Nanostructured Calcium Silicate Phase Change Materials for Thermal Buffering in Packaging Applications

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ABSTRACT

This paper reports the development and use of a nanostructured calcium silicate – phase change material to provide thermal buffering in packaging applications. Nano-structured calcium silicate (NCS) is a proprietary new material comprising nanosize platelets stacked together in an open framework structure with a particle size of about 1-5 microns. The material has a high pore volume and hence liquid absorbency of up to about 500 g oil $100g^{-1}$ silicate. Phase change materials (PCMs), typical examples of which are alkane paraffins, absorb and release heat energy (latent heat) associated with the liquid-solid transition at their melting point. The major practical problem of containing the liquid phase on melting has been overcome by incorporating these alkane PCMs into the porous NCS structure in amounts of about 3-4 times the weight of the NCS. The resulting NCS-PCM composite remains as an easily useable powder above the alkane melting point and can be readily incorporated into packaging materials to provide heat buffering properties of about 110 kJ kg^{-1} of NCS-PCM composite. This has been demonstrated by filling plastic bubblewrap bags with a NCS-PCM composite containing a *Rubitherm RT6* paraffin as the phase change material with a meltimg point of about 6 ºC, and using them as liners in a paperboard package. As the package is cooled the PCM in the NCS-PCM-*RT6* liner solidifies and as the package is warmed up the PCM melts. Hence the NCS-PCM-*RT6* liner maintains the inside temperature of the package below about 10 ºC for about 110 minutes longer than without the NCS-PCM-*RT6* thermal buffering liner.

Keywords: phase change materials, nano-structured calcium silicate, thermal buffering, packaging, geothermal.

1 INTRODUCTION

This paper presents the formation and use of a novel composite nanostructured calcium silicate phase change material with significant thermal buffering capacity for use in thermally responsive packaging applications.

Phase change materials (PCMs) provide the opportunity for passive heat storage and release across a liquid-solid phase transition, due to the associated latent heat. The energy required to melt the PCM solid can be absorbed from the warmer surroundings and stored in the liquid phase. This can released back to the environment when the liquid solidifies. The ice-water phase change can store and release some 330 kJ kg^{-1} of thermal energy at 0 ºC. Alkane (paraffin wax) materials have latent heats of about 160-200 kJ kg^{-1} with the melting point being determined by the hydrocarbon chain length, typically ranging from about 0-100 ºC. Inorganic salts with their water of crystallization e.g. $Na_2CO_3.10H_2O$ can function as a PCM due to the release and recapture of the water of crystallization in a closed environment. The energy for this transition is 247 kJ kg^{-1} at the crystallization temperature of about 33 ºC for $Na_2CO_3.10H_2O$ [1-3]. However, this is difficult to use in practice as there must not be any loss of water from the system on melting since the decahydrate will not reform on freezing.

The technical challenge in using PCMs is that of containing the liquid phase after melting. One method is to contain the liquid PCM in micro polymer capsules, which are incorporated into the end use composite material [4]. The robustness of the capsules and binding them into the host material to form the composite can be an issue.

Nanostructured calcium silicate (NCS) is our proprietary material [7]. It comprises nanosize platelets stacked together in a unique open framework structure forming discrete particles of about 1-5 microns in size (Figure 1). It is prepared from either a sodium silicate source or geothermal water under appropriate conditions. The composition can be changed according to the preparation conditions and can be generally represented as being $CaSiO_{3-x}(OH)_{2x}.H_2O$, where x is typically about 2. We have developed a novel approach and technology to produce NCS from the dissolved silica in separated geothermal water which is present at supersaturation levels following steam flashing for electricity production. This desirably obviates the worldwide problem of silica deposition in pipes, heat exchangers and reinjection wells carrying this water, in geothermal resource utilisation for electricity production [5-7]. The material has a high pore volume with a consequent high liquid absorbency of up to about 500 g oil $100g^{-1}$ solid (ASTM Oil Absorption test), and a high surface area of up to about 500 m^2 g^{-1}, depending on the preparation method [7].

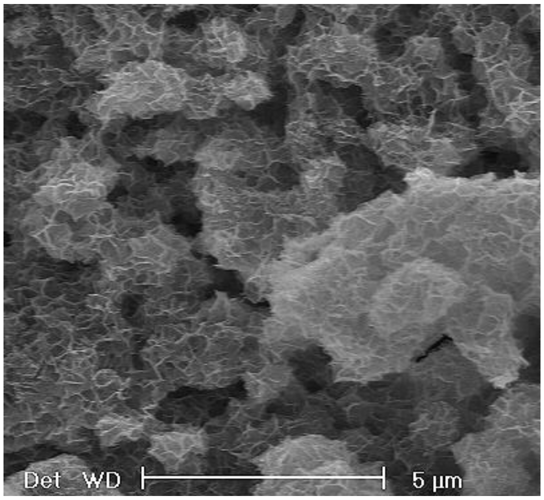

Figure 1: A scanning electronmicroscope image of nanostructured calcium silicate.

This NCS material with its high pore volume provides an innovative approach to the technical problem of containing the liquid paraffin wax following melting in a PCM, by incorporating it into the highly porous matrix of the nanostructured calcium silicate. Typically 300-400 wt % PCM can be accommodated in the matrix. Above the melting point the liquid PCM phase is fully contained in the pores of the nanostructured calcium silicate with the overall NCS-PCM composite remaining as a solid powder. This powder can be incorporated into packaging and other materials such as those used in construction, to provide thermal buffering properties of about 110 kJ kg^{-1}. The effective temperature range for the thermal buffering is determined by the melting point of the PCM used.

2 METHODOLOGY, RESULTS AND DISCUSSION

A range of NCS-PCM composites utilising *Rubitherm RT* paraffin PCMs [8] with melting points of about 6, 20 and 25 ºC respectively, have been prepared by blending the liquid paraffin into the NCS powder to produce a material that is still a solid powder in nature but with the pores being largely filled with PCM. This nicely captures the liquid PCM yet provides a composite NCS-PCM material that has the handling properties of a powder.

Differential scanning calorimetry was used to measure the heat energy absorbed and released by a NCS-PCM composite with these Rubitherm PCMs respectively, for their solid-liquid melting endothermic phase change and their liquid-solid freezing exothermic phase change. The measurements were recorded over two cycles of heating and cooling between -10 ºC to +50 ºC. An example is shown for the NSC-PCM composite with the *Rubitherm RT25* PCM in Figure 2. This shows that the endothermic and exothermic phase changes involve the absorption or release of about 110 kJ kg^{-1} for the NCS-PCM composite. The Rubitherm data sheet lists the phase change energy for *RT25* as 170 kJ kg^{-1}. Hence the NCS-PCM composite has a significant thermal buffering capacity.

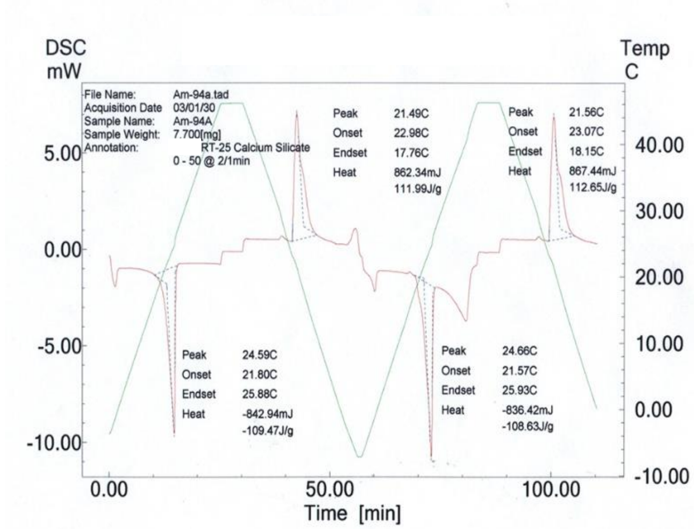

Figure 2: The Differential Scanning Calorimetry curves for NCS-PCM-*RT25* composite recorded for two cycles of heating and cooling over the temperature range from -10 ºC to +50 ºC showing the endothermic and exothermic peaks at about 25 ºC, corresponding to a phase change energy of about 110 kJ kg^{-1} for the composite.

Samples of a NCS-PCM composite with *Rubitherm RT6*, *RT10* and *RT25* were prepared and incorporated as a functional phase change filler into fluted paperboard, sealed plastic bags and sealed bubblewrap plastic bags to provide various configurations of thermal buffering liners and their thermal buffering properties measured.

The liners with the lower melting point PCMs could be placed inside packages that are used to transport temperature sensitive perishable products, notably those relating to the food and medical industries. In the transportation of such products it is usually important to ensure the temperature of the product does not increase above a certain value, at which its quality is adversely compromised or irreparably damaged. Ice is often used as the PCM. However its use is limited to the buffering temperature of 0 ºC corresponding to the ice-water phase change. For many food products 0 ºC is too low and only a chilled temperature rather than a freezing temperature is required. This is particularly true for the transportation of fresh vegetables, dairy and live shellfish products where such a chilled temperature is required. The use of the paraffin type PCMs contained in the NCS host enables a range of buffering temperatures to be achieved, either below of above the ambient temperature.

In this packaging application, the thermal buffering properties, notably the heat energy associated with the phase change can be absorbed and released. This enables the internal temperature of the package to remain close to the buffering temperature for extended periods, much longer than can be achieved by the insulation alone, even though the outside temperature of the package is higher.

A versatile application of the use of NCS-PCM with *Rubitherm RT6* which has a melting point of about 6 ºC, as a thermal buffering agent in packaging is presented here. This buffering temperature was chosen as it is applicable to the transportation of live shellfish wherein the temperature has to be kept below about 10 ºC to keep them alive. For this, a NCS-PCM composite was prepared by blending *Rubitherm RT6* with NCS in the weight ratio of 3:1 to produce a free flowing NCS-PCM powder. This was then loaded into plastic bubblewrap bags which were sealed and then used as liners in a paperboard packaging box.

The thermal performance of the package was characterised by recording the temperature at various points inside and outside the package, as it was cooled from ambient temperature down to about 2 ºC in a refrigerator over about a day, and then taken out and allowed to warm back up again to ambient temperature of about 22 ºC. This procedure was carried out for the paperboard package itself and then again with the NCS-PCM-*RT6* filled bubblewrap plastic bag liners placed against the inside walls of the package. The temperatures were recorded using Thermochron ibuttons placed on the outside and inside walls of the package. In addition, three ibuttons were placed on the inside walls of the NCS-PCM-*RT6* bubblewrap plastic bag liners when these were placed against the paperboard walls inside the package. The temperature profiles recorded by each of these ibuttons as the package was cooled down and then allowed to warm back up are presented in Figure 3.

Ibutton 4 is the temperature profile of the outside of the package and ibutton 3 is that for the inside paperboard wall of the package. The temperature profiles show there is negligible difference between the outside and inside temperatures and hence that the walls of the paperboard package do not provide any effective insulation. The on-off cycling of the thermostat in the refrigerator is evident when the package temperature cools below about 5 ºC (Figure 3).

Ibuttons 1, 2 and 5 which were placed on the inside walls of the NCS-PCM-*RT6* filled bubblewrap plastic bag liners showed similar temperature profies, but quite different from those of ibuttons 3 and 4 above. These show that it takes about 40 minutes longer for the volume space of the package with the thermal buffering liners inside the walls to cool down to about 7 ºC, which demonstrated the better thermal insulation properties of the bubblewrap bag and of the NCS (Figure 3). As cooling proceeds from 7 ºC to 6 ºC the rate of cooling slows markedly and is nearly constant with time, as a result of the *RT6* PCM solidifying and releasing the latent heat energy from this phase change into the system. From here the temperature profiles show a slow cooling down to the lowest temperature of the refrigerator. When the package was taken out of the refrigerator, the heat up time to reach about 5 ºC is about 40 minutes longer than that without the liners. Between 5 ºC and 10 ºC the shape of the temperature profiles clearly show the effect of heat energy being absorbed from the surroundings to provide the latent heat required to melt the PCM in the solid to the liquid phase. As a result the time taken for the inside of the package to reach 10 ºC is about 110 minutes longer than that without the NCS-PCM-*RT6* filled bubblewrap plastic liner being used. This result clearly demonstrates the effectiveness of the NCS-PCM composite as a thermal buffer in maintaining the inside environment of the package at a lower temperature than that of the ambient temperature (Figure 3).

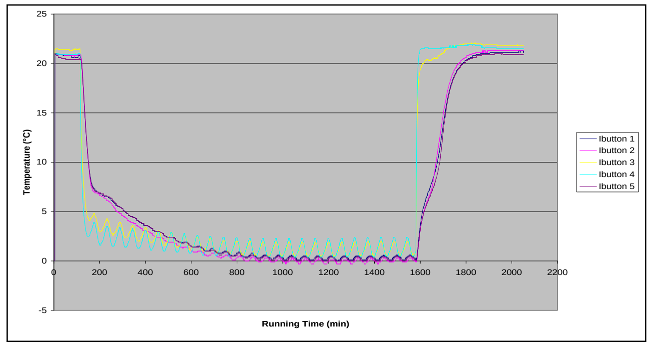

Figure 3: Temperature profiles of a paperboard package lined with bubblewrap plastic bags filled with NCS-PCM-*RT6* thermal buffering composite, showing thermal buffering properties. The vertical profiles show the temperature outside the package (ibutton 4) and on the inside wall (ibutton 3). The stepped profiles show the temperature inside the package on the inside walls of the NCS-PCM-*RT6* liners (ibuttons1, 2, 5).

The results show that a paperboard package by itself had little thermal insulation capacity and that the inside temperature and hence the contents of the package quickly equilibrated with the outside temperature. However, when liners containing the NCS-PCM composite were introduced into the package, improved insulation and significant thermal buffering capacity were achieved. For example, a NCS-PCM-*RT6* liner with a buffering temperature of 6 ºC enabled the inside temperature of the package to remain below 10 ºC for about 110 minutes longer than the package without the NCS-PCM, as the package was warmed to ambient temperature (Figure 3).

3 CONCLUSION

The research has shown that the proprietary nano-structured calcium silicate can accommodate alkane paraffin phase change materials to form NCS-PCM composites which effectively contain the liquid PCM in the large NCS pore volume when the composite is at temperatures above the PCM melting point. The composite remains as a powder which can be handled easily and incorporated in plastic liners or other containments, that can then be readily inserted into packaging or building materials to provide them with thermal buffering capacities. This has been demonstrated by filling plastic bubblewrap bags with a NCS-PCM composite containing the *Rubitherm RT6* paraffin as the phase change material with a meltimg point of about 6 ºC, and using these bags as liners in a paperboard package. As the package is cooled the PCM solidifies and as the package is warmed up the NCS-PCM-*RT6* liners maintain the inside temperature of the package below about 10 ºC for about 110 minutes longer than without the NCS-PCM thermal buffering liners.

This is one of a number of applications of this proprietary nanostructured cacium silicate material prepared from either sodium silicate or geothermal water.

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