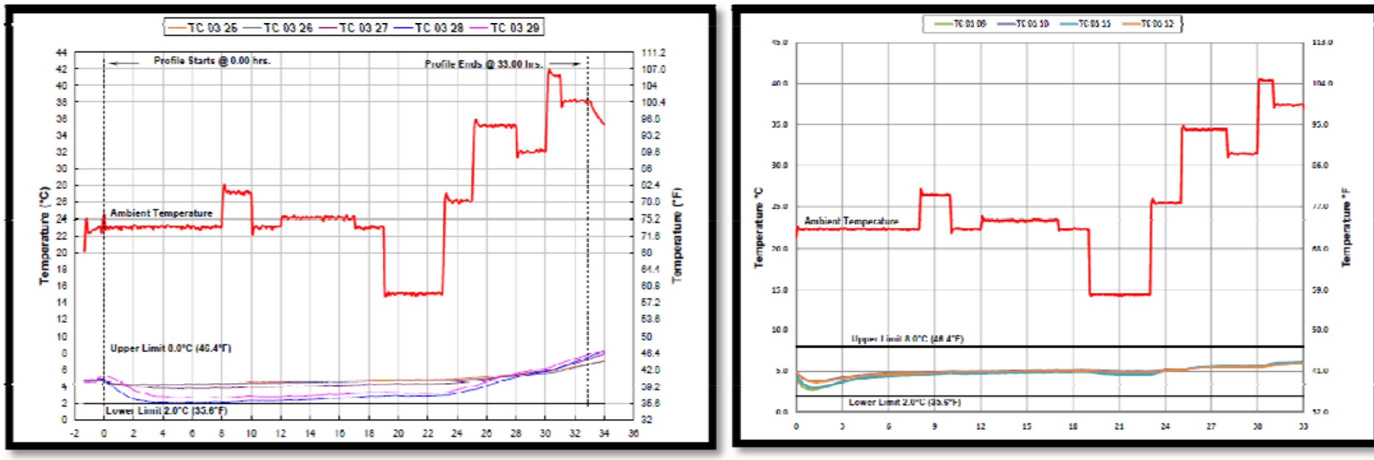
> <u>WATER</u>: Energy removal to lower [1kg] of liquid water from (+5°C) to (+2°C) = **12.6 kJ**
> <u>+5°C PCM</u>: Energy removal to lower [1kg] of liquid PCM (+5°C) to frozen PCM (+2°C) = **233.3 kJ**

In the above scenario, almost nineteen times (233.3 kJ ÷ 12.6 kJ) more energy is needed to change the temperature of the PCM compared to liquid water! The result is that considerably less (weight) of PCM is required to protect the product from low temperature exposure as compared to water. Efficient use of PCMs will result in <u>smaller</u>, <u>lighter</u> (reduced freight) thermal packaging designs that <u>outperform</u> their water-based counterparts. This benefit can be used for both summer and winter cycles (melting or freezing of PCM) as long as the PCM phase change temperature is within the desired product temperature range.

Figure 1, below, illustrates the increased performance that can be achieved by using PCM in place of water-based refrigerants: The figure shows a graph of product temperature versus time of a PCM-based solution (right) vs. a water-based solution (left). As shown, the product temperature at the end of the profile (test) is approximately 2°C lower for the PCM-based solution which results in increased duration of temperature control. It is also important to note the minimum product temperatures in the water-based solution compared to the PCM-based solution. The water-based solution product temperature is very close to the +2°C lower temperature limit, while the +5°C PCM-based solution maintains the product temperature within +/- 1°C of +5°C after the initial stabilization period (first few hours) in the shipping solution. As such, relatively small changes to the ambient temperature profile could result in a lower temperature limit failure in the water-based design whereas the PCM-based solution is much more robust.

Figure 1: Comparison of a typical Water-based design vs. PCM-based design

Water-based Solution | +5°C PCM-based Solution



PCMs are specialty, not commodity, materials and as a result are much more costly than their water-based counterparts. However, in many cases the added cost of the PCM is more than offset by reduction in freight, resulting in lower total system costs (packaging plus freight). Table 1, below, compares several PCM designs developed to replace existing qualified water-based designs for refrigerated (+2°C to +8°C) product shipments.

Table 1: Comparison of [2 to 8°C] PCM designs vs. Water-Based designs

Comparison Characteristic	Example 1		Example 2		Example 3	
	Water-Based	**PCM-Based**	**Water-Based**	**PCM-Based**	**Water-Based**	**PCM-Based**
Insulation Type	Polyurethane		Polyurethane	Expanded Polystyrene (EPS)	Polyurethane	Vacuum Insulation Panel (VIP)
Qualified Duration at 2-8°C	48 hours	72 hours	48 Hours	48 Hours	48 Hours	72 Hours
Weight of Solution (no product)	24 lbs	17.5 lbs	36 lbs	15.3 lbs	36 lbs	23 lbs
Dimensional Weight (Factor of 166)	30 lbs	27 lbs	48 lbs	27 lbs	48 lbs	15 lbs
System Cost	$70	$65	$85	$30	$105	$135
Estimated Freight Costs ($1.20 / lb)	$36	$32	$58	$35	$58	$28
Total Cost of Ownership	$106	$97	$143	$65	$163	$163

Types of PCMs Typically Used in Thermal Packaging

PCMs typically used in thermal packaging are usually grouped by their chemical makeup (“organic” or “inorganic”), with the most common being organic. Organic PCMs, which are oil-based, have the $(CH_2)_n$ group that provides their high latent heat. A number of types of organic PCMs are currently used by packaging providers including: n-alkanes, fatty acid methyl esters (“methyl esters”), fatty acids and fatty alcohols. The inorganic PCMs are aqueous (water-based) salt hydrates (e.g. $Salt{\cdot}nH_2O$). There are a number of key attributes for a PCM that should be considered. Overall, the attributes of a “perfect” PCM are:

- Phase change temperature in desired range with sharp melting/freezing point
- High latent heat of fusion (solid to liquid)
- Non-toxic (to humans/animals) & non-carcinogenic
- Commercially available at low cost
- Does not react with and/or act as a solvent for packaging materials
- Landfill disposable and/or waterway disposable
- Biodegradable
- Low/non-flammable (high flash point, low vapor pressure)
- Non-corrosive
- Good stability upon thermal cycling (no super-cooling)
- Limited volumetric expansion/contraction upon freeze/thaw

Table 2, below, summarizes, by generic type, PCMs that have been used in Cold Chain applications, along with the (Pros) and (Cons) of each.

Table 2: Organic/Inorganic PCMs used in Cold Chain Applications

Generic Name: Formula	Pros (Cold Chain Applications)	Cons (Cold Chain Applications)
n-Alkanes: $CH_3(CH_2)_nCH_3$	High latent heat; inert, non-toxic, non-corrosive	Limited availability, limited biodegradability
Fatty Acid Methyl Esters: $CH_3(CH_2)_nCOOCH_3$	Biodegradable, non-toxic, non-corrosive	Limited availability, strong odor, solvent for EPS, latent heat below alkanes
Fatty Alcohols: $CH_3(CH_2)_nCH_2OH$	Biodegradable, non-toxic	Limited availability, odor, flammable, easily oxidized, latent heat below alkanes
Fatty Acids: $CH_3(CH_2)_nCOOH$	Biodegradable, good cycling stability, limited super-cooling	Limited availability, causes burns, corrosive, latent heat below alkanes
Salt Hydrates (inorganic): $Salt{\cdot}nH_2O$	Water based systems, packaging compatible, good latent heat	Very limited availability, poor cycling stability, may be corrosive

Challenges Associated with PCMs

While there can be a significant advantage to using PCMs in certain thermal packaging applications (as outlined above), there are also a number of challenges regarding their manufacture and use that need to be understood and addressed by both the PCM manufacturer and the end-user. The key challenges include:

- Material Compatibility
- Material Properties and Thermal Performance
- Packaging for Use
- Conditioning for Use
- Cost and Availability
- Health & Safety and Disposal

The following sections cover these specific challenges in greater detail and explain Cold Chain Technologies' approach to address each including the PCM selection process, ongoing research & development efforts, and manufacturing improvements.

Material Compatibility

Since PCMs are oil-based their compatibility with packaging materials must be evaluated. This evaluation must include both the materials used to encase the PCM (i.e. films) and other packaging materials used in the thermal shipping solutions (i.e. insulation and corrugate). The most important factors to be considered are permeability and solubility of the PCM with the packaging materials. If the PCM and the material used to encase it are not compatible, the PCM can permeate through the packaging material relatively quickly after it is manufactured. Considering solubility, in the event of a leak (puncture) caused by the physical stresses of distribution (vibration, drop and/or pressure) the leaking PCM material could act as a solvent for, or in the worst case dissolve, the other packaging materials. An example of this is shown below (Figure 3a) when a commercially available used organic, fatty acid methyl ester PCM (about 100 ml or 3.4 oz) is placed in direct contact with an Expanded Polystyrene (EPS) shipper. The hole shown through the EPS shipper wall occurred after only 10 minutes of exposure. Figure 3b shows the same shipper after an overnight exposure.

Figure 3a: Fatty Acid Methyl Ester PCM on EPS Shipper - 10 minutes

Figure 3b: Fatty Acid Methyl Ester PCM on EPS Shipper - Overnight

Cold Chain Technologies has performed extensive permeability and solubility testing with the various types of PCMs to evaluate them with commonly used packaging materials for flexible "gel pack" refrigerants. **Table 4** below summarizes this testing. Additionally, solubility testing was completed on typical shipper components and materials including: Expanded Polystyrene (EPS), Polyurethane Foam (PUR), Vacuum Insulation Panels (VIPs) and corrugate.

Table 4: Summary of Permeability Testing with alkane PCM

Sample	# of Days	# Samples	Transmission Rate [g*mil/(100in^2*day)]	% Weight Loss/Year (%/year)
Flexible Barrier Film #1	28	8	0.0164	-2.12%
Flexible Barrier Film #2	707	11	0.0009	-0.12%
Flexible Barrier Film #3	203	6	0.0013	-0.18%

Material Properties and Thermal Performance

As mentioned previously there are a number of key material attributes that should be characterized for any PCM including the phase change temperature, existence of a sharp melting/freezing point, latent heat of fusion, toxicity, flash point, vapor pressure, corrosiveness, material purity, odor and thermal stability upon thermal cycling. Among the commonly used PCMs in thermal packaging today, the following negative attributes were studied and used in the selection process for Cold Chain Technologies' PCM:

- Fatty alcohols were eliminated due to their pungent odor and flammability.
- Fatty acids were removed due to their corrosive nature and burn potential.
- Salt Hydrates were rejected due to poor cycling stability and potential for corrosion.
- Fatty acid methyl esters were excluded due to their solubility with common insulation materials (as shown above, see Figure 3).

Of the organic materials, n-alkanes exhibited the highest latent heat values at a given phase change temperature, which makes sense considering their large number of $(CH_2)_n$ repeat groups. Testing also showed that purity and/or contaminants have a significant effect on the latent heat of a PCM. An exhaustive evaluation by Cold Chain Technologies didn't uncover the "perfect" PCM but alkanes exhibited the best combination of attributes.

Packaging for Use

One of the biggest challenges for **all** PCM thermal packaging manufacturers is providing "leak-proof" PCM packaging. All (liquid) PCMs have a lower surface tension than water which results in the PCM easily wetting a surface followed by its free migration. This is a challenge for our industry because they are more difficult to contain than their water-based counterparts. Very small seal defects, that are acceptable for water-based refrigerants, will not be acceptable for PCMs. Additionally, these defects may not be present at the time of manufacture. **Figure 4a shows** the % weight loss of a several (n=15) flexible PCM packages; some of these packages have "delayed" (months) leaks. This is in part due to the ridged seal type used and the inner (sealing) layer of film, which is shown in **Figure 4b**. Over time, the inner layer of the film can swell/crack with PCM exposure, leading to leaks. The "delay" occurs since the seal has a small cross sectional area (normal to flow) and a large relative length.

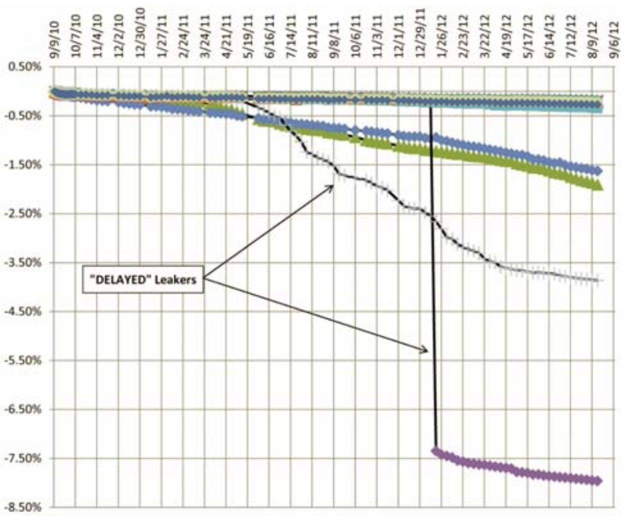


Figure 4a: % Weight Change – Flexible PCM Package vs. Time

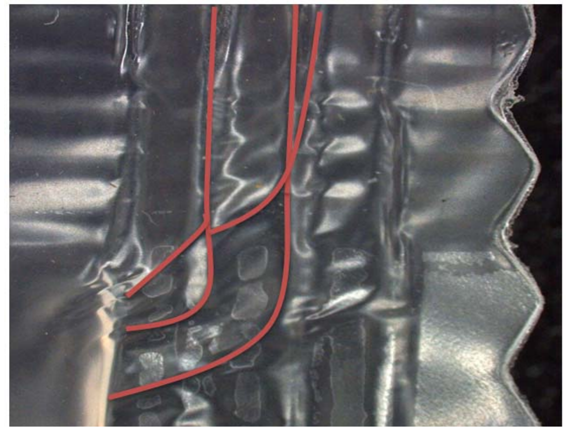


Figure 4b: Delayed Leaks Caused by Ridged Seals

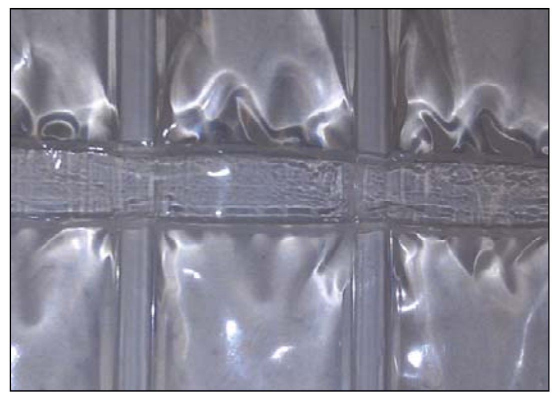


Figure 5: Higher Quality Seals

Due to these issues Cold Chain Technologies' current production methods are subjected to a heightened level of quality control. After a thorough analysis and understanding of the challenges of packaging PCMs, CCT has invested in new sealing equipment that will produce consistent, higher quality seals for products containing PCMs as shown in **Figure 5** (right). Evaluation of the new alkane sealing process showed no seal/edge defects, low permeability (1.72%/yr. weight loss at 60°C), and no leakage after combination drop and freeze/thaw testing (30 cycles).

Additionally, CCT has developed and patented (patent pending) the ability to "gel" its PCM material. In the event that the PCM packaging is breached/punctured for any reason, even with the high quality seals intact, the gelled PCM will retain its form and not leak as if it were in pure liquid form. This process, currently being tested for commercialization, produces a gel similar in texture and viscosity to those now used with water-based refrigerants.

<u>Conditioning for Use</u>

As stated earlier, the most efficient way to use PCMs is within the required temperature range of the product being shipped. Unfortunately this can lead to some challenges when conditioning the refrigerant to the proper phase (liquid or solid) prior to use. Since three temperature ranges are common in typical healthcare distribution centers, refrigerated (+2°C to +8°C), controlled room temperature (+15°C to +25°C for example) and frozen (-20°C for example), conditioning to a specific temperature can be challenging and/or costly.

For example, a client with a refrigerated application may use a +5°C PCM in a liquid phase. If this PCM is stored in a standard refrigerator set to +2°C to +8°C it may freeze depending on the "actual" temperature in the refrigerator and/or its location in the refrigerator. Refrigerated applications are not the only ones that cause challenges. PCMs used for controlled room temperature (CRT) applications may require liquid +20°C PCM and/or a solid +25°C PCM in the shipping solution to hold for a tight CRT requirement. In this example the +20°C PCM may need to be "heated" for use in the liquid state, but its temperature cannot be too high (i.e. +25C or +30C) to reach the liquid state, since the ambient temperature in the distribution center may be below +20°C.

Cold Chain Technologies has performed extensive conditioning studies on its PCMs to understand these potential conditioning issues and provides various methods of achieving the proper conditioning. However, each customer's storage situation is different and CCT partners with its clients to develop the best method for each client.

Cost and availability
For all PCMs, cost and availability is an issue since these materials are not commodities. Cold Chain Technologies has multiple qualified sources for the raw materials used to manufacture their PCM products. Manufacturing of PCM refrigerants is an expensive process, both in terms of raw material costs and the process, as compared to water-based refrigerants. However, with proper thermal design techniques, their use in thermal packaging can result in a total costs savings. CCT only recommends the use of PCM refrigerants in specific applications, where their phase change temperature and latent heat will result in a highly efficient thermal packaging design. Additionally, CCT strives to minimize the amount used in solutions as much as possible to decrease the cost impact.

Health & Safety and Disposal
The health and safety of every company's employees and clients/patients is of the upmost importance. While most of the PCMs used in the industry are non-toxic to humans and animals, ingestion and long-term exposure to skin should be avoided. In regards to disposal, PCM materials are land-fillable (subject to federal, state and local regulations), and are not considered a hazardous waste or hazardous material. However, given their high energy content, incineration (i.e. cement kiln) is preferred over landfill disposal.
It is CCT's experience that both suppliers and end-users must be better educated regarding the re-use, recycling and disposal of PCMs. Every distribution channel is different and some may lend themselves to re-use while others to recycling and/or return. CCT is committed to helping our clients achieve their sustainability goals and works to develop the appropriate plan for each scenario.

Conclusion

Phase Change Materials have changed the way thermal packaging solutions are designed. When used to address certain specific applications, like refrigerated product shipments, efficient use will result in smaller, lighter (reduced freight) thermal packaging designs that outperform their water-based counterparts. There are also many challenges in the manufacture and use of PCMs that must be considered. It is imperative that the manufacturer of the PCM refrigerants understand these key challenges to ensure their packaging will perform as designed and maintain the highest level of quality. Additionally, the user must understand the use of the PCM refrigerant in their specific application to ensure that the packaging will perform as designed and that they are being environmental responsible. Cold Chain Technologies understands all these challenges as they pertain to their PCMs, and strives to educate and assist their clients to ensure the successful use of PCMs.

For more information, please contact us at info@coldchaintech.com or 800.370.8566.