Development of Micro-Encapsulated Phase Change Materials

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Abstract

Phase change materials (PCM) are often used as heat storage media, providing heat buffering to thermal systems. Conventional PCMs have a number of problems, some of which are being addressed by researchers. Two of the more serious problems are the poor thermal conductivity of most PCM materials and that the PCM must fixed in place by its physical size and solid nature. The authors propose a microencapsulated PCM that is suspended in a solution, thus creating a fluid of very high specific heat capacity over a narrow temperature range. Microencapsulation has previously been applied to solid materials such as wallboards and in the food and pharmaceutical industries, but seldom as heat transfer fluids Using this technique, not only is a high surface area to volume ratio possible, but the heat store is effectively mobilised. Furthermore, the stored heat creates essentially isothermal conditions where they are required. This paper discusses early research into the manufacture of such material using the complex coacervation technique and some of the resultant PCM colloidal solution properties.

1. INTRODUCTION

Energy storage is undertaken in an effort to bridge the mismatch that exists between supply and demand. One way of storing this resource is through *thermal* energy in the form of heat, and can be characterised by the change in internal energy of the absorbent material. Three basic thermal energy storage (TES) strategies exist. They are sensible heat storage (SHS), latent heat storage (LHS) and thermo-chemical heat-transfer (Sharma et al. 2004).

Phase change materials (PCMs) provide a means by which latent heat can be stored and released with minimal temperature change to the TES. For practical purposes, the phase change between liquid and gas is not often used since it is associated with a large increase in volume (and hence a low gaseous energy density). All further reference to PCM will regard the melting phase change which is used as an example to demonstrate heat capacity of the LHS (eqtn 1). Here, a PCM is subject to heating from $T_{initial}$ to T_{final}, spanning its melting temperature, T_{melt}.

$$Q = m\left[c_{p\,solid}\,(T_{melt} - T_{initial}) + a_m \Delta h_m + c_{p\,liquid}\,(T_{final} - T_{melt})\right] \tag{1}$$

where the percentage PCM melted, or state of charge is denoted by a_m and the heat of fusion denoted by Δh_m.

There are three broad categories for PCM based stores; organic, inorganic and eutectic compounds (figure 1).

The two most widely used organic phase change materials are paraffin waxes and fatty acids. The latter include esters, alcohols and glycols. Perhaps the most useful PCMs are the paraffin waxes. Paraffins are constructed of a combination of straight chain hydrocarbons. Their chemical inertness, commercial availability and low cost have made them the focus of a large number of research studies and practical applications (Hasnain, 1998).
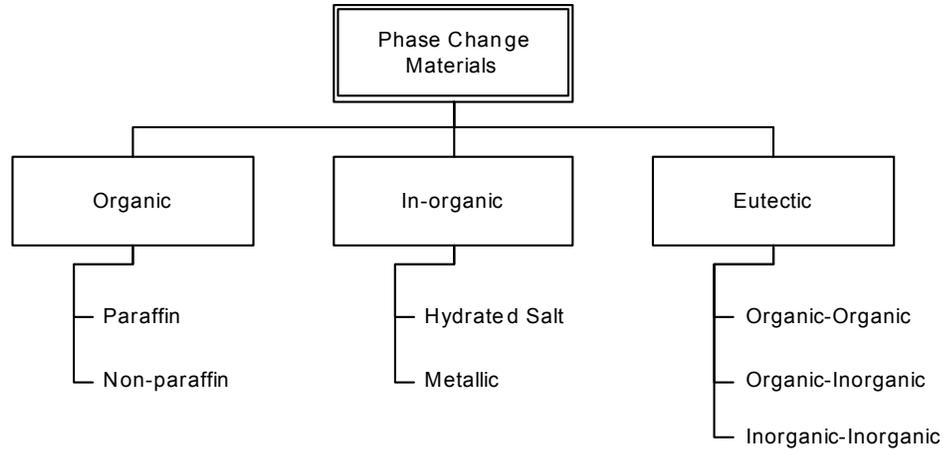
Figure 1: Phase change material classification

Sharma et al. (2004) highlight a major drawback of paraffin PCMs to be their low thermal conductivity upon cooling. Many researchers have attempted to overcome this problem by impregnating the material with conductive material, thus accepting a penalty in heat storage capacity for improved heat transfer rates into the material (Mehling et al. 2000). A further potential hazard of waxes is their flammability.

The PCM itself must be isolated from the system in which it operates, or at least contained in the liquid phase. Encapsulation is the term used to describe the method of isolation of the PCM. In this paper, we present a microencapsulation system for PCM in which the PCM material is broken up into small particles and each particle is coated in a protective layer so that the material does not disperse in the liquid phase. The predominant focus of PCM research has been concerned with energy industry in a search to limit the effect of solar energy intermittency (Hawlader et al. 2002, Farid et al. 2004). Zalba et al. (2003) state that such technology can be applied to the protection of temperature sensitive materials in the medical and food industries, while Peng et al. (2004) provide a study of µPCMs in the use of cooling electronic circuitry. A rapidly developing field of research into µPCM technology has been integration into building materials (BASF Micronal® is a good example) and in high-end military and space technology textile applications (BASF 2005).

In each of these cases, the PCM or uPCM has remained spatially static within the application. One might envisage such particles mixed with a carrier fluid to form a phase change slurry (PCS). A slurry of uPCM would be a good heat transfer fluid. In such cases, a heat exchanger might benefit from having one fluid acting in an essentially isothermal manner. A solar collector might benefit from lower collector temperatures using a PCS circulating fluid (Hawlader et. al 2002, Yamagishi et al. 1999). One might consider ice slurries used for air conditioning thermal stores as an example of a non-encapsulated PCM slurry.

The PCS approach has a number of benefits. Firstly, it provides an alternative means of increasing the surface area available for convective heat transfer to the surface of the PCM encapsulation and shorter heat conduction paths to the core of the PCM. Secondly, the PCM can be made mobile within the system. Not only does this allow the potential distribution of the thermal store, but also allows the design of heat transfer fluids of high heat capacity. This has potential benefits for the design of heat exchangers, solar collectors and other devices utilising heat transfer.

2. THE MAKEUP OF UPCM

Microencapsulation implies that the PCM material must first be reduced to small particles and that these particles must then be coated in a way that the liquid phase PCM is contained. Chemical and mechanical processing methods, as well as post-production techniques, provide means to alter the final uPCM particle properties.

In this case, production of the micro-encapsulated particles was undertaken using a chemical process known as complex coacervation or associative phase separation. This technique has been well documented in the pharmaceutical and food industries as an organic and environmentally friendly means of encapsulation (Baziwane & He 2003, Chilvers & Morris 1987, Densai & Park 2005, Schrooyen et al. 2001, Tsung & Burgess 1997, Ofner et al. 2001, Saxena et al. 2005). Chemical processes have proven superior to mechanical processes because of their ability to achieve smaller and more consistently sized particles.

A paraffin wax with a melting temperature of 43ºC and latent heat capacity of 186 kJ/kg is used in this preliminary study. A range of natural and synthetic coating materials may be used to envelop the core PCM. Our selection was based on previous research into the coacervation technique.

Four main complex coacervation theories have been developed over the past 60 years. The Voorn-Overbeek theory applied to the gelatin/acacia system is used in this work (Overbeek & Voorn 1957, Schmitt et al. 1998). Before discussing coacervation in detail, it is appropriate to revise the properties of colloidal systems.

3. THEORY OF COLLOIDAL CHEMISTRY

A colloidal system involves the suspension or dispersion of one or multiple phases distributed throughout another. The dispersed or suspended component is commonly known as the discontinuous phase, while the other in known as the continuous phase. When a micro-encapsulated phase change material (µPCM) is suspended within a fluid it can be considered a dispersion phase in a colloid system. Distilled water makes up the continuous phase in our system.

A colloidal solution is commonly achieved by two processes; dispersion and condensation (Hunter 1993, Tauer 2001, Tadros 1987). Dispersion or comminution involves breaking a larger bulk material into smaller particles. Considerable mechanical agitation is required to disperse insoluble wax material within a continuous phase (distilled water) through the use of a mechanical mixer. Condensation processes are dependent upon particles being coated through a chemical reaction, involving a nucleation and growth stages.

The uPCM shell material, described in the Voorn-Overbeek theory, is a combination of two organic compounds; a protein and a glycoprotein / saccharide mixture. The condensation process by which these two compounds react is known as polymerisation, involving the joining of monomers (Callister 2000).

Colloidal systems are either lyophilic or lyophobic (Hunter, 1993). This distinction categorises the behaviour of the colloid system in terms of its ability to redisperse the discontinuous phase within a continuous phase (or solvent) after being left to dry.

A lyophilic colloid can easily be redispersed as it has the capacity to absorb a dispersion medium. A suitable solvent is usually used, as this can easily be "taken up" by the dry colloidal product. This process may take some time, however it will eventually form a stable colloid solution once again.

Lyophobic colloids often require addition of external energy to the system in order for the original state to be restored. This energy most commonly takes the form of mechanical agitation, however other methods such as ultrasound have also been documented (Tauer 2001). The two coating products associated with this theory are gelatin (protein) and acacia (glycoprotein), which are lyophilic and lyophobic respectively

3.1. System Stability

The two main concerns of colloid production for this application are its physio-chemical behaviour with respect to stability, as well as the system's mechanical behaviour and flow dynamics.

A micro-encapsulated product is only useful if it remains in its intended state after a prolonged period of time. If the uPCM particles begin to settle within the continuous phase or group together into flocs,

undesirable fluid and heat transfer characteristics will become evident, indicating instability. Achieving stability in the dispersion of one phase within another is difficult, and must be performed within a controlled environment.   Many factors determine the interaction between the phases including electrostatic forces, steric forces and van der Waals bonds (Bijsterbosch 1987). External influences, such as temperature and pressure, can also cause changes in the colloid's arrangement. One of the most common theories of colloid stability is the DVLO theory, based upon the attractive and repulsive nature of colloids (Pashley & Karaman 2004).

DVLO Stability Theory
Characterisation of these stability factors led to a theory devised by four scientists during the early 1940s. Deryaguin, Landau, Voorn and Overbeek collaborated to produce the DVLO theory. It is this theory that states that the combination of electrostatic repulsive forces and Van der Waals attractive forces determine the kinetic stability of a colloid system on a macroscopic level (Tiberg et al. 2001). Resistance to clumping is maximised when the inter-particle distance provides the highest DLVO potential (figure 2).
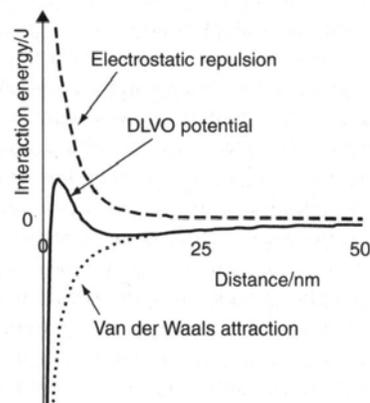

Figure 2: Attractive and repulsive forces resulting in the DVLO interaction for spherical particles

Electrostatic charges are a predominant cause of particle instability by clumping. One way to overcome these electrostatic forces within a colloid suspension is to create a protective layer around the solid particle. This barrier prevents electrostatic interaction between adjacent particles and is commonly known as steric stabilisation.

This form of stabilisation is possible through absorbing monomers onto the surface of the particle in the form of a polymer or through the use of surfactants, which are also known as dispersing or stabilising agents (Hunter 1993).   The structure of the molecules allows them to be absorbed at the interface between two phases, such as between the water and the coating material of a μPCM particle. Surfactant molecules consist of a *head* group (hydrophobic) and a *tail* group (hydrophilic), which allows one end to be absorbed within the hydrophilic compound with the other is exposed acting as a barrier at the water interface (Aveyard 1987).

The stability implication means that post manufacture treatment of the uPCM may be required. Our first few batches showed a tendency to flocculate and a surfactant will be used subsequently.

3.2.   PCS Viscosity

If a colloidal suspension such as PCS is to be pumped around a hydraulic circuit, it is important to quantify the viscosity of the PCS. Einstein developed a useful equation for the viscosity of a system of suspended spherical particles within a liquid continuous medium, stating that the viscosity of the system will increase in proportion to the volume fraction (Φ) occupied by the particles (Catherine Lam et al. 2001).

$$\frac{\mu}{\mu_0} = 1 + 2.5\phi \qquad\qquad (2)$$

In equation 2, μ_o represents the viscosity of the suspending medium. This relationship can be used to determine the viscosity (or particle volume fraction) of a solid-liquid dispersion provided the system is neutrally buoyant and homogeneous (Hunter 1993). Our product PCS was approximately neutrally buoyant but not homogeneous.

There are three flow classifications for slurry flows in pipes; homogenous, heterogeneous and saltation. A homogenous fluid can be characterised by its high solid volume percentage, small particles in comparison to the size of the pipe which it is travelling though, and relatively uniformly dispersed through the continuous medium (Darby 1986). Such a system can be modeled as a Newtonian fluid, with a higher viscosity due to the introduction of a dispersed solid phase.

Pashley & Karaman (2004) describe three primary influences on fine solid particles in a continuous medium; gravitational forces highlighting density variations, continuous phases' viscosity and the *natural* energy of particles. The latter of these has been described in detail, however the first two influences are evident in a heterogenous flow situation. Over time, settling of particles will become a problem due to differences between the discontinuous and continuous phase densities. Ideally (such as in the homogenous case), identical densities will result in neutral buoyancy. This implies that the viscosity of the continuous medium is the defining factor in heterogenous flow characterisation. If the fluids viscosity is high enough, then it will resist particles moving downwards under gravitational forces. On the other hand, low viscosity will result in particles settling resulting in a heterogeneous flow regime. The complexity associated with optimising the viscosity of continuous medium is increased with inconsistent particle size.

The third flow behaviour which is common in solid-liquid dispersion is known as saltation (Darby 1986). Saltation results from multiple particles within the fluid body grouping on the edges of the pipe, thus partially blocking the flow. Agglomeration due to DVLO instability will contribute to the severity of the blockage.

We propose to make the PCS more homogeneous by adding surfactant to the product to reduce its tendency to clump. We would also conclude that it is important to control the particle size distribution during the dispersion process.

4. COMPLEX COACERVATION

The four known theories of complex coacervation where developed mid way through last century. There are two initial pioneering theories of Voorn-Overbeek and Veis-Aranyi, with Nakajima, Sato and Tainaka completing further theories more recently (Schmitt et al. 1998). Some criticism has been raised over the accuracy of any and all of these models, as their qualitative and quantitative findings partly contradict each other (Burgess 1990). This project uses the Voorn-Overbeek theory and its capacity for production of a biopolymer coating material.

The studies of Bungresberg into the gelatin/acacia coacervate were the foundation of the Overbeek and Voorn theory that found that the coacervate shell around a solute molecule occurred spontaneously (Schmitt et al. 1998). That is, once the correct environmental conditions were created for the coacervation to occur, such as temperature and pH level, the attractive forces between biopolymers (predominantly electrostatic) would supersede the repulsive ones.

The term complex coacervation was introduced by Bungresberg and Kruyt in a paper published in 1929 (Overbeek & Voorn, 1957). The process involves mixing various raw materials under a high shear, causing them to aggregate within a controlled environment. Controlling the experimental environment is critical in order to achieve a successful result using complex coacervation. The two most critical parameters are temperature and pH level. By reducing the temperature of the system, coacervation will increase due to hydrogen bonding between polymer molecules. At higher temperatures, lyophobic interactions such as covalent bonding are encouraged, which can change the structure of polymers

(Schmitt et al. 1998). The result is colloid rich and colloid poor phases that can be separated using an appropriate filtration method. Both centrifuging and grate filtering have been tried with moderate success.

Gelatin and acacia gum are the most common colloids studied under the Voorn-Overbeek coacervation theory and have been well documented in previous literature (Overbeek & Voorn 1957, Hawlader et al. 2002, Hawlader et al. 2003, Mayya et al. 2003 and Densai & Park 2005).

Figure 3: Gelatin (left) and Acacia (right) used for complex coacervation

Both are proteins composed of complex organic molecules of high molecular weight, however they vary in the way in which their amino acids are attached. Due to their high molecular weight they can both be considered *polyelectrolytes*. Gelatin is a hydrophilic protein commonly containing carbon, hydrogen, oxygen, nitrogen, and sometimes sulphur (Baziwane & He 2003). Acacia is hydrophobic and can be classified as a *glycoprotein* consisting multiple proteins as well as carbohydrate components.

The ability of the gelatin and the acacia to combine to form a uniform coating material around the wax droplets is dependent upon the isoelectric point (pI) of gelatin. At pH values above 4.8 the gelatin molecules are positively charged, repelling the positively charged acacia molecules and hence resulting in the two colloids not aggregating. If the pH of the solution is reduced to below this critical value, the gelatin will become negatively charged and attract with the acacia molecules. Therefore, electrostatic forces are being utilised to draw the lyophilic and lyophobic components together.

The ultimate stability and mechanical integrity of the coating material can be increased through cross-linking the by-products of the surrounding shell material. Cross-linking is a method use to branch chemical and physical junctions within polymeric materials (Roylance 1996). This phenomenon has been studied for several decades, and one of the most common cross-linking agents used in association with gelatin is formaldehyde (Hawlader et al. 2003, Densai & Park 2005, Uddin et al. 2002). Hardening of the coating material is caused by the formaldehyde connecting with the protein chains within the gelatin (Tengroth et al. 2005).

As mentioned earlier, the use of a surfactant can assist in achieving system stability. A surfactant (such as Sodium dodecyl sulphate or SDS) has not yet been used as other researchers have reported that the suspension was stable without its presence (Mayya et al. 2003).

4.1.   Development of the Coacervation Methodology

The formation of coacervates is dependent upon the methodology used and controlled environment in which this process must be performed. Parameters such as material quantities, temperatures, pH level, shear rate and mixing time all contribute to the processing environment.
The main steps in making a uPCM are:
1. Dispersion of bulk PCM in a carrier fluid (figure 4) using high shear mixing
2. Processing to obtain the desired particle size range
3. Coating the particles with coacervates
4. Cross linking to strengthen the particle coating
5. Filtering to isolate the product
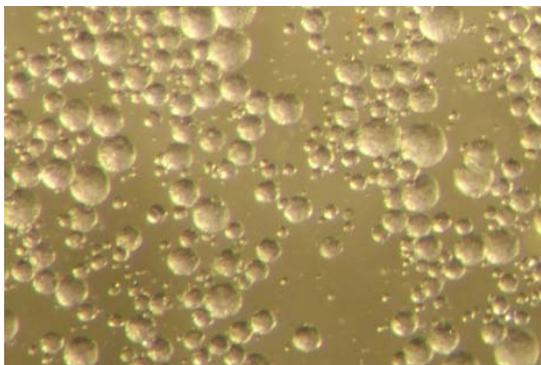6. Drying the product (if necessary)

Figure 4. Uncoated wax particles

The recipe for manufacture of uPCM is still under development and is not published in this paper. We have made a small number of batches, each taking several hours to complete. The thermal and mechanical properties are being evaluated at the time of writing of this paper. It should be noted that there are a large number of variables in this process and the refinement of this technique is a high priority.

5. STRUCTURAL ANALYSIS OF UPCM PARTICLES

The diagrams in figure 5 show samples of product solution from various levels within the reactant vessel. It can be seen that the phase separation has occured, however it must be determined how much of the top precipitate layer is useful as a final microencapsulated product.
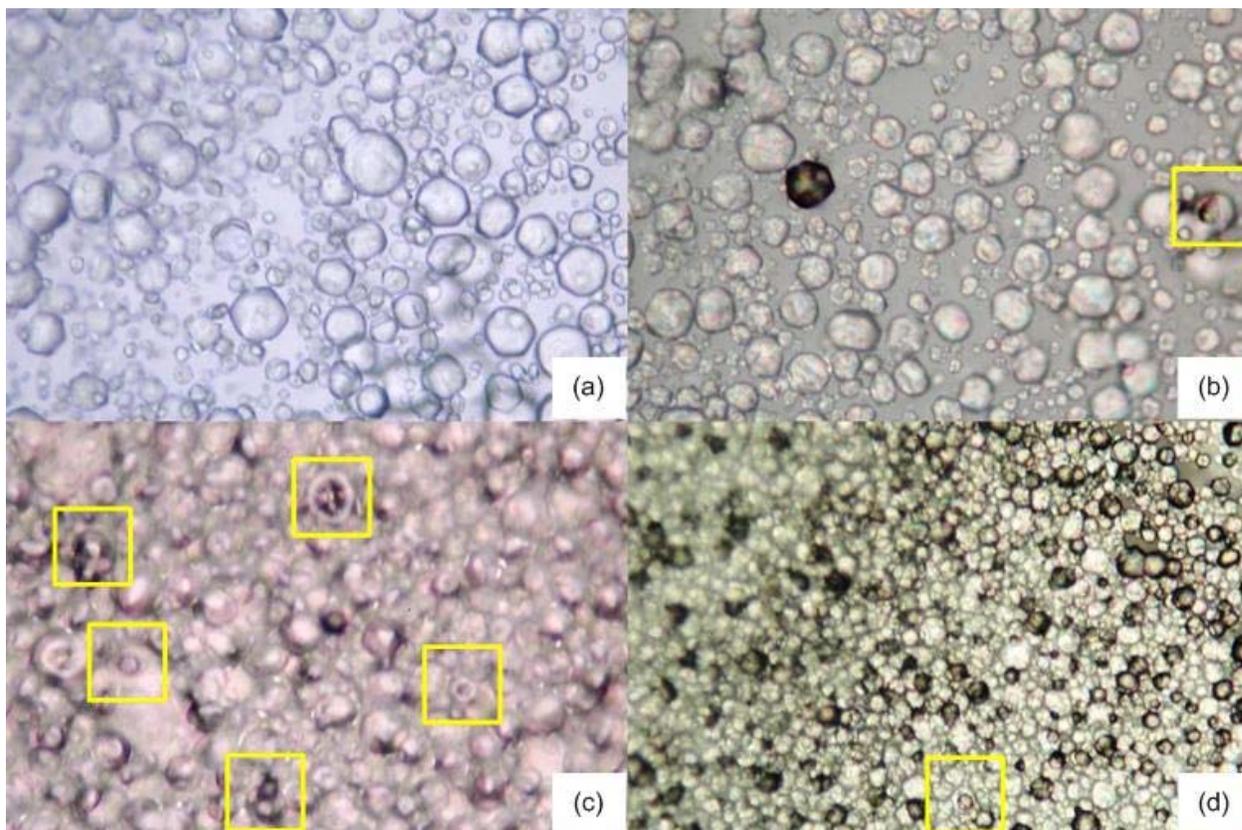

Figure 5(a) - (d). Colloid layers from bottom to top of the beaker using E200 with x30 magnification, with coacervated particles highlighted

It can be seen that the quantities of gelatin, paraffin wax and coacervated particles vary significantly from the bottom of the vessel through to the top of the sample. In figure 5(a), the suspension consists purely of transparent gelatin molecules. In (b), the darker particles are paraffin, the larger of which is uncoated. More coated wax particles are seen in (c) and their size (70-100um) is smaller than those found in (d). Finally, the (d) sample contains many smaller paraffin particles, however many of them are uncoated.

Several important observations can be taken from these four samples. Firstly, the phase which has the highest concentration of coacervated particles is at the bottom of the precipitate layer. Secondly, the smaller particles tend to be located towards the very top of the system due to their lower density. Thirdly, coacervation seems to be more efficient on the smaller medium size particles.

5.1.   Particle Morphology

The exterior appearance of the µPCM particles were studied throughout the coacervation process using the *Nikon Eclipse E200* optical microscope. The average structure of the particles was spherical, however variations existed.
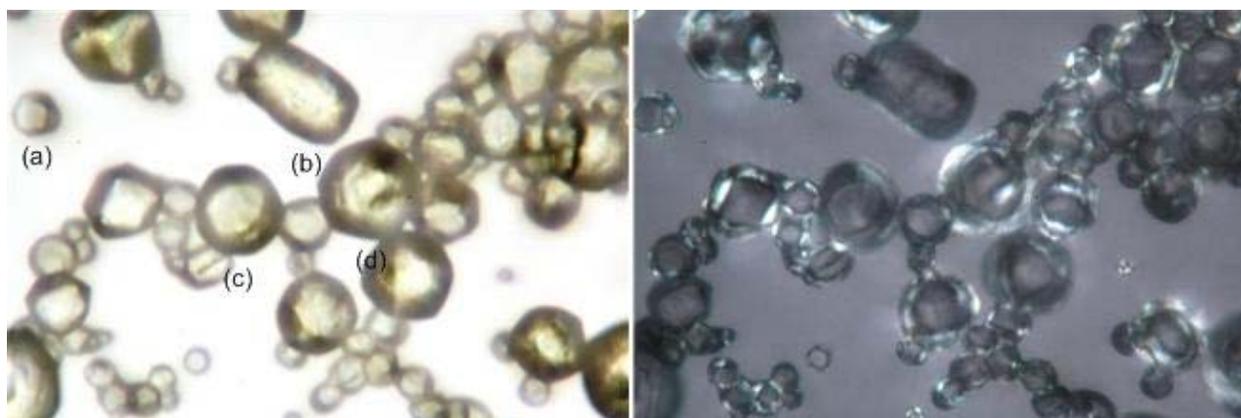

Figure 6. Standard (left) and phase contrast pictures (right) of a typical sample of coacervated particles produced using a coating to wax ratio of 1:2

In figure 6 it can be seen that the particles varied in both size and shape. The majority of particles featured are spherical in shape, such as particles (c) and (d). However, some microencapsulated particles have formed in distorted elongated shapes such as (d). Alternatively, in the top left it can be seen that two wax particles have been coated together, producing a single µPCM particle.

The gelatin/acacia coating material is distributed relatively evenly around the surface of the particles. Some inconsistency exists when the core material has defects upon it. For example, particle (d) has a small discrepancy in it surface, and hence this is replicated in the coacervate coating.

5.2.   Encapsulation Yield

One determinant of the suitability for the production of µPCM particles is encapsulation yield. This is defined as a ratio of the weight of the final products produced during the coacervation process to the weight of raw materials.

For this project the raw materials are defined as the paraffin wax, gelatin, acacia and formaldehyde. The final coacervate rich phase after separation was taken as the total weight of the final product. A small amount of distilled water and excess uncoated material remained present in this phase, however it was neglected for calculations. The encapsulation efficiencies for the 1:2 and 1:1 (coating to wax ratio) experiments are listed in the table 1.

Table 1. Encapsulation yield of coacervation process

Experiment (Coating:Wax)	Total System Weight [g]	Raw Material Weight [g]	Coacervate Rich Weight [g]	Encapsulation Yield [%]
1:2	491.7	38.0	21.8	57.4
1:1	429.4	51.0	26.1	51.1
Average Encapsulation Yield				54.3

The average encapsulation yield of the coacervation process is approximately 50%. Hawlader et al. (2003) state that encapsulation yields in excess of 80% using coating to wax ratios of 1:2 and 1:1 are achievable. The reduced yield in this case is caused by poor control of the process. During experiments, a considerable amount of raw materials accumulated on the equipment and hence did not contribute to the coacervation process. With more sophisticated processing equipment allowing a more controlled processing environment, encapsulation yields will be increased. Factors such as electrostatic attraction between polyelectrolytes, mixing time and rate, quantity of formaldehyde, presence of a surfactant and temperature are just some of the critical factors impacting on the formation of complex coacervates (Hawlader et al. 2003, Schmitt et al. 1998, Mayya et al. 2003).

5.3. Thermal and Mechanical Testing

We have limited data on the performance of the product material to date. The primary goal of microencapsulation is to protect the core material from its external environment. Successful encapsulation will allow the core material to remain within the protective shell for a prolonged period of time, by withstanding variable environmental conditions.

A simple pump cycle was set up to determine the ability of the particles to withstand mechanical pressure and their behavior as a result of continuous collisions. An inline centrifugal pump was used for this experiment.
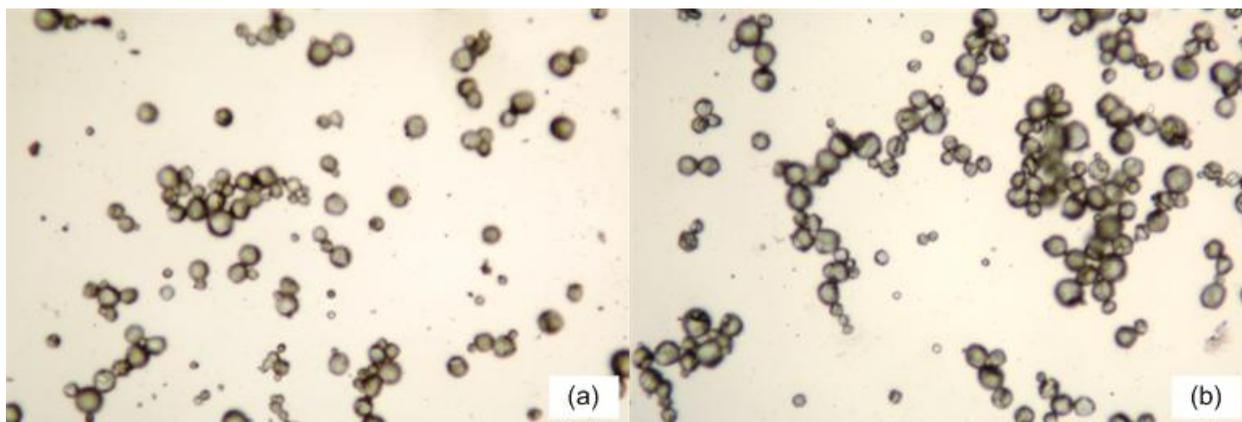

Figure 7. Typical samples of microencapsulated particles pumped for 5 minutes (a) and 10 minutes (b)

It can be seen in figure 7, that flocculation between particles has increased over the 5 minute time frame between samples. By pumping the slurry continuously through, the Brownian motion and continuous particle interactions are repeatedly occurring. From the previous discussion regarding the DVLO theory concerning stability, if the particles are brought close enough together, the close range Van der Waals forces become prominent, hence, the interaction energy is increased (see figure 2).

These results highlight the importance of steric stabilisation layer. Clearly the gelatin, acacia and formaldehyde coating have not provided sufficient stabilisation. The use of a surfactant may be a viable option to reduce flocculation. This protective coating is necessary to allow particles to come into close

proximity of each other, and posses the ability to not stick to one another.

Through observation, it appeared that the shell coating remained intact around the surface of the core wax material. Even though the particles were only pumped for 10 minutes, these results are promising. If the coating material was going to significantly deteriorate, it is predicted that this will occur relatively soon after cycling has begun. Uddin et al. (2002, 114) highlight that the gelatin-formaldehyde cross-linked combination can create a suitable coating for paraffin waxes, capable of withstanding thermal and physically cycling. In their study, they show that a particles surface contour changes with cycling, however its overall profile can remain relatively unchanged. By pumping this particular sample, it is apparent that the coating system is robust for a short period of time. The long term stability of this coating combination will be determined with more in-depth experimental analysis.

Thermal testing involving heating the solution until the water boiled also showed no material degradation in the PCM particles, indicating that the encapsulation process was successful.

6. CONCLUSIONS AND FURTHER WORK

An exploratory investigation into the production of a micro-encapsulated phase change material has been carried out. It is further proposed that this material be used in a fluid suspension as a heat exchange fluid of high heat capacity and thus benefit heat transfer and heat storage applications.
The PCM core material, paraffin wax, was coated in a protein layer using a chemical process known as complex coacervation, developed by Overbeek and Voorn. The ingredients of the coating were acacia and gelatin, and the strength of the coating was increased by cross linking using formaldehyde. Filtering is required at several steps.

The control of the coacervation and dispersion processes is difficult as there are many variables. It is also desirable to maintain tight control of particle size for fluid dynamic considerations. These considerations also demand that a surfactant be added to the solution to prevent clumping and settling of the colloidal uPCM suspension.

We aim to refine the recipe for production of uPCM and continue thermal and mechanical testing of the product.

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