15

Nano-Structured Calcium Silicate Phase Change Materials for Packaging Temperature Sensitive Products

James H. Johnston
School of Chemical & Physical Sciences and The MacDiarmid, Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, New Zealand

1. Introduction

The safe transportation together with en route and temporary storage of temperature sensitive and perishable materials, particularly chilled food and medical products, often require the use of packaging that provides thermal buffering against unwanted transient temperature rises and falls as a result of rapid changes in the temperature of the immediate environment of the package. Effective insulation can alleviate unwanted temperature rises or falls to some extent for a short time. However, this is often insufficient when the packages are exposed to higher or lower temperatures for several hours without effective temperature control (Dodds, 2009; Johnston et al., 2007).

New Zealand and other food producing countries export considerable quantities of fresh food to international markets in response to the increasing global demand for such produce. Much of this food cannot be frozen as the quality and nutritional value are adversely affected, but has to be chilled to maintain freshness. After harvesting and packing, chilling is usually carried out in a coolstore. A major issue is the unwanted warming of the food when the packages are exposed to warm temperatures on airport tarmacs and in temporary (un-refrigerated) storage in transit during air transportation, which can adversely affect the food quality and export value. This is due to the limited thermal insulation and poor thermal buffering capacity of the paperboard containers that are typically used. Polystyrene containers with better insulating properties can be used but there is now a move away from them due to environmental issues associated with their production and disposal. The warm temperature fluctuations often encountered are for durations typically up to 1 hour or so, but can be up to several hours, which is sufficient time to cause spoilage of the perishable food in the package. Hence there is a need for an effective material that provides insulation and thermal buffering properties and can be accommodated in readily re-useable liners for inserting into these packages to insulate against and also absorb the transient heat from the external environment, thereby protecting the valuable and perishable products in the package (Amcor Kiwi Packaging Ltd, 2011; Carter Holt Harvey Packaging, 2011; Cool pack, 2011; Johnston and Dodds, 2011; Johnston et al., 2007; Plastics New Zealand, 2011; Powell and Mathews, 1987).

A similar application is in the transportation of temperature sensitive medical products, often of a high value, which must be kept at a requisite low temperature, but not frozen. Also, comparable problems arise with the transport of products which require maintaining temperatures above ambient. Such products include the delivery of hot fast foods to homes and functions where the desired serving temperature of the food has to be maintained. Similarly in specialist applications such as the transportation of tropical fish, the water has to be maintained within a small temperature range above ambient temperature.
Phase change materials (PCMs) such as alkanes (paraffin oils and waxes) can provide passive thermal buffering properties due to the relatively large latent heat content (~140-210 kJ kg^{-1}) associated with their reversible solid-liquid phase transition. They are non-toxic and the operating temperature (melting point) can be tuned by altering the hydrocarbon chain length (Farid et al., 2004; Rubitherm Technologies GmBH, 2011; Feldman et al., 1986, Zalba et al., 2003). Hence they can absorb heat energy from the immediate environment on melting and release it back on solidifying or freezing. Farid et al., (2004) and Zalba et al., (2003) have reviewed the properties and use of phase change materials in energy storage applications. Khudhair and Farid (2004) have similarly reviewed energy conservation approaches in buildings using phase change materials to capture heat energy from the sun during the day and release it at night. In packaging applications, if the alkane PCM is in thermal contact with a temperature sensitive material or is contained in the surrounding packaging material, the PCM has the effect of buffering or minimising the unwanted sudden temperature changes due to heating and cooling transients in the immediate environment. Here the heat energy is absorbed or released accordingly to counteract the unwanted change in temperature (Farid et al., 2004; Feldman et al., 1986; Hawlader et al, 2003; Johnston and Dodds, 2011; Rubitherm Technologies GmBH, 2011; Schossig et al., 2003; Tyagi and Buddhi, 2007; Zalba et al., 2003; Zhang et al., 2007). However in the practical application of this concept, it is necessary to contain the liquid phase of the PCM upon melting in order to prevent loss of the PCM and the contamination of the material it is thermally protecting. This poses a major problem as the PCM has to be accommodated in robust leak proof and preferably flexible containers around or within the package. This has been addressed by encapsulating the PCM in a microcapsule and then incorporating these microcapsules into the final product such as building materials (Hawlader et al., 2003; Schossig et al., 2003). It is possible these microcapsules can rupture or become dislodged whereupon the PCM thermal buffering capacity is reduced. An alternative approach is to contain the PCM in a highly porous matrix as is discussed here. For this, a composite proprietary nano-structured calcium silicate (NCS) material with a high pore volume has been used to accommodate the alkane PCM to provide a novel nano-structured calcium silicate – phase change material (PCM) in the form of a dry powder (NCS-PCM) (Johnston et al., 2006) that can be contained in flexible plastic packaging liners made of polythene or bubblewrap as detailed below.

2. Preparation of nano-structured calcium silicate – phase change materials

Nano-structured calcium silicate is a proprietary new material comprising nano-size platelets stacked together in a unique open framework structure forming discrete particles of about 1-5 microns in size Fig. 1 (Johnston et al., 2006). It can be prepared by the reaction of Ca^{2+} with the silicate anion, typically $H_3SiO_4^-$ at room temperature under alkaline conditions at a pH typically about pH=11, according to the following general equation:

$$Ca^{2+} + H_3SiO_4^{-} + OH^{-} \rightarrow CaSiO_x(OH)_y + H_2O \qquad \text{Where } x \approx 2 \text{ and } y \approx 2$$

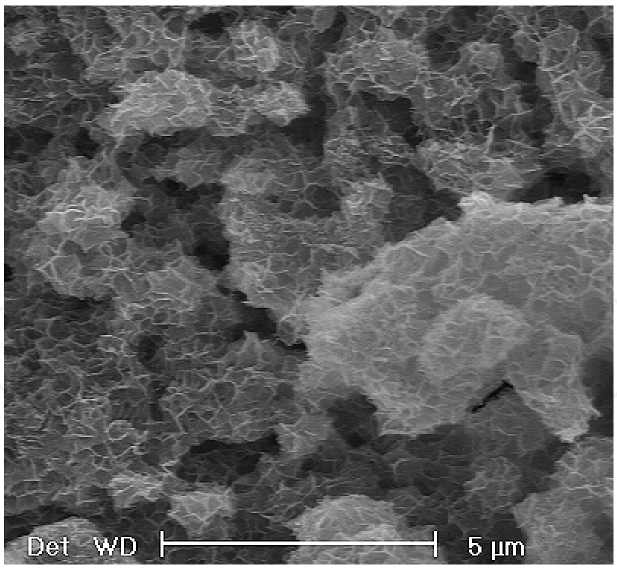


Fig. 1. Nano-structured Calcium Silicate showing the framework of nano-size platelets stacked together to form discrete particles. Some agglomerates are visible.

The $H_3SiO_4^-$ species can be provided by sodium silicate or another source of dissolved silica such as geothermal water. The Ca^{2+} and OH^- can be provided separately from a soluble calcium salt and sodium hydroxide, or provided collectively by a partially neutralised slurry of $Ca(OH)_2$ to remove 1 mole of OH^- ions. Upon mixing the reactants, the NCS precipitates immediately and is then aged for up to several hours to develop the nano-structure shown in Fig. 1. During ageing, the pore volume or oil absorption capacity and the surface area increase with time (Fig. 2) to provide a material with a high pore volume with a consequent high liquid absorbency of up to about 500-600 g oil $100g^{-1}$ silicate (ASTM Oil Absorption test D281), and a high surface area of up to about 500 $m^2\ g^{-1}$ (Johnston et al., 2006).

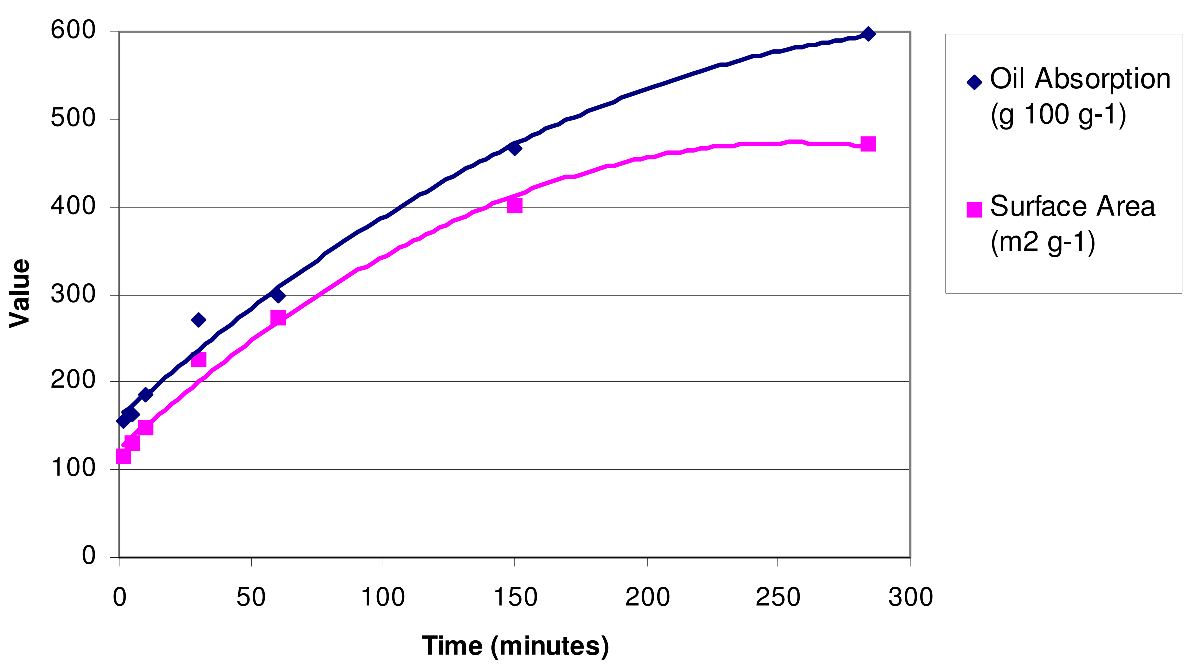


Fig. 2. The increase in oil absorption and surface area of nano-structured calcium silicate as the framework and pore structure develop with ageing.

Alkane PCMs are commercially available from a number of suppliers. For example *Rubitherm GmbH* in Germany currently offers a number of such PCMs with melting points ranging from -4 ^{o}C to 100 ^{o}C (Rubitherm Technologies GmbH, 2011). The practical problem mentioned above of containing the liquid phase on melting, has been overcome here by incorporating the alkane PCM into the highly porous NCS matrix. It is a relatively simple process to mix and work the liquid PCM into the readily accessible pores of the NCS with a spatula for small test samples, or with a food mixer or other such mixing equipment for larger scale preparations. In the transportation and temporary storage of chilled food where it is desirable to maintain a temperature of about 7-10 ^{o}C to retain freshness, a NCS-PCM composite containing either *Rubitherm* RT2 or RT6 alkane phase change materials can be used to provide thermal buffering in this temperature range. The RT2 has an approximate melting point of 6 ^{o}C, a congealing point of 2 ^{o}C and a heat storage capacity of 214 kJ kg^{-1}. RT6 has an approximate melting point of 8 ^{o}C, a congealing point of 6 ^{o}C and a heat storage capacity of 174 kJ kg^{-1} (Rubitherm Technologies GmbH, 2011).
Levels of 100–400 wt % RT6 PCM in the NCS have been tested to determine the highest loading achievable whilst still retaining the free-flowing powder characteristics. An optimum loading level of PCM in the NCS was found to be about 300 wt % PCM on a NCS basis (i.e. 1 kg of NCS-PCM composite comprises 250 g NCS and 750 g PCM). The resulting composite NCS-300PCM remains a powdery solid above the alkane melting point and can be readily incorporated into flexible packaging materials to provide heat buffering of about 100-120 kJ kg^{-1} of composite. In addition, the open framework structure of the NCS itself provides some insulation properties. This thermal buffering packaging can be a simple robust plastic bag containing the NCS-PCM or a common bubble wrap lined plastic bag containing the NCS-PCM which provides both thermal insulation and thermal buffering properties. These can be placed as thermal buffering liners inside conventional paperboard packages. Alkane PCMs are commercially available from a number of suppliers.
Hence by accommodating a PCM of a particular melting point in the NCS pores, it is possible to produce a NCS-PCM composite powdered material and contain it in a conventional plastic bag or bubble wrap plastic bag to form a flexible liner with effective thermal buffering properties at selected temperatures in the range from -4 ^{o}C to 100 ^{o}C (Fig. 3). This can therefore provide thermal buffering capacity to negate or minimise the deleterious effect of short term, high or low temperature fluctuations on temperature sensitive perishable produce and materials.

Fig. 3. The polythene bag containing a sample of NCS-PCM (left) being inserted into a bubblewrap bag (right).

3. Thermal properties of nano-structured calcium silicate – phase change materials

The thermal buffering properties of the NCS-PCM composites with 300 wt% and 400 wt% PCM loadings of different PCMs have each been measured by Differential Scanning Calorimetry (DSC) using a Shimadzu DSC-60 Differential Scanning Calorimeter. The results showed that 300 wt% PCM could readily be accommodated into the NCS without unwanted weeping out of the PCM in repeated heating and cooling cycles and at the same time provide useful thermal buffering properties. The DSC curves of the NCS-300PCM composite material with *Rubitherm* RT6 showed the typical reversible endotherms and exotherms across the solid-liquid and liquid-solid phase transitions respectively with a measured thermal buffering capacity of about 101 kJ kg^{-1} (Fig. 4). Some small hysteresis is observable.

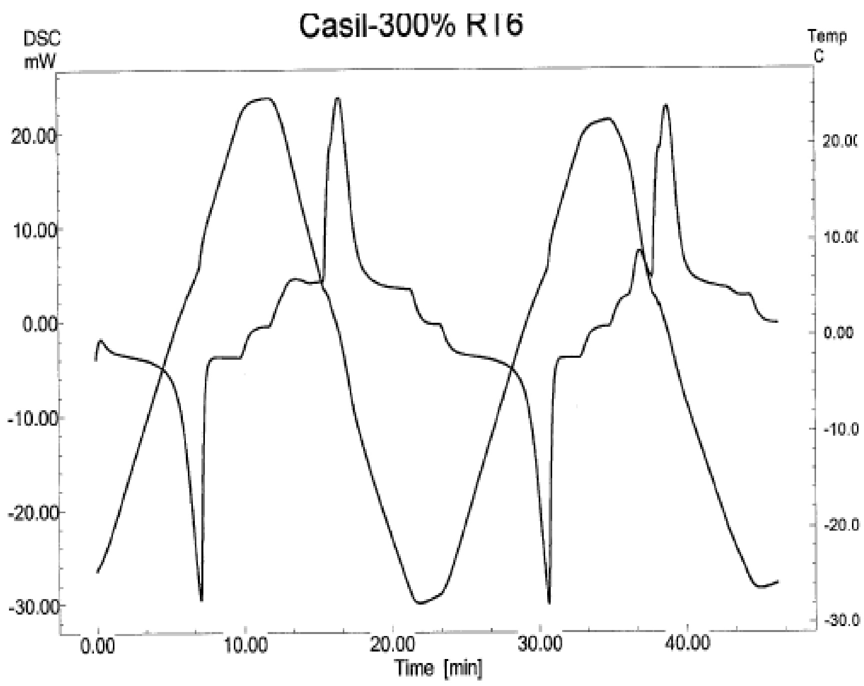


Fig. 4. The Differential Scanning Calorimetry results for the NCS-300PCM composite material for two heating and cooling cycles from -25 ^{o}C to 25 ^{o}C. The triangular curve is the temperature sweep. The DSC curve shows the energy absorbed (endotherm) on melting and released (exotherm) on freezing.

When considering the usefulness of a composite phase change material it is important to also consider the thermal insulation properties by measuring their thermal resistance and thermal conductivity and comparing them with conventional insulation materials. Hence measurements of thermal resistance and thermal conductivity of NCS-300PCM composites containing *Rubitherm* RT2 and RT6 respectively in polythene and bubblewrap bags were carried out with a Togmeter (Fig. 5) (Johnston and Dodds, 2011; Dodds, 2009). This is a device used to measure the temperature difference and the heat flow across a flat plate-like sample from which the thermal resistance and thermal buffering properties can be determined. It comprises a 30 cm diameter thermostatically controlled bottom plate which can be heated above ambient temperature and a 30 cm diameter top plate which can be held at or below ambient temperature by refrigeration. Amounts of 429 g of NCS-RT2, 394 g of NCS-RT6 and 151 g of NCS by itself were placed in a 773 cm^2 polythene bags respectively to

form essentially flat sheet like liners (Fig. 3) for which heat transfer and thermal buffering properties could be measured across the liner using the Togmeter. The liners were also placed inside 280 mm x 325 mm bubblewrap bags and similarly measured to show the additional effect of a layer of bubblewrap insulation surrounding the liners (Fig. 3). Overall the density of NCS-PCM in the liner was about 0.5 g cm^{-2} (Dodds, 2009).
The sample being measured is sandwiched between the plates under an appropriate pressure and uniform thickness to ensure good contact between the plates and the sample (Fig. 5 (left). The respective temperatures of the bottom plate (*T1*), the sample lower surface (*T2*), the sample upper surface (*T3*) and ambient air temperature (*T4*) are measured by thermocouples as shown in Fig. 5 (right). Measurements were carried out in accordance with the international standard ISO 5085-1.

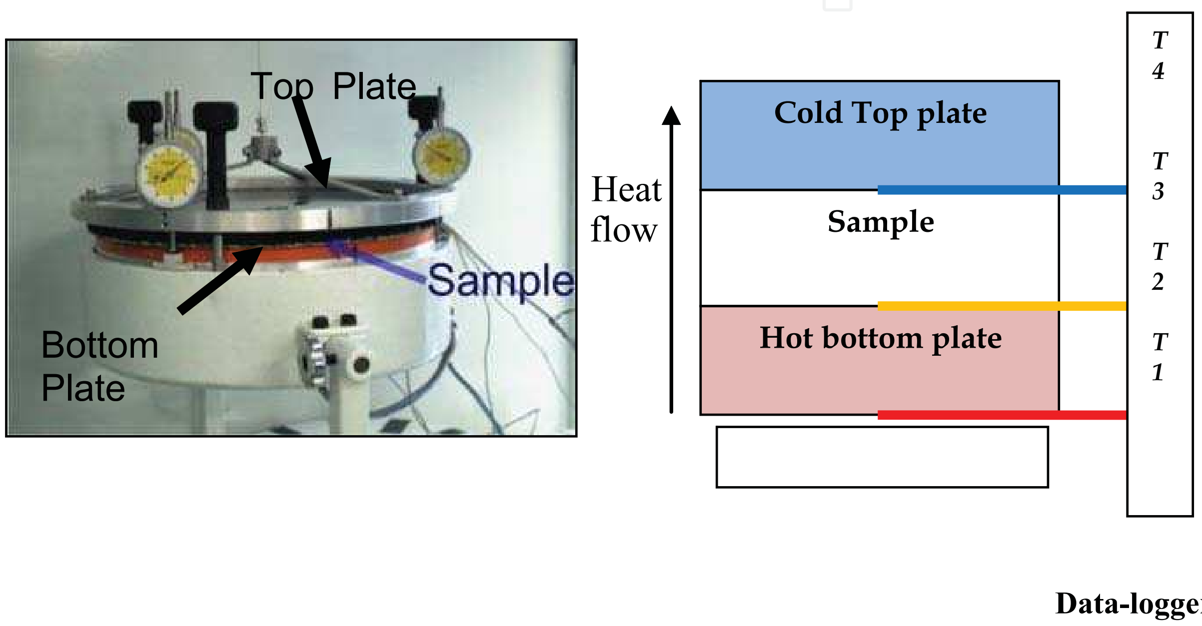


Fig. 5. (left) The Togmeter showing the heated bottom plate, cooled top plate and sample positioned between these plates. The thickness gauges ensure uniform sample thickness and contact between the plates; (right) the placement of thermocouples *T1-T4*. *T1* measures the temperature of the hot plate, *T2* the lower surface of the sample, *T3* the upper surface of the sample, and *T4* the ambient temperature (Dodds, 2009).

The measurement of thermal resistance *Rs* is made by measuring the temperatures *T1*, *T2* and *T3* across the sample under the condition of steady state heat transfer between the hot bottom plate and cooler top plate (Fig. 5).

$$Rs = Rst - Rc\ (T2 - T3)/(T1 - T2) \qquad \left(m^2 K\, W^{-1}\right)$$

Where:
Rs = thermal resistance
Rc = contact resistance (known for instrument)
Rst = resistance of calibration standard
The Thermal Conductivity *k* is calculated from the thermal resistance and the sample thickness *d*

$$k = d / Rs \qquad \left(\mathrm{W\,m^{-1}K^{-1}}\right)$$

For thermal resistance and thermal conductivity measurements the sample is placed between the plates, the bottom plate temperature set and the temperatures *T1-T3* recorded on a data logger until they reach constant values, confirming a steady state heat flow across the sample is reached. These temperature values were used to calculate thermal resistance and thermal conductivity for the sample (Dodds. 2009).

The thermal resistance and thermal conductivity values for NCS and NCS-PCM in the polythene bags and bubblewrap bags are presented in Table 1. The values measured here for corrugated paperboard and expanded polystyrene (EPS) are also provided as a comparison.

Sample ID	*d* mm	*Rs* m^2KW^{-1} *±0.002*	*k* $Wm^{-1}K^{-1}$ *±0.002*
NCS in polythene bag	12.5	0.427	0.030
NCS in polythene bag in bubble wrap bag	19.5	0.520	0.038
NCS-RT2 in polythene bag	12.5	0.337	0.037
NCS-RT2 in polythene bag in bubble wrap bag	19.5	0.367	0.053
NCS-RT6 in polythene bag	12.5	0.183	0.068
NCS-RT6 in polythene bag in bubble wrap bag	19.5	0.264	0.069
Bubble wrap bag	5.05	0.139	0.036
Corrugated paperboard	11.9	0.243	0.049
10mm Expanded polystyrene	10.3	.372	0.032

Table 1. Thermal resistance and thermal conductivity values (Dodds, 2009).

The results (Table 1) show that the thermal conductivity *k* of NCS contained in the polythene bag is similar to that for 10 mm expanded polystyrene which is a widely used insulating and packaging material. The NCS thermal conductivity is slightly better than the bubblewrap bag and much better than that for corrugated paperboard. The excellent insulation properties of NCS result from its open framework and low density structure due to its high pore volume and consequent large number of air voids. When a PCM is incorporated into the NCS pores, the thermal conductivity of the NCS-PCM composite increases as the air is displaced by the PCM which has a higher thermal conductivity. This is shown for the NCS-PCM with RT2 and RT6 in the polythene and bubblewrap bags. Even though these thermal conductivity values have increased with the incorporation of the PCM into the NCS pores, they are substantially better than the value of 0.2 $Wm^{-1}K^{-1}$ quoted for RT2 and RT6 (Rubitherm Technologies GmbH, 2011). This clearly shows the advantage of incorporating these PCMs into the NCS material to provide the composite NCS-PCM products developed here.

4. Thermally buffered paperboard packages

The thermal buffering effectiveness of the NCS-PCM composite for chilled packaged food was tested using a paperboard package containing asparagus as a typical food that requires chilled temperatures of about 7-10 °C during storage and transportation to maintain optimum freshness. The package was a rectangular container (box) with dimensions 270 mm long x 200 mm wide x 180 mm high, constructed from 4 mm fluted paperboard and filled with 2 kg of freshly picked asparagus sealed in a polythene bag (Fig. 6). A series of six bubblewrap bags of the same dimensions as the walls, base and top of the package respectively, were prepared as removable and re-useable liners (Figs. 3 and 6). These were filled with the NCS-300PCM containing the *Rubitherm* RT6 alkane as the PCM to provide thermal buffering around 7-10 ^{o}C. Three different total amounts of NCS-300PCM collectively in the six liners of 200g, 400g and 600g being 10 wt%, 20 wt% and 33 wt% of the asparagus respectively were used. The results showed that the thermal buffering properties depended linearly on the amount of NCS-PCM as expected and hence only those detailed results for the 400 g quantity of NCS-PCM in the liners surrounding the paperboard package are presented here.

Fig. 6. Paperboard package with bubble wrap bag liners containing 400 g NCS-300PCM composite with RT6, and 2 kg of asparagus sealed in a polythene bag. The positions of the *Dallas Semiconductor* I-buttons used to measure the temperature / time profiles are shown by the arrows.

The thermal buffering properties of the paperboard package by itself, with the bubblewrap liners containing the NCS-300PCM, and also with the 2 kg of asparagus were each measured by recording the temperature / time profiles for the particular package configuration as it was cooled down in refrigerator to about 0 ^{o}C, then warmed up in the ambient environment to room temperature. The temperature / time profiles were recorded using *Dallas Semiconductor* I-buttons placed outside the package, inside the package on the inner side of the NCS-300PCM liner and at the centre of the package. When the package was filled with asparagus, I-buttons were placed throughout the package amongst the asparagus (Fig. 6). The temperature was recorded every 4 minutes. These temperature/time profiles are shown in Figs. 7-10.

The temperature / time cooling and heating profiles for the empty package without the liners or asparagus, measured on the outside, inside wall and centre of the package show the paperboard package walls provide no effective insulation and no thermal buffering capacity (Fig. 7). The inside of the package cools down and warms up at essentially the same rate as the outside temperature / time profile. There is a very slight lag in the heating up profile between the inside and outside of the package but this is negligible.

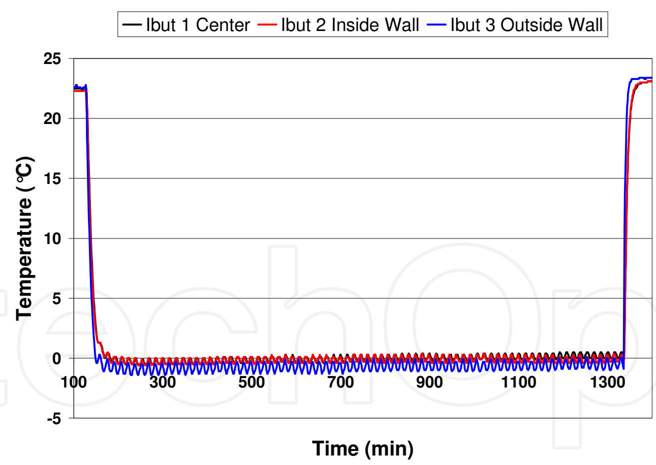


Fig. 7. The temperature / time cooling and heating profiles for the empty paperboard package.

The temperature / time profiles for the package with the empty bubblewrap liners (Fig. 8) show a small lag in the cooling and heating profiles for the inside wall and centre of the package when compared with the outside temperature, demonstrating a relatively small insulating effect of the bubblewrap liners. For comparison purposes a temperature of 10 °C which is at the higher end for chilled foods and a temperature of 7 °C which is more typical were chosen. These of course vary for particular foods but serve as a general guideline here to evaluate the thermal buffering performance of the paperboard package and the NCS-300PCM composite material. Using this approach, the heating up profiles show that it took about 8 minutes longer and 6 minutes longer for the inside temperature of the package to warm to 10 °C and 7 °C respectively, than for the time taken for the outside temperature to similarly increase. This shows that the bubblewrap liners do serve to increase the thermal insulation properties of the paperboard package, but not markedly so.

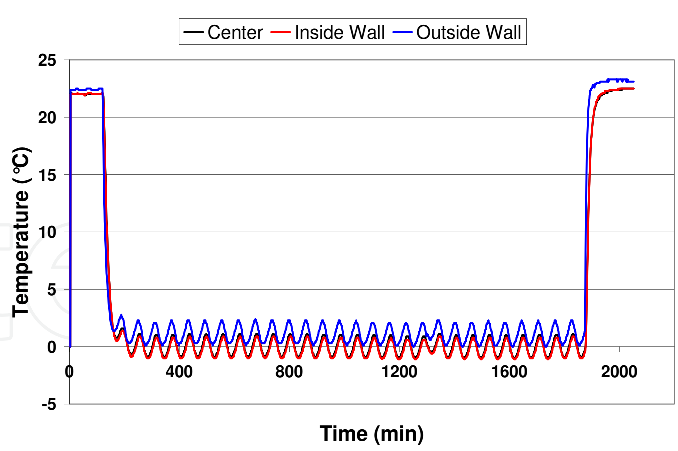


Fig. 8. The temperature / time cooling and heating profiles for the paperboard package with empty bubblewrap liners placed on the inside walls, base and top of the package.

When the bubblewrap liners collectively containing 400 g of NCS-300PCM composite were placed inside the package there was a distinct lag in the cooling down and heating up temperature / time profiles between the inside and outside of the package (Fig. 9). The cooling profiles for inside and outside the package are similar down to about 7 °C which is around the freezing point of the RT6 PCM. The freezing process takes additional (phase change) heat energy from the immediate environment and hence the cooling rate is slowed significantly. Below 7 ºC the cooling profile inside the package plateaus somewhat for about 100 minutes during which time the RT6 solidifies progressively and the cooling then continues at a slower rate until it reaches the outside temperature. On warming, the heating profiles for inside and outside the package are similar until a temperature of about 5 ºC is reached whereupon the RT6 starts to melt and this continues progressively up to about 10 ºC as the additional heat energy (phase change) required to melt the PCM must come form the immediate outside environment (Fig. 9). For comparison, the time lag for the inside temperature of the package with the bubblewrap liners containing the NCS-300PCM to reach 10 ºC is 97 minutes and to reach 7 ºC is 67 minutes. These are much longer periods and show that the 400 g of NCS-300PCM contained in the bubblewrap liners provides effective thermal buffering to the inside of the package for about 1-1.5 hours. The temperature / time profiles on the inside wall and the centre of the package are very similar showing the heat spreads quickly and uniformly through the inside of the box. Also, the small differences between the temperature / time profiles inside and outside the package between about 10 ºC and ambient temperature reflect the thermal insulation properties of the bubblewrap as noted above in Fig. 8.

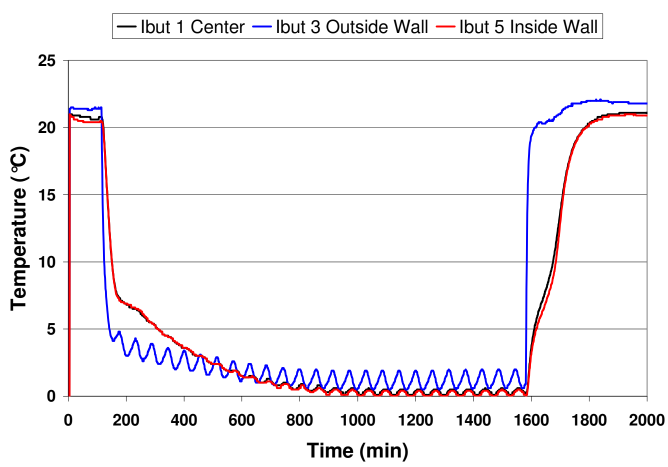


Fig. 9. The temperature / time cooling and heating profiles for the paperboard package with bubblewrap liners collectively containing 400 g of the NCS-300PCM composite and placed on the inside walls, base and top of the package.

Fig. 10 shows the temperature/time profiles for the paperboard package lined with bubblewrap liners collectively containing 400 g of the NCS-300PCM composite and placed on the inside walls, base and top of the package which is also filled with 2 kg of asparagus in a sealed plastic bag to ensure moisture retention. There is a noticeable difference between the profiles measured on the inside wall of the bubblewrap liner and the centre of the package resulting from the progressive absorption of the heat energy by the asparagus which is close to the wall of the package and the progressive flow of this heat energy through the asparagus to the centre of the package. This also shows the inherent thermal capacity for the asparagus itself. At 10 ºC the time lag in the heating up profile between the asparagus at the centre of the package and the outside environment is an impressive 550 minutes or over 9 hours. The time lag between the inside wall of the liner and the outside environment is 260 minutes or over 4 hours which is also very significant. At 7 ºC these time lags are 426 minutes and 171 minutes respectively. These large time lags collectively demonstrate considerable thermal buffering at such temperatures.

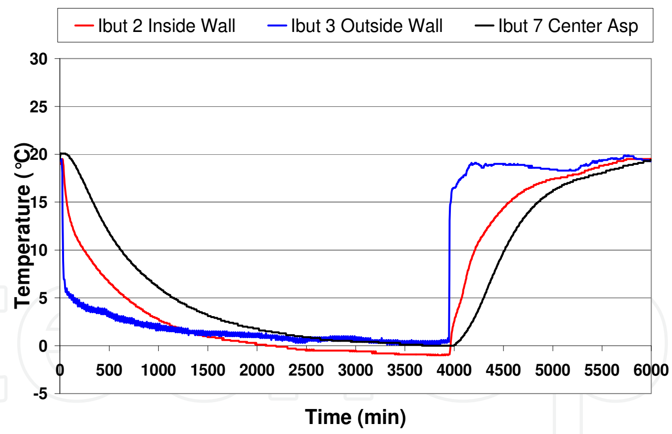


Fig. 10. The temperature / time cooling and heating profiles for the paperboard package with bubblewrap liners collectively containing 400 g of the NCS-300PCM composite and placed on the inside walls, base and top of the package and filled with 2 kg of asparagus.

The results show that this model system clearly demonstrates the thermal buffering capacity and effectiveness of our novel NCS-300PCM thermal buffering composite material when contained in bubblewrap liners. These flexible liners can easily be inserted inside a paperboard package containing temperature sensitive perishable food to maintain the temperature of the food at a suitably chilled level for about 4-9 hours even though the outside of the package has warmed up to higher temperatures during this time. This thermal buffering capacity is ideally suited to protect chilled and temperature sensitive food and other products against unwanted higher outside temperatures which are often encountered during the transportation and temporary en route storage from the coolstore to the international market place. The PCM which is incorporated in the high pore volume nano-structured calcium silicate host is selected such that the melting temperature is close to the optimum chilled temperature required for maintaining the freshness of the food. Hence, the use of flexible bubblewrap liners for containing the NCS-PCM is an ideal way to provide such required thermal buffering capacity to paperboard packages containing the food. These liners are readily recyclable and re-useable. The food, NCS-PCM liners and package are all cooled to just below the PCM melting point for a long enough time to ensure thermal equilibrium is reached and all the PCM is in the solid form. The package is then usually transported in a chilled container to the airport where may sit on the tarmac or in uncontrolled temporary storage for a few hours before being loaded onto an aircraft for international export. The NCS-PCM will prevent the perishable food contents of the package from warming up and spoiling as the PCM will slowly melt and absorb the unwanted ambient heat before it reaches the perishable food in the package. Once in further chilled storage, the PCM will solidify again ready to provide thermal buffering against the next unwanted transient temperature rise. The same system can be used to provide thermal buffering for other temperature sensitive materials such as medical supplies, where again the PCM is chosen to give the required temperature range.

5. Thermally buffered water containers

The NCS-PCM composite can also be used in maintaining the temperature of the contents of a package above that of ambient and to temporarily prevent or buffer the cooling rate of the contents of the package. This is useful for slowing the cooling of hot fast foods during delivery and in boutique applications such as maintaining the required water temperature for transporting tropical fish. In this application, a PCM with a suitably higher melting point is selected. The PCM is a solid up to the required buffering temperature range but has to be heated above the buffering temperature to ensure it is in the liquid phase initially. Upon cooling, the liquid to solid phase change releases heat energy to the inside of the package which buffers or slows down the cooling process, thereby enabling the above ambient temperature to be maintained in the package for a longer period of time. An example of the use of the NCS-PCM in the transportation of tropical fish where it is desirable to keep the water temperature slightly above about 18 – 20 °C is presented here. *Rubitherm* RT20 PCM which has a melting point and hence thermal buffering range of about 20 °C was chosen. This was heated to a liquid and worked into the pores of the NCS to a level of 300 wt %. The resulting NCS – 300PCM was similarly placed in bubblewrap liners. An 11 kg quantity of water was placed in a rectangular plastic container and heated to about 26 °C. I-buttons were placed in the centre of the water volume and also outside (beside) the container to record temperature / time profiles. The container was then placed in a room where the temperature was about 13 °C and the temperature / time cooling profiles were recorded over 2000 minutes as the container cooled down from about 26 °C to about 13 °C (Fig. 11). The temperature profile is characteristic of a typical exponential cooling curve.

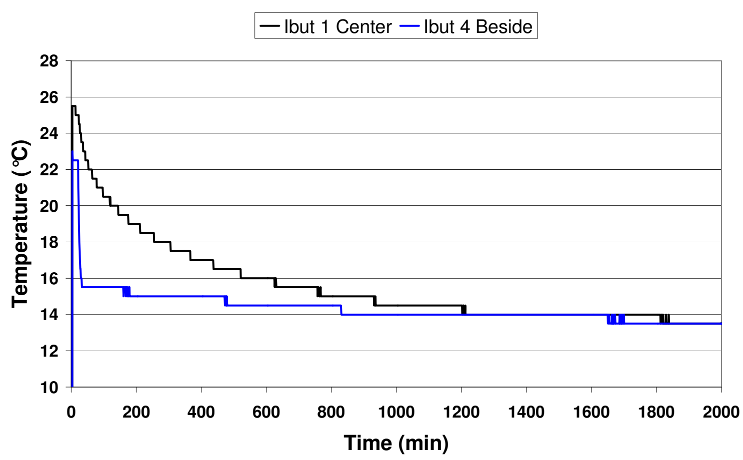


Fig. 11. The temperature / time cooling profile for an 11 kg volume of water in a rectangular plastic container.

The plastic container of water was then surrounded by 6 bubblewrap liners containing a total of 600 g of the NCS - 300PCM composite with RT20 to provide thermal buffering at about 20 °C. The water was again heated to about 26 °C together with the liners to make sure all the PCM in the NCS-PCM composite was in the liquid phase. The liners were then placed around the container and the temperature / time cooling profiles recorded (Fig. 12). A comparison of the cooling profile for the water with and without the NCS-PCM liners clearly shows that the rate of cooling when the container is surrounded by the NCS-PCM composite bubblewrap liners is significantly slower. (Figs. 11 and 12). This is particularly noticeable in the region from about 26 – 18 °C which spans the freezing point of the PCM. Here the PCM gives out heat on freezing which buffers the cooling rate of the water. The results show that the times taken for the water to cool to 18 °C and to 14 °C without the PCM liners are 265 minutes and 1220 minutes respectively. With the PCM liners these cooling times are much longer being 690 minutes and 1770 minutes respectively. The slower cooling rate achieved with the use of the NCS-PCM bubblewrap liners makes it possible to maintain water above a particular temperature for a longer period of time without additional external heating, as is required in the transport of hot food and tropical fish.

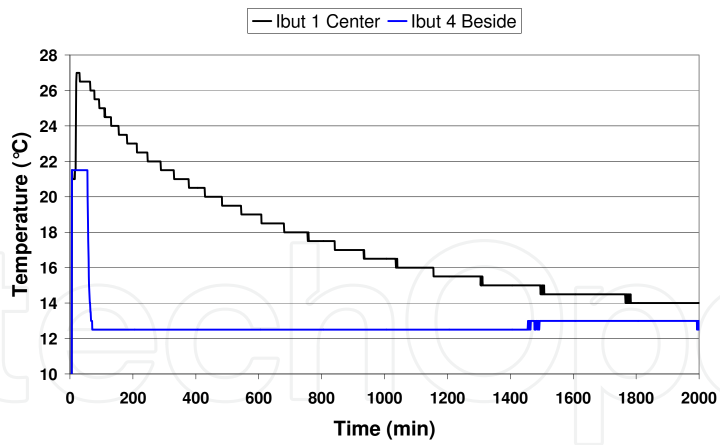


Fig. 12. The temperature / time cooling profile for an 11 kg volume of water in a rectangular plastic container surrounded by bubblewrap liners containing 600 g of RT20 NCS-PCM.

6. Conclusion

The research has shown that the proprietary nano-structured calcium silicate material can accommodate alkane phase change materials to form NCS-PCM composites which effectively contain the liquid phase PCM in the large NCS pore volume when the composite is at temperatures above the PCM melting point. Below the melting point the NCS-PCM contains solid alkane PCM in the solid NCS host and above the melting point the NCS-PCM contains liquid PCM in the solid NCS host, but the overall composite is still a dry free flowing powder. The optimum level of PCM was found to about 300 wt% PCM on a NCS basis. The NCS-PCM composite can readily be contained in bubblewrap plastic bags as liners inside paperboard packages to provide thermal buffering for the contents. It has been successfully shown that a NCS-PCM composite containing 300 wt% of *Rubitherm* RT6 alkane PCM in bubblewrap liners inserted into a paperboard package around the inside walls, can provide effective thermal buffering for temperature sensitive chilled food to prevent unwanted warming and hence food spoilage, during temporary storage and transportation enroute from the supplier to the international market place. For a package containing 2 kg of chilled asparagus and lined with bubblewrap liners containing 400 g of NCS-PCM using RT6 PCM, the inside temperature of the asparagus can be maintained below about 10 ^{o}C for some 4-9 hours even though the ambient temperature had warmed well above this. In a similar way the cooling rate of temperature sensitive contents such as hot food or tropical fish can be reduced by using these NCS-PCM liners in which the PCM has a higher melting point consistent with the preferred temperature for the contents of the package. The NCS-PCM composite material developed here and contained in easily useable and re-useable bubblewrap liners therefore has wide range of potential applications in the packaging industry for the safe transport of temperature sensitive and perishable produce and materials, below and above ambient temperature.

7. Acknowledgement

Financial support received from the NZ FRST RFI Grant C04X0401 as well as the work of Margaret Dodds and James Grindrod are gratefully acknowledged.

8. References

Amcor Kiwi Packaging Ltd. (2011) <www.amcor.com>

Carter Holt Harvey Packaging. (2011) <www.chhpackaging.co.nz>

Cool Pack Cold Chain. (2011) <coolpack.com/learning_center>

Dodds, M.M. (2009) The Development of thermally responsive Packaging Materials for Transporting Perishable Foods. *MSc Thesis* Victoria University of Wellington.

Farid, Mohammed M.; Khudhair, Amar M.; Razack, Siddique Ali K.; & Al-Hallaj Said (2004) A Review on Phase Change Energy Storage: Materials and Applications. *Energy Conversion and Management*, 45 (9-10) pp 1597-1615

Feldman, D.; Shapiro, M.M.; & Banu, D. (1986) Organic Phase Change Materials for Thermal Energy Storage. *Solar Energy Materials*, 13, pp 1-10

Hawlader, M.N.A.; Uddin, M.S.; & Khin, Mya Mya. (2003) Microencapsulated PCM Thermal-energy Storage System. *Applied Energy*, 74, Issues 1-2, pp 195-202

Johnston, J. H.; Borrmann, T.; & Mcfarlane, A. J. (2006) Nano-structured Silicate, Functionalised Forms Thereof, Preparation and Uses. *NZ Patent Specification No. 537747* ; *International PCT Application PCT/NZ2006/000003*

Johnston, James H.; & Dodds, Margaret. (2011) The Development of a Flexible Re-useable Thermal Buffering and Insulating Liner for Packaging Temperature Sensitive Products. *Appita*, 64(2), pp 153-157

Johnston, J.H.; Grindrod, J.E. & Dodds, M.M. (2007) Nano-structured Calcium Silicate Phase Change Material: A New Product for Thermal Buffering In Packaging. *Proceedings of the 61st Appita Conference*, pp 366-369, Brisbane, May 2007

Khudhair, Amar M.; & Farid, Mohammed M. (2004) A Review on Energy Conservation in Building Applications with Thermal Storage by Latent Heat Using Phase Change Materials. *Energy Conversion and Management*, 45 (2), pp 263-275

Plastics New Zealand (2011) <www.plastics.org.nz>

Powell, F.J.; & Matthews, S.L. (1987) Thermal Insulation: Materials and Systems, ASTM Committee C-16 on Thermal Insulation. *Published by ASTM International, 1987 ISBN 0803104936, 9780803104938,* 755 pages

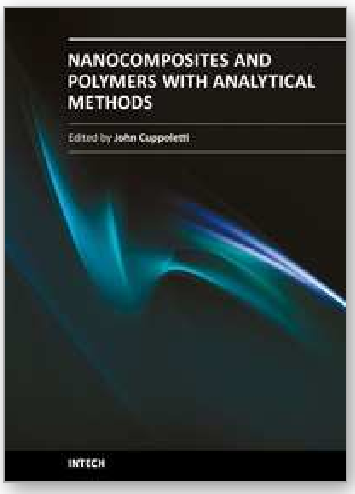
Rubitherm Technologies GmbH. (2011) <www. Rubitherm.com>

Schossig, P.; Henning, H.-M.; Gschwander, S.; & Haussmann, T. (2005) Micro-encapsulated Phase-change Materials. Integrated into Construction Materials *Solar Energy Materials and Solar Cells*, 89, pp 297-306

Tyagi, Vineet Veer; & Buddhi, D. (2007) PCM Thermal Storage in Buildings: A State of Art. *Renewable and Sustainable Energy Reviews*, 11, pp 1146-1166

Zalba, Belén; Marín, José; Cabeza, Luisa F.; & Mehling, Harald (2003) Review On Thermal Energy Storage With Phase Change: Materials, Heat Transfer Analysis and Applications. *Applied Thermal Engineering,* 23, pp 251–283

Zhang, Yinping; Zhou, Guobing; Kunping, Qunli; Zhang, Lin; & Di, Hongfa. (2007) Application of Latent Heat Thermal Energy Storage in Buildings: State-of-the-art and Outlook. *Building and Environment*, 42, pp 2197-2209



Nanocomposites and Polymers with Analytical Methods
Edited by Dr. John Cuppoletti

ISBN 978-953-307-352-1
Hard cover, 404 pages
Publisher InTech
Published online 09, August, 2011
Published in print edition August, 2011

This book contains 16 chapters. In the first part, there are 8 chapters describing new materials and analytic methods. These materials include chapters on gold nanoparticles and Sol-Gel metal oxides, nanocomposites with carbon nanotubes, methods of evaluation by depth sensing, and other methods. The second part contains 3 chapters featuring new materials with unique properties including optical non-linearities, new materials based on pulp fibers, and the properties of nano-filled polymers. The last part contains 5 chapters with applications of new materials for medical devices, anodes for lithium batteries, electroceramics, phase change materials and matrix active nanoparticles.

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821