Journal of Phase Change Materials

J-PCM

Article

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Published from the Department of Computer Engineering, Modeling, Electronics and Systems - DIMES, Italy by Royallite Global UK

Volume 2, Issue 2, 2022

Article Information
Submitted: 9 August 2022
Accepted : 14 October 2022
Published: 07 December 2022

Additional information is available at the end of the article

How to Cite:
Rangan, K., Forbesa, H. ., & Kumar, N. (2022). Inorganic salt hydrates-hydrogel composites as phase change materials for energy storage in buildings. Journal of Phase Change Materials, 2(2); 35-41.

DOI:
https://doi.org/10.58256/jpcm.v2i2.25

Inorganic salt hydrates-hydrogel composites as phase change materials for energy storage in buildings

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Abstract

There are few drawbacks to implementing hydrogel phase change materials (PCMs) for building applications requiring long duration stability of over 20 years. Both inorganic salts and functional groups of hydrogel polymers compete for interaction with water molecules. In the highly saline solutions, a competition for hydration water occurs between salt ions and polymer chains, resulting in a dramatic effect of salt on the polymer solubility and gelation. The three-dimensional network of hydrogels is damaged, and polymer solubility and gelation properties are influenced by the addition of large amounts of inorganic salt salts. On the other hand, functional groups such as hydroxyl and carboxyl also electrostatically bond strongly with metal cations affecting their crystallization as hydrates. For instance, calcium salts formed hydrophobic precipitates with sodium acrylate hydrogels resulting in a phase separation (stratification) of water and Ca-hydrogel precipitate. Thus, traditional hydrogel materials based on sodium acrylate and acrylamide are unsuitable for PCM applications. Therefore, a new hydrogel PCM system based on polyvinyl pyrrolidone (PVP) was investigated to avoid incompatibility issues with hydrated salts and polymer hydrogel systems.

Keywords: Phase Change Materials, Salt Hydrate, Energy Storage, Building materials, Thermal storage

Public Interest Statement

While many of the advances in materials science have been driven by breakthroughs in material design and fabrication, understanding the changes that occur in a material during its utilization or operation in devices is of immense importance for its successful integration. Considering these aspects and the continued growth in materials research, there is a clear need for new topical journals which can serve researchers to understand the phase transitions and exploit the phenomena to current, state-of-the-art research in the field of materials science, moreover with full accessibility.

1. Introduction

The electricity consumption of residential and commercial buildings accounts for over 40% of the nation's total energy demand [1]. The US Department of Energy's Building Technologies Office (BTO) supports technologies that could lead to a significant reduction in energy consumption Heating and cooling in buildings and process heating in industry consume considerable amounts of energy. Storing thermal energy from "waste" heat and using them as and when needed could significantly improve energy efficiency. Thus, Thermal Energy Storage (TES) technology plays a significant role in achieving BTO's goal of reducing US buildings' energy use by 30% by 2030, relative to 2010 consumption.

Thermal energy storage can be achieved by latent heat storage using phase change materials (PCMs). The main advantages of PCMs include high thermal storage density and small temperature swings. Paraffin materials are the common PCMs used in building applications [2]. Due to their high cost, low volumetric energy capacities, and high combustibility, alternative PCMs are needed for the wide implementation of PCMs in building applications. Inorganic salt hydrate PCMs are particularly attractive as thermal energy storage materials because of their high volumetric energy densities and optimum transition temperatures, and low costs. However, technical barriers such as inherent supercooling, phase separation, and liquid leakage in solid-liquid phase change must be overcome [3].

Typical methods used to avoid these issues are microencapsulation or impregnation of hydrated salts onto supporting materials such as metal foam, porous ceramics, and porous minerals [4]. The main problem with the microencapsulation method is the volume and phase changes and the inflow of crystal water into the cavity of the polymer shell materials [5]. Hydrated salt composite PCMs prepared through impregnation onto porous supports degraded easily and reduced the heat storage density due to the increased loading of the porous adsorbent [6]. The melting enthalpy of the composite materials decreased significantly, which was often lower than the theoretical value calculated from the encapsulation amount. Xie *et al.* impregnated inorganic salt hydrate into expanded vermiculite to prepare a shape-stabilized composite PCM [7]. The melting enthalpy of the composite and eutectic salt hydrate was 110.3 and 195.3 J/g, respectively. A similar phenomenon occurred with composite PCMs that were prepared by encapsulation in other porous minerals [8,9,10]. One of the critical factors that affect the thermal storage capacity is the crystal water stability in the porous composite PCMs [11]. The loss of crystal water from the PCM composite can be reduced by introducing hydrogen bonds into the salt hydrates with the encapsulating polymers [12]. One approach is to use hydrogels with a large capacity to hold water through charge interactions and hydrogen bonding.

The hydrated salt/hydrogel composites systems have a low melting point in the desired range of 15-30 °C for building applications and relatively large latent heat of fusion (>160 kJ/kg). The volumetric energy storage density is approximately double the energy density values of comparable organics PCMs (such as paraffin) with similar melting points. Thus, inorganic salt hydrate/hydrogel composites are amenable for realizing compact and lightweight thermal energy storage platforms (TES). Hydrogels are a class of three-dimensional polymeric network materials obtained from physical and/or chemical cross-linking. Hydrogels are consisted of functional groups, such as carboxyl and hydroxyl groups which can readily form hydrogen bonds with crystal water. Hydrogels exhibit high tensile and compressive strengths and higher water absorption capacity [13]. Hydrogels have been considered as dispersion media for hydrated salts to produce a phase change hydrogel (PCH) for thermal energy storage. Wang *et al.* fabricated a cross-linked polymer hydrogel with Glauber's salt, sodium sulfate decahydrate ($Na_2SO_4.10H_2O$) [5]. The PCH stayed stable during the thermal-phase-transformation process. Poly (acrylamide-co-acrylic acid) copolymer (PAAAM) was used for leakage prevention of inorganic hydrate salts

[14]. Poly(vinyl alcohol) (PVA) – a non-toxic, biocompatible polymer has also been used in the preparation of phase change hydrogels [15]. Recently, Xiao *et al.* showed the use of acrylamide-based hydrogels in stabilizing sodium acetate hydrate [3]. Some of the typical shortcomings of the traditional PCMs were eliminated or reduced by incorporating the inorganic hydrated salts in the hydrogels. For example, hydrogel stabilization reduced liquid leakage during the phase change process by over 87%. Scanning electron micrographs confirmed that the $CH_3CH_3COONa.3H_2O$ particles were confined to the three-dimensional hydrogel networks. Differential scanning calorimetry tests showed that the melting temperature of hydrogel/sodium acetate trihydrate was close to that of sodium acetate trihydrate, and its latent heat was as high as 202.4 J/g. Other studies have shown that acrylic acid hydrogel is effective in preventing undesirable phase separation of the high hydrate inorganic salts (Na_2SO_4 hydrate) [16, 17]. These reports indicate that the formation of PCM composites of inorganic hydrated salts with hydrogels is a promising approach to designing PCM materials that can be used in building energy management.

However, there exist a few drawbacks to implementing hydrogel systems for building applications requiring long-duration stability of over 20 years. Both inorganic salts and functional groups of hydrogel polymers compete for interaction with water molecules. In the extremely saline solutions, a competition for hydration water occurs between salt ions and polymer chains, resulting in a dramatic effect of salt on the polymer solubility and gelation. The three-dimensional network of hydrogels is damaged, and polymer solubility and gelation properties are influenced by the addition of large amounts of salt inorganic salts [18]. On the other hand, functional groups such as hydroxyl and carboxyl also electrostatically bond strongly with metal cations, affecting their crystallization as hydrates. For instance, calcium salts formed hydrophobic precipitates with sodium acrylate hydrogels resulting in a phase separation (stratification) of water and Ca-hydrogel precipitate. Thus, traditional hydrogel materials based on sodium acrylate and acrylamide are not suitable for PCM applications. Therefore, a new hydrogel material system based on polyvinyl pyrrolidone (PVP) was investigated to avoid incompatibility issues with hydrated salts and polymer hydrogel systems.

2. Material and methods

Inorganic hydrated salts and PVP polymers were purchased from Millipore Sigma, Saint Louis, MO. The expandable graphite flakes were purchased from Millipore sigma and dried in a vacuum oven at 80 °C for 24 h. Then the dried flakes were heated in a microwave oven at a power of 1,000 W for 30 s. The graphite expanded over ten-fold, and fluffy expanded graphite was obtained after the microwave treatment.

Differential scanning calorimetry (DSC) (TA Instruments, Model #DSC 2500) was used to evaluate the thermal properties of the samples. The scanning temperature ranged from -60 to 60 °C and the scanning rate was 5 $C \cdot min^{-1}$.

The thermal conductivities of the samples were measured using 4" length x 4" width x 1 mm thickness molded samples. A constant 100°C temperature difference was established between both sides of the sample plate using ice. Thermal conductivity was measured after reaching a steady state based on the amount of water collected from the melting of ice due to heat transfer.

The interaction between the hydrogel and metal cations and anions was investigated using Fourier transform infrared (FTIR) spectroscopy (Nexus 670 fitted with ATR module). The

data were recorded between 600-4000 cm^{-1} at 4 cm^{-1} resolution for 72 scans.

Powder X-ray diffraction patterns of hydrated salts and hydrogel composites were acquired on a Rigaku Miniflex X-ray diffractometer with Co Kα radiation at 30 kV with 2 degrees per minute scan rate.

2.1. T-History

The T-History method is simple to measure the specific heat, phase change temperature, and latent heat during melting and freezing of hydrogel PCM composites. The T-History method is a simple method to measure the specific heat, phase change temperature, and latent heat during melting and freezing for inhomogeneous materials using a much larger sample size than DSC. In the T-History method, the temperature profile of the PCM hydrogel composites during heating and cooling is recorded above and below the transition temperature, along with water, a known reference. Any change in the thermophysical properties of the test sample will show up in the temperature profile. The T-History method is based on a lumped capacitance heat transfer assumption and assumes the same heat transfer coefficient between the sample and reference (water) when measured at the same temperature.

The T-History experimental set-up was accomplished using a benchtop environmental chamber (Tenny Environmental, Model TJR), test tube (1.0 cm diameter x 19 cm length, Pyrex), and insulated box as illustrated in Figure 4. A photograph of a typical hydrogel composite ($CaCl_2.6H_2O$/2.5wt% $SrCl_2.6H_2O$/5wt% PVP) in a test tube used in T-history testing is provided in Figure 1.

Figure 1. Photograph of $CaCl_2.6H_2O/SrCl_2.6H_2O$/PVP hydrogel composite in a test tube

The test tubes were insulated inside a Styrofoam insulated box to reduce the effect of the forced convection on the sample and reference from the chamber and to maintain a natural convection heat transfer coefficient of less than 5 $Wm^{-2}K^{-1}$. Each T-history cycle lasted for approximately 5 hours (3.125°C per minute ramp to 15°C, 90 minutes soak time, 3.125°C per minute ramp to 40°C, 90 minutes soak time, 3.125°C per minute ramp back to 15°C, at least 60 minutes soak time) and mass of the sample was ~12 g.

The test tubes for the sample and reference were designed to have a sample length greater than 10 times of tube diameters to reduce axial heat transfer effects. The test tube measured 190 mm in length and 10 mm in diameter. The test tube was insulated with a layer of plastic measuring 2 mm in thickness to further reduce the overall heat transfer coefficient between the ambient air and the samples (test and reference). The accuracy of the T-history technique was calibrated and verified with 99.9% pure n-octadecane organic PCM run.

2.2. Preparation of $CaCl_2.6H_2O$/hydrogel composites

In a typical process, 240 g of $CaCl_2.6H_2O$ and 9.6 grams of $SrCl_26H_2O$ were added to 140 mL of the 10% polymer solution. [solution of what solvent?] The mixture was heated to 36 °C with constant stirring. When the solution was clear, the stir bar was removed, and the beaker was ~~set~~ placed in an oven set at 36°C in order to evaporate any excess water present in the solution. Once, approximately 140 g of water had been removed from the solution, the sample was used for further testing. The resulting product was a highly viscous gel, which turned into a solid product after cooling to 15 °C.

2.3. Preparation of $CaCl_2.6H_2O$/$SrCl_2.6H_2O$ /PVP hydrogel/expanded graphite composites

A mixture of $CaCl_2{\cdot}6H_2O$ and $SrCl_2.6H_2O$ was added to the 10% PVP solution in water. The excess water was removed from the hydrogel composite by placing the solution at 36°C in an oven. Then the required amount of expanded graphite powder was added to the mixture. The resulting mixture was thoroughly mixed with a glass rod and then placed in a refrigerator to solidify the product before using it in T-history testing.

3. Results & Discussion

3.1. Hydrogel Composite Preparation

In this work, a unique hydrogel system was developed that can work with all types of inorganic hydrated salts (sodium, calcium, ammonium, and multivalent metal ions). The PVP polymer hydrogel acts as a host for storing water molecules without strongly binding to metal cations. In the presence of water, the resonance structure of PVP provides $N\text{-}C{=}O \leftrightarrow {}^{+}N{=}C\text{-}O^{-}$ groups to hold water molecules through hydrogen bonding. As the hydrate crystallization starts, the PVP polymer reverts to its anhydrous state smoothly. The hydrated and anhydrous state transition happens with ease and keeps the overall PVP hydrogel/hydrated salt system stable through melting/freezing cycling. Selective inorganic hydrate-based PCMs with superior thermal storage cycling and free of leakage/phase separation were prepared by incorporating them into non-toxic PVP hydrogel composites. The thermal properties of the inorganic hydrate/PVP hydrogel composites were characterized using a variety of techniques, including differential scanning calorimeter, T-history, X-ray diffraction, thermal conductivity measurements, and FTIR spectroscopy. The hydrated salt/hydrogel system's performance was measured experimentally for 300 thermal cycles of repeated melting and solidification by incorporating additives (nucleators) into the PCM samples. The experimental measurements show that these nucleators reduced supercooling significantly (< 2 °C for $CaCl_2.6H_2O$ and <3 °C for $Na_2SO_4.10H_2O$), and the system demonstrated energy storage capacity <3% degradation after 500 cycles and enhanced reliability.

3.2. Thermal stability of Hydrate Salt/Hydrogel Composites

A mixture of $CaCl_2.6H_2O$, 2.5% $SrCl_2.6H_2O$, 5% PVP (MW 360,000) was prepared in a cylindrical mold. After cooling to 15 °C, the sample was removed from the mold, placed on a Pyrex dish, and subjected to increasing temperature for 10 minutes in a preheated oven. The purpose of this test was to observe the dimensional stability at the temperature of use. The sample remained stable without any noticeable difference in the dimensions of the sample, as

demonstrated in Figure 2. With the decreased diffusion capacity of particles due to the solid-state nature of the PCM, the contact probability of particle nucleation effectively increases in this composite.

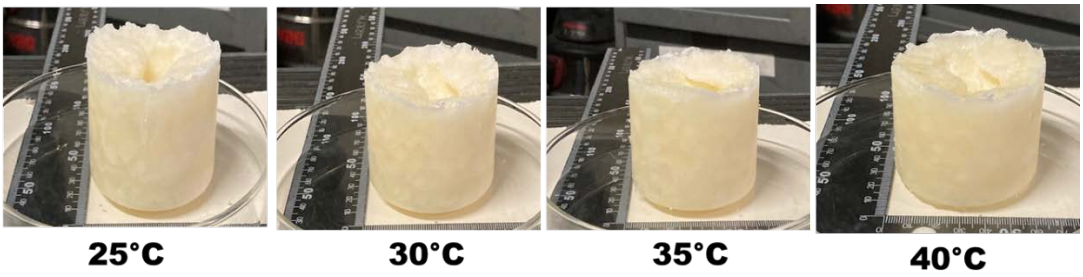

Figure 2. Thermal stability of $CaCl_2.6H_2O$/PVP hydrogel composites

3.3. T-History

The T-History method is a simple and economical method to measure the specific heat, phase change temperature, and latent heat during melting and freezing for inhomogeneous materials using a much larger sample size than DSC. In the T-History method, the temperature profile of the PCM composites during heating and cooling is recorded simultaneously with known reference materials. The accuracy of the T-history technique was calibrated and verified with 99.9% pure n-octadecane organic PCM over three runs. The data for a typical T-history run is provided in Figure 3.

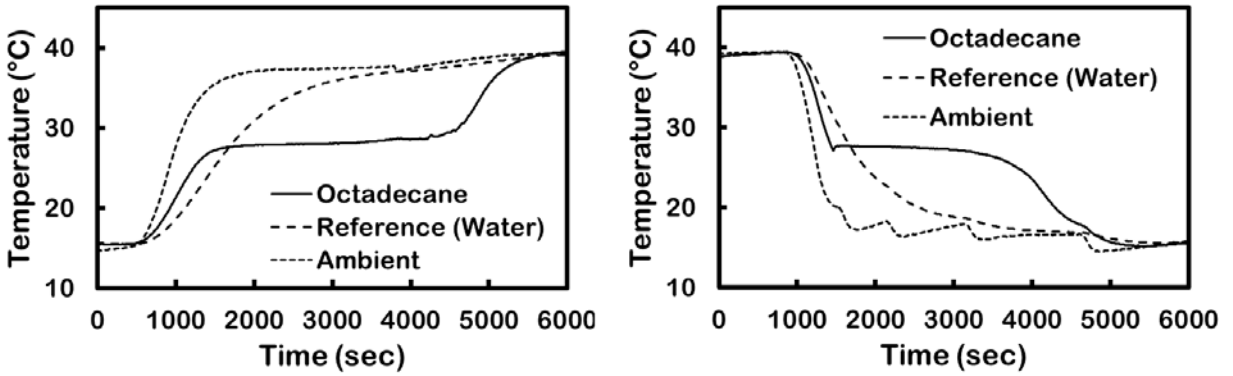

Figure 3. T-history of an n-octadecane calibration, and a reference (water) with only sensible heat with varying constant ambient temperature (A) Heating and (B) Cooling curves.

Any change in the thermophysical properties of the test sample will show up in the temperature profile. The T-History method is based on a lumped capacitance heat transfer assumption and assumes the same heat transfer coefficient between the sample and reference when measured at the same temperature. In this work, the original method described by Zhang et al. [19] was modified to account for the varying ambient temperature, supercooling, and phase change temperature glide by calculating the heat transfer coefficient as a function of temperature over very small time intervals (< 10 s) and then computing the enthalpies as a function of temperature.

The T-History experimental set-up was accomplished using a benchtop environmental chamber and insulated box, as illustrated in Figure 4.

Figure 4. T-history samples setup in a benchtop environmental chamber; Samples were kept inside an insulation box to reduce the rate of heat transfer from the sample to ambient

The test tubes for the sample and reference were designed to have a sample length greater than 10 tube diameters to reduce axial heat transfer effects. The test tube measured 190 mm in length and 10 mm in diameter.

T-history $CaCl_2.6H_2O$/ $SrCl_2.6H_2O$ /PVP hydrogel samples as a function of PVP concentration

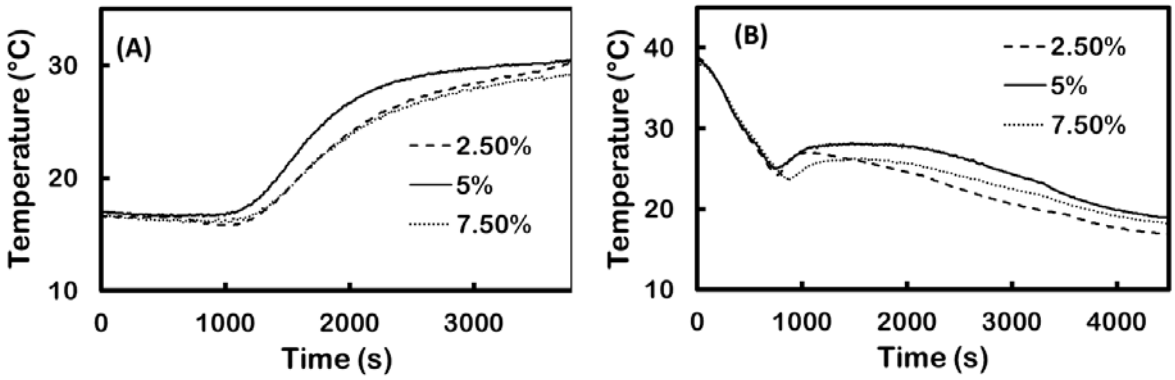

Figure 5. T-history of $CaCl_2{\cdot}6H_2O/SrCl_2{\cdot}6H_2O$/PVP composites as a function of PVP concentration (A) Heating curves and (B) Cooling curves

The samples with 2.5wt%, 5.0wt%, and 7.5wt% of PVP were melted in an oven at 45°C and kept for 1 h to ensure the three samples were completely phase-transformed to the melted stage. The sample vials were visually observed phase separation. A sample with 2.5wt% PVP exhibited liquid leakage. Both 5.0% and 7.5% PVP samples remained stable as solid without any residual water separating from the samples indicating that the PVP composite gel samples can keep a stable form during the phase change. The supercooling effect for 5.0wt% was less than 7.5wt% samples. Therefore, in the current work, the PVP containing five wt% PVP was selected for further study.

T-history $CaCl_2.6H_2O$/ $SrCl_2.6H_2O$ /PVP hydrogel samples as a function of the type of PVP

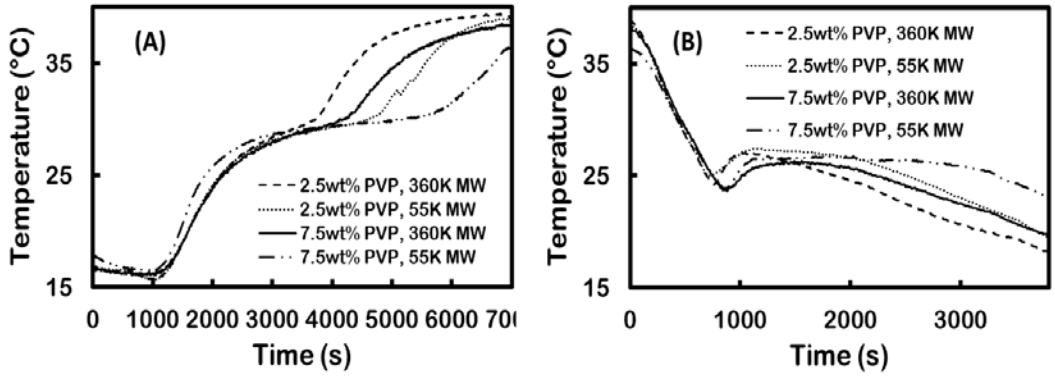

Figure 6. T-history of $CaCl_2{\cdot}6H_2O/SrCl_2{\cdot}6H_2O$/PVP composites with varying molecular weight of PVP (MW 55000 and 360000).

The molecular weight of the PVP is expected to play a key role in the viscosity of the composite, thermal conductivity, and dispersion of hydrated salts in the hydrogel medium. The data in Figure 5 show that PVP with MW 360,000 dissipates heat at a faster rate than PVP with MW 55,000. This could be attributed to the higher thermal conductivity of MW 360,00 PVP. It is known that the thermal conductivity of PVP increases with the increase in molecular weight [20]. Therefore, PVP MW 360,000 was selected for further study.

Data $CaCl_2.6H_2O$/PVP as a function of $SrCl_2.6H_2O$

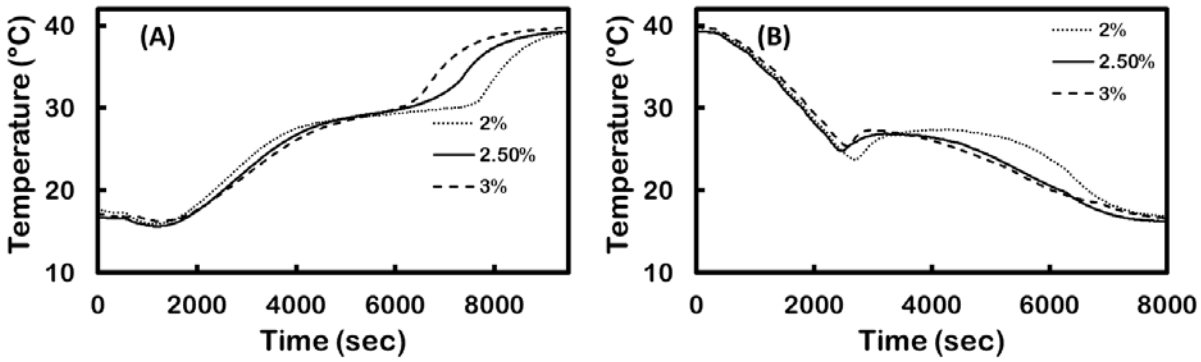

Figure 7. T-history of $CaCl_2{\cdot}6H_2O/SrCl_2{\cdot}6H_2O$/PVP composites as a function of $SrCl_2.6H_2O$ concentration (A) Heating curves and (B) Cooling curves

Figure 7 shows the relationship between $SrCl_2{\cdot}6H_2O$ concentration and the degree of supercooling of $CaCl_2{\cdot}6H_2O$. The supercooling degree of the $CaCl_2{\cdot}6H_2O$ PCM after adding increasing mass fractions (2.0wt%, to 12.0%) of $SrCl_2{\cdot}6H_2O$ is provided in Table 1. As the concentration of $SrCl_2{\cdot}6H_2O$ increases, the supercooling degree of the $CaCl_2{\cdot}6H_2O$ PCM decreases until the content of $SrCl_2{\cdot}6H_2O$ reaches 3% (on a mass basis) where the supercooling degree begins to increase; therefore, 3% $SrCl_2{\cdot}6H_2O$ content is effectively the ideal concentration for the optimum effect to reduce the supercooling phenomenon.

Table 1. Supercooling temperature as a function of $SrCl_2.6H_2O$ nucleating agent

Sample #	SrCl2.6H2O (wt%)	Freezing Temperature	Latent Heat Peak	Supercooling (°C)

		(°C)	(°C)	
1	2.0	23.4	27.4	3.0
2	2.5	24.5	26.9	2.4
3	3.0	24.7	26.6	1.9
4	4.3	19.8	22.5	2.7
5	6.0	14.7	19.3	4.6
6	9.0	14.2	23.0	6.8
7	12.0	16.5	24.6	8.1

3.4. $CaCl_2.6H_2O$/2.5% $SrCl_2.6H_2O$/5%PVP hydrogel composite thermal cycle stability

The stability of hydrogel composites after thermal cycling at 15-40 °C was examined using T-history measurements after 1 cycle, 100 cycles, 200 cycles, and 300 cycles. The data provided in Figure 8 demonstrate that the PVP hydrogel composite has no significant phase change on the heating and cooling curves after several cycles. The exothermic time decreased from 931 seconds to 911 seconds (~2.1%) after 200 cycles. However, the exothermic time remained at 911 seconds after 300 cycles without any significant change in the melting or freezing cycle curves. The exothermic temperatures are found at 27 °C, the phase transition temperature was 29.3 °C. The supercooling temperatures are 2.7 °C after 1 cycle, which increased to 3.4 °C after 200 cycles, and remained at 3.4 °C even after 300 cycles. After several time cycles, the hydrogel composite salt performance was stable, and there was a clear phase change flatline observed on both the heating and cooling curves. From the DSC test result presented in Figure 9, it can be seen that the phase transition enthalpies are 155 J/g.

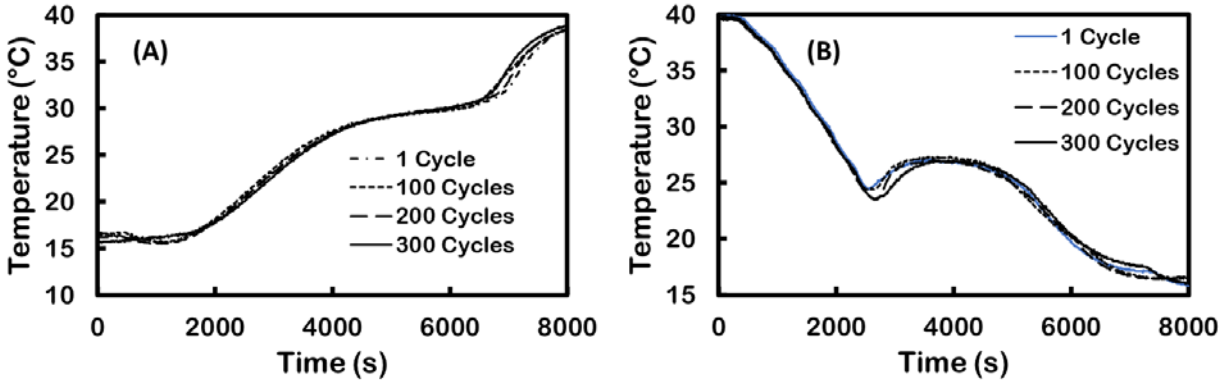

Figure 8. Thermal cycling of $CaCl_2{\cdot}6H_2O$/2.5% $SrCl_2{\cdot}6H_2O$/5%PVPcomposite (A) Heating curves and (B) Cooling curves

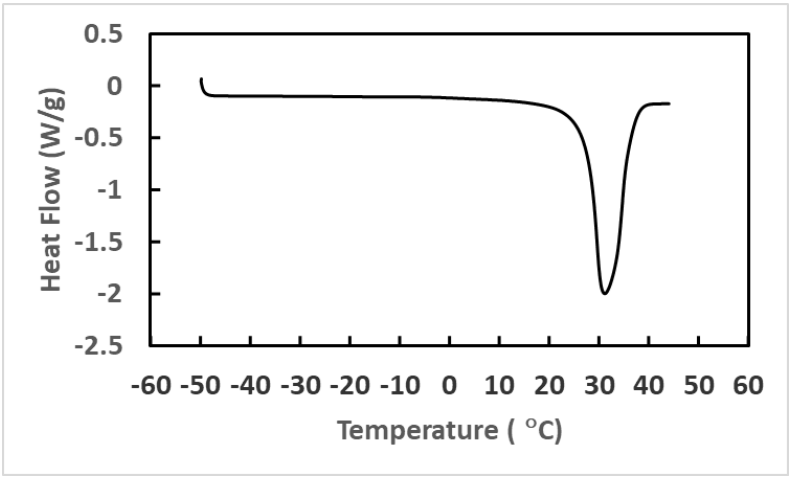

Figure 9. DSC curve of $CaCl_2.6H_2O$/2.5wt% $SrCl_2.6H_2O$/5 wt% PVP (MW 360,000) for measurement of the latent heat capacities.

3.5. $CaCl_2.6H_2O$/2.5wt% $SrCl_2.6H_2O$/5wt%PVP/EG hydrogel composite as a function of expanded graphite content

Expandable graphite (EG) has been used in PCMs to increase the thermal conductivity and to support the host medium for the crystallization of hydrated salts. Duan et al. [13] investigated the influence of the expandable graphite on the supercooling and phase separation behavior of $CaCl_2{\cdot}6H_2O$, and the results indicated that EG could effectively increase the thermal conductivity and promote phase-change performance. Phase change behavior of $CaCl_2{\cdot}6H_2O$/$SrCl_2{\cdot}6H_2O$/EG/PVP hydrogel composite PCMs, including supercooling degree, phase change temperature, latent heat, density, thermal conductivity, and thermal stability were studied. The objective of this effort was to explore the more efficient mechanism that optimizes the thermal properties of the hydrated salt/PVP hydrogel composites for thermal energy storage applications.

Figure 10 shows the heat storage curves of $CaCl_2{\cdot}6H_2O$/$SrCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}6H_2O$/$SrCl_2{\cdot}6H_2O$/EG/PVP/ composites PCMs. As can be seen from the heat storage curve, it takes 380 min for $CaCl_2{\cdot}6H_2O$/ $SrCl_2{\cdot}6H_2O$ to increase the equilibrium temperature from 15°C to 35 °C. Besides, the temperature rises rather slowly with quite a long heat storage platform at *ca.* 29°C. When adding 0.2, 0.4, and 0.6 wt% EG, the time taken for the temperature from 15°C to 35°C is reduced from 79 to 75, 73, and 56 min, showing improved heat transfer rate of the composites. This is attributed to the fact that the addition of EG improves the thermal conductivity of the composite PCMs, facilitating heat transfer in the heat storage process. Thus, the heat storage time to get equilibrium temperature is reduced for $CaCl_2{\cdot}6H_2O$/$SrCl_2{\cdot}6H_2O$/EG/PVP composites PCMs.

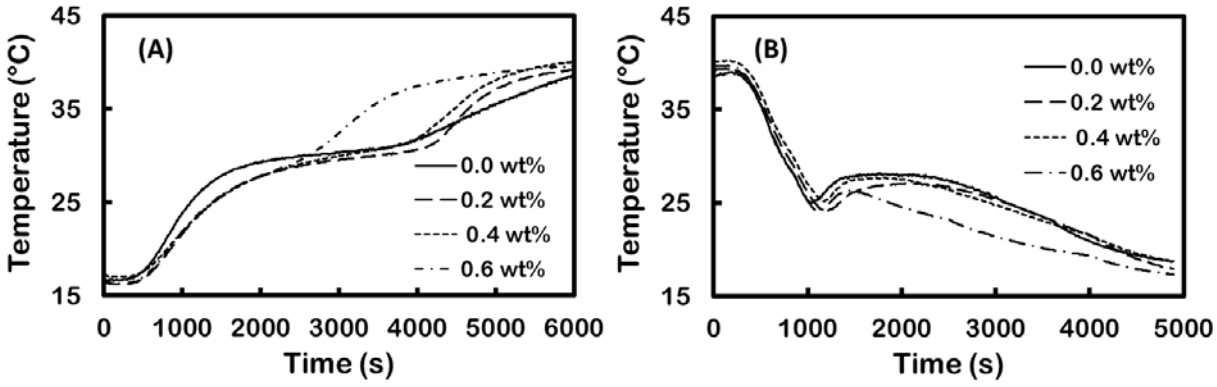

Figure 10. Thermal cycling of $CaCl_2 \cdot 6H_2O$/2.5% $SrCl_2 \cdot 6H_2O$/5%PVPcomposite as a function of EG content (A) Heating curves and (B) Cooling curves

3.6. FTIR Analysis

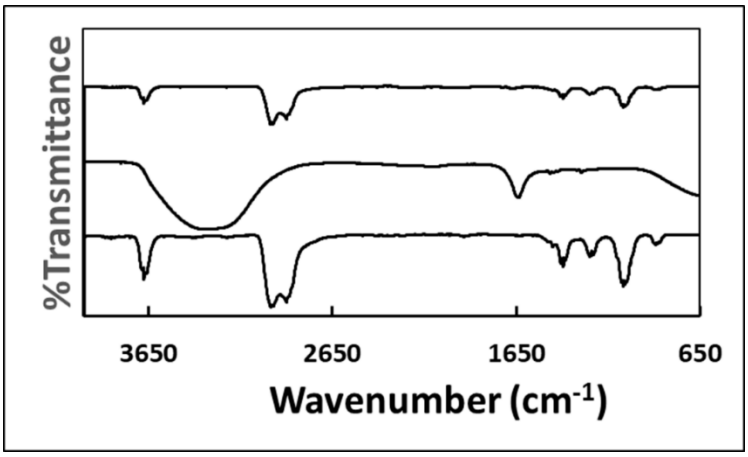

Figure 11. ATR/FTIR spectra of (A) PVP MW 360,000 powder (B) as-prepared $CaCl_2.6H_2O$/2.5wt% $SrCl_2.6H_2O$/5wt%PVP hydrogel composite at 35 °C temperature, (C) $CaCl_2.6H_2O$/2.5wt% $SrCl_2.6H_2O$/5wt%PVP hydrogel composite after freezing and crystallization of $CaCl2.6H_2O$ at 20 °C. [Please indicate which curves in this figure correspond to (A), (B), and (C)]

The FTIR/ATR spectrum of $CaCl_2.6H_2O$/2.5wt% $SrCl_2.6H_2O$/5wt%PVP hydrogel composite is provided in Figure 11, along with the spectra correspond to PVP and $CaCl_2.6H_2O$/2.5wt% $SrCl_2.6H_2O$/5wt%PVP hydrogel composite after freezing and crystallization of $CaCl2.6H_2O$ at 20 °C. The main absorption bands for PVP powder C=O (1669 cm^{-1}), C–N (1250 cm^{-1}), and CH_2/CH (2971–2900 cm^{-1}) groups could be identified in

the FTIR spectra. We found that the 10% aqueous solution of PVP showed mainly broad peaks corresponding to water molecules and a strong C=O stretching band at around 1638 cm^{-1}. More interestingly, the FTIR spectrum of $CaCl_2.6H_2O$/PVP hydrogel composite is identical to that of dried PVP. This indicates minimum interaction between PVP and water molecules under temperatures below the melting point of $CaCl_2.6H_2O$. However, as the salts melt, the water liberated was readily absorbed by the PVP forming hydrogel. To study the interaction of water and PVP solutions in the presence of $CaCl_2$, FTIR studies should be conducted at temperatures above 30 °C.

PVP has found an additional use in the manufacture and stabilization of metallic nanoparticles (NPs) (e.g., Ag). Such NPs are prepared by reducing aqueous metal salts in the presence of PVP, which coats them as they form, stabilizing them by preventing their contact and agglomeration and limiting their growth. The characterization of the PVP-coated metal NPs has been studied by many groups, almost exclusively by vibrational spectroscopy, with the general conclusion that the 2-pyrrolidone ring binds to the NP through reaction with the carbonyl to form an alkoxide >C = O + metal → >C – O – metal. [21] This conclusion was made by the researchers based on the slight (~10 cm^{-1}) shift of an IR peak, located at ~ 1660 cm^{-1}, and attributed to the carbonyl stretch when reacted with metal nanoparticles. However, metal-O-C chemical bonding is not justified by a small spectral shift of 10 cm^{-1} [21]. This shift could be attributed just to the interaction of PVP with water molecules, as reported here.

The FTIR spectrum of PVP in water shows a shift in C=O peaks from 1669 cm^{-1} to 1638 cm^{-1} compared to dry PVP powder. This shift could be attributed to the hydrogen bonding of C=O groups with H_2O molecules. The addition of inorganic salts does not shift this peak further, indicating there is no strong bond between metal ions and PVP amide groups. Water molecules mostly surround the PVP molecules. This weak interaction with metal ions favors the crystallization of metal hydrates without strongly binding the metal ions like carboxylate groups in acrylate-based hydrogels. The weak interaction with water also allows the water molecules to shuttle between metal ions (during crystallization of hydrates and melting of hydrated salts). This effectively retains the heat capacity of hydrated salts over 100's cycles.

3.7. X-ray Diffraction

XRD is commonly used for the structural characterization of materials and identification of the crystal structure and potential composition of solid materials. The XRD patterns can act as the fingerprint for a particular metal hydrate composition. Salt hydrates tend to be phase-separated after preparation,-melting, and freezing. In Figure 12, powder X-ray diffraction pattern of $CaCl_2.6H_2O$/2.5wt% $SrCl_2$. $6H_2O$ /5wt% PVP composites after 1 cycle and after 300 cycles are provided along with a standard $CaCl_2.6H_2O$ from the literature. The XRD pattern shows negligible difference even after 300 cycles of heating and cooling between 15 to 40 °C.

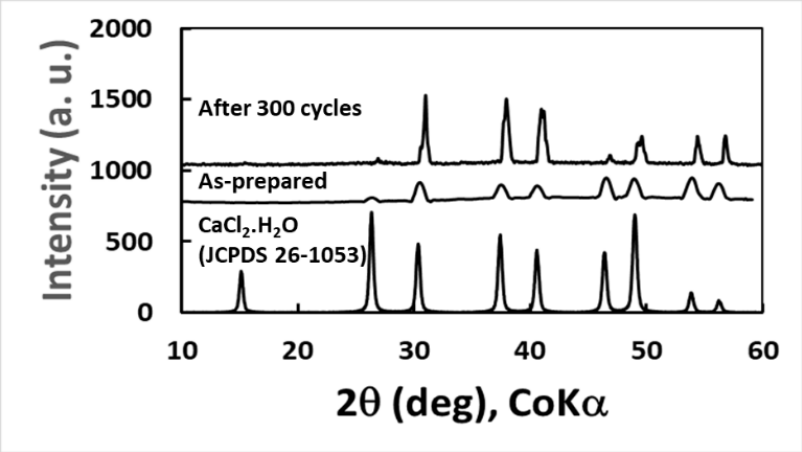

Figure 12. Powder X-ray diffraction pattern of $CaCl_2.6H_2O$/2.5wt% $SrCl_2.6H_2O$/5wt%PVP (MW 360,000) hydrogel composite at 20 °C. The data for as-prepared hydrogel composite (1 cycle) and after 300 thermal cycles between 15 deg C to 40 °C.

In this work, a unique hydrogel system was demonstrated to work with all types of inorganic hydrated salts (sodium, calcium, ammonium, and multi-valent metal ions). The PVP polymer hydrogel acts as a host for storing water molecules without strongly binding to metal cations. In the presence of water, the resonance structure of PVP provides N-C=O ↔ $^{+}$N=C-O^{-} groups to hold water molecules through hydrogen bonding. As the hydrate crystallization starts, the PVP polymer reverts to its anhydrous state smoothly as schematically provided in Figure 13.

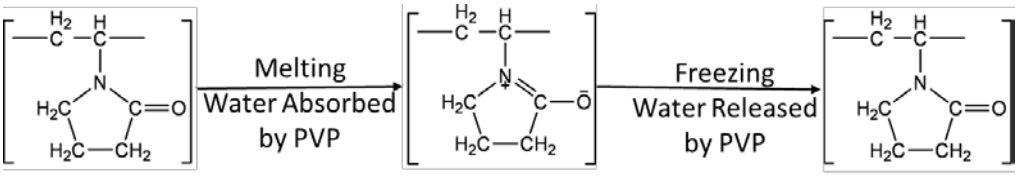

Figure 13. Resonance structure of PVP as a function of hydrated/anhydrous state

The hydrated and anhydrous state transition happens with ease and keeps the overall PVP hydrogel/hydrated salt system stable through melting/freezing cycling. Selective inorganic hydrate-based PCMs with superior thermal storage cycling and free of leakage/phase separation were prepared by incorporating them with the PVP hydrogel composites. The thermal properties of inorganic hydrate/PVP hydrogel composites were characterized using a variety of techniques, including differential scanning calorimeter, T-history, X-ray diffraction, thermal conductivity measurements, and FTIR spectroscopy. The hydrated salt/hydrogel system's performance was measured experimentally for 300 thermal cycles of repeated melting and solidification by incorporating additives (nucleators) into the PCM samples. The experimental measurements show that these nucleators reduced supercooling significantly (< 2 °C for $CaCl_2.6H_2O$ and <3 °C for $Na_2SO_4.10H_2O$), and the system demonstrated energy storage capacity with <3%

degradation after 300 cycles and enhanced reliability.

4. Conclusions

1. Selective inorganic hydrate-based phase-changing materials (PCMs) with superior thermal storage cycling and free of leakage/phase separation were prepared by incorporating them into non-toxic hydrogel composites.
2. Demonstrated that the conventional acrylate-based hydrogels are not suitable to produce hydrogel PCMs due to their interaction with di- and multi-valent cations of the hydrated salts. [Please re-write]
3. Polyvinyl pyrrolidone (PVP) is more suitable to form hydrogel PCMs with mono and multi-valent metal ion-containing hydrated salts.
4. The thermal properties of inorganic hydrate hydrogel composites were characterized using a variety of techniques, including differential scanning calorimeter, T-history, X-ray diffraction, thermal conductivity measurements, and FTIR spectroscopy. The thermal energy storage and the thermal cycling performance were evaluated, and a universal hydrogel media for inorganic hydrated salts was down-selected for further study.

Acknowledgements

Financial support from the Department of Energy through SBIR contract No. DE-SC0020728 (2020) is gratefully acknowledged. The authors thank Kyle R. Glusenkamp, *Oak Ridge National Laboratory, Oak Ridge, TN, USA* for helpful discussions.

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