



Mitigation of Leakage and Water Ingress for a Promising Phase Change Material (PCM) Containing Polyethylene Glycol (PEG)

Preprint

Kerry Rippy,¹ Judith Vidal,¹ Shuang Cui,² and Sumanjeet Kaur³

1 National Renewable Energy Laboratory

2 University of Texas and Dallas

3 Lawrence Berkeley National Laboratory

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National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, CO 80401
303-275-3000 • www.nrel.gov

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MITIGATION OF LEAKAGE AND WATER INGRESS FOR A PROMISING PHASE CHANGE MATERIAL (PCM) CONTAINING POLYETHYLENE GLYCOL (PEG)

Kerry Rippy¹, Judith Vidal¹, Shuang Cui², Sumanjeet Kaur³

¹National Renewable Energy Laboratory, Golden, CO

²University of Texas and Dallas, Dallas, TX

³Lawrence Berkeley National Laboratory, Berkeley, CA

ABSTRACT

A promising and cost-effective phase change material (PCM) containing polyethylene glycol (PEG) 600, 800, and/or 1000 has been synthesized. It is shape stabilized using a sol-gel method and displays promising thermal properties. These properties make the PCMs good candidates for thermal batteries and other thermal energy storage applications in the building sector. However, PEG leakage is observed at elevated temperatures, and due to the hygroscopic nature of PEG, moisture ingress is also observed, which can have a significant effect on performance and durability. Thus, we have developed hydrophobic coatings to prevent PEG leakage and mitigate moisture ingress. The selected approach involves a secondary sol-gel process during which a thin layer formulated with hydrophobic precursors is deposited onto the surface of the PCM samples. Several coating formulations have been investigated, including formulations composed of tetraethyl orthosilicate (TEOS), diethoxy(dimethyl)silane (DEDMS), triethoxymethylsilane (TEMS), and n-octyltriethoxysilane (OTES). We find that this is effective at increasing hydrophobicity of the PCM substrates. It also decreases substrate leakage.

Keywords: Phase Change Materials; Hydrophobic Coatings; Thermal Energy Storage

1. INTRODUCTION

New approaches to energy storage and thermal management in buildings can increase the reliability and resiliency of our energy systems. [1-4] One application for these technologies is the building envelope, which has been envisioned as an energy storage opportunity for decades because of the large surface area available. [5] Our current work focuses on development of new approaches to solid-state thermal energy storage materials to control the flow of heat in space and time. This will enable thermal micro-grids within a building envelope that can shift

thermal loads, for example to exploit nighttime cooling the following afternoon or the ability to precool (or preheat) the envelope and store the energy until it is needed.

As a part of this work, we have developed a promising and cost-effective phase change material (PCM) containing polyethylene glycol (PEG) with average molecular weights of 600, 800, and/or 1000. We employ a sol-gel method to make this material. It displays promising and unique thermal properties. These properties make our PCMs good candidates for thermal batteries and other thermal energy storage applications in the building sector. However, moisture ingress into the material plays a key role in performance and durability. As is common for such materials, PEG leakage is observed at elevated temperatures. Furthermore, due to the hygroscopic nature of PEG, moisture ingress is common. Thus, we have developed hydrophobic coatings to prevent PEG leakage and mitigate moisture ingress.

Here, we report the process for formulation and application of these coatings. A secondary sol-gel process is employed, during which a thin layer formulated with hydrophobic precursors is deposited onto the surface of the PCM samples.

Several different coating formulations have been investigated, including formulations composed of tetraethyl orthosilicate (TEOS), diethoxy(dimethyl)silane (DEDMS), triethoxymethylsilane (TEMS), and n-octyltriethoxysilane (OTES). Multiple deposition methods have been compared for synthesis of the hydrophobic layer, including dip-coating, use of a mold, and vapor deposition. Conditions have been optimized to ensure gelation of the hydrophobic layer. Leakage tests and water contact angle measurements have been made to assess the success of the hydrophobic coating at preventing leakage and moisture ingress. Ultimately, we will utilize these findings to

develop an approach that increases durability, feasibility, and potential applications of our novel PCM material.

2. MATERIALS AND METHODS

2.1 Substrate Preparation

A water bath was preheated to 60 °C using a hot plate. Using micropipette, ethanol, DI water, sulfuric acid, and TEOS were added to a 250 mL beaker. A watch glass and parafilm were used to seal the beaker, and the mixture was stirred for 45 min at 60 °C and 250 rpm. After 45 minutes, PEG-800 which had been pre-melted in an oven at 80 °C was added to the mixture. It was stirred for 45 min at 60 °C and 250 rpm for an additional 2 h. After this time period elapsed, NaOH was added and the solution was stirred for approximately 1 minute, until it began to thicken. At this point, it was poured into a silicon mold and placed in an oven at 60 °C for 24 h. This produced substrate cubes of approximately 1 cm³. The cubes were uniform, with smooth surfaces and an opaque appearance. Volume reduction during the gel process in the mold caused the top surface of each cube to become slightly convex. Several of these samples were analyzed by differential scanning calorimetry (DSC) confirming that an appropriate melting point (between 23 °C and 25 °C) had been achieved. Homogeneity of substrate cubes produced by this method was also confirmed by sampling several different cubes by DSC. The mass of the coated cubes was taken, then they were placed in an oven on a paper surface at 60 °C for 24 h. After 24 hours, samples were again massed. The paper surface upon which the samples had been placed was visually inspected for signs of PEG leakage and was photographed. To measure water contact angle, sample was placed on a stage such that the surface of the sample was level with the lens of a camera. A 15 µL drop of distilled water was pipetted onto the surface of the sample. The water droplet was photographed from the side. From this photograph, water contact angle was measured. Furthermore, digital calipers were used to measure the diameter of the water droplet to assess spreading of the droplet.

2.2 One-Stage Dip Coating

The amounts of each reagent used in this synthesis are listed in Table 1. A metal scintillation vial holder was preheated to 60 °C using a hot plate. Using micropipette, ethanol, DI water, sulfuric acid, and silanes were added to a 20 mL scintillation vial. The vial was closed tightly, and the mixture was stirred for 45 min at 60 °C and 250 rpm. After 45 minutes, NaOH was added and the solution was stirred for approximately 1 minute, until it began to thicken. At this point, substrate cubes, prepared according to the method listed above, were dipped into the solution and immediately removed. The mass of the coated cubes was taken, then they were placed in an oven on a paper surface at 60 °C for 24 h. After 24 hours, samples were again massed. The paper surface upon which the samples had been placed was visually inspected for signs of PEG leakage and was photographed. To measure water contact angle, sample was placed on a stage such that the surface of the sample was level

with the lens of a camera. A 15 µL drop of distilled water was pipetted onto the surface of the sample. The water droplet was photographed from the side. From this photograph, water contact angle was measured. Furthermore, digital calipers were used to measure the diameter of the water droplet to assess spreading of the droplet.

2.3 Two-Stage Dip Coating

The amounts of each reagent used in this synthesis are listed in Table 1. In 20 mL scintillation vial 1, a solution of 0.5 M NaOH was prepared. Then a metal scintillation vial holder was preheated to 60 °C using a hot plate. Using micropipette, ethanol, DI water, sulfuric acid, and silanes were added to 20 mL scintillation vial 2. The vial was closed tightly, and the mixture was stirred for 45 min at 60 °C and 250 rpm. After 45 minutes, substrate cubes were dipped into vial 1 (the NaOH solution), removed, and immediately dipped into vial 2 (Silane solution). The mass of the coated cubes was taken, then they were placed in an oven on a paper surface at 60 °C for 24 h. After 24 hours, samples were again massed. The paper surface upon which the samples had been placed was visually inspected for signs of PEG leakage and was photographed. To measure water contact angle, sample was placed on a stage such that the surface of the sample was level with the lens of a camera. A 15 µL drop of distilled water was pipetted onto the surface of the sample. The water droplet was photographed from the side. From this photograph, water contact angle was measured. Furthermore, digital calipers were used to measure the diameter of the water droplet to assess spreading of the droplet.

2.4 Vapor deposition

Silane (0.05 mL) was loaded into a glass vial. This vial was placed on its side in a quartz tube (diameter 1 inch) in the center of a tube furnace. Substrate cubes were placed in the tube at distances of 1, 2, and 3 inches from the vial containing silanes. Under a flow of N₂(g), the tube was heated to 80 °C. The tube furnace was then turned off and allowed to cool to room temperature. The mass of the coated cubes was taken, then they were placed in an oven on a paper surface at 60 °C for 24 h. After 24 hours, samples were again massed. The paper surface upon which the samples had been placed was visually inspected for signs of PEG leakage and was photographed. To measure water contact angle, sample was placed on a stage such that the surface of the sample was level with the lens of a camera. A 15 µL drop of distilled water was pipetted onto the surface of the sample. The water droplet was photographed from the side. From this photograph, water contact angle was measured. Furthermore, digital calipers were used to measure the diameter of the water droplet to assess spreading of the droplet.

2.5 TEOS/OTES/PEG and TEOS/PF-OTES/PEG Preparation

The amounts of each reagent used in this synthesis are listed in Table 1. A water bath was preheated to 60 °C using a hot plate. Using micropipette, ethanol, DI water, sulfuric acid, and silanes

were added to a 20 mL scintillation vial according to the amounts listed in Table 1. The mixture was stirred for 45 min at 60 °C and 250 rpm. After 45 minutes, PEG-800 which had been pre-melted in an oven at 80 °C was added to the mixture. It was stirred for 45 min at 60 °C and 250 rpm for an additional 2 h. After this time period elapsed, NaOH was added into the solution in 0.12 mL increments, until it began to thicken. Once gelled, the mass of the coated cubes was taken, then they were placed in an oven on a paper surface at 60 °C for 24 h. After 24 hours, samples were again massed. The paper surface upon which the samples had been placed was visually inspected for signs of PEG leakage and was photographed. To measure water contact angle, sample was placed on a stage such that the surface of the sample was level with the lens of a camera. A 15 μ L drop of distilled water was pipetted onto the surface of the sample. The water droplet was photographed from the side. Furthermore, digital calipers were used to measure the diameter of the water droplet to assess spreading.

TABLE 1: COMPOSITION OF COATINGS USED TO ACHIEVE HYDROPHOBICITY

| | DEDMS (mL) | TEOS (mL) | TEMS (mL) | OTES (mL) | EtOH (mL) | H ₂ O (mL) | H ₂ SO ₄ (mL) | 5M NaOH (mL) |
|---------------------|------------|-----------|-----------|-----------|-----------|-----------------------|-------------------------------------|--------------|
| DEDMS-based coating | 1.6 | 2.24 | -- | -- | 0.4 | 0.022 | 0.72 | 0.134 |
| TEMS-based coating | -- | 2.24 | 1.85 | -- | 0.4 | 0.022 | 0.72 | 0.134 |
| OTES-based coating | -- | 2.24 | -- | 2.99 | 0.4 | 0.022 | 0.72 | 0.134 |

3. RESULTS AND DISCUSSION

The relative success of each of the coating methods listed above was evaluated. One stage dip coating was found to be the simplest method and was effective at increasing the hydrophobicity of the materials. The water contact angle for the original substrate and for samples coated with each of the coating types via one-stage dip coating are shown in Figure 1. Furthermore, shape stability was maintained for samples coated via one stage dip coating, and leakage tests showed good shape stability. This was the case for all samples. It is illustrated for the TEOS and DEDMS sample in Figure 2. Note that no leakage of PEG is observed. Were there leakage, a dark stain would be visible on the paper upon which the samples rested.

We note that water contact angle is significantly reduced by the surface coatings. As expected, the more hydrophobic silanes resulted in more hydrophobic surface coatings. The coating containing OTES, which features a long hydrophobic moiety, was the most effective at increasing water contact angle, achieving a hydrophobic water contact angle of over 90°. The coating containing TEMS, with hydrophobic methyl moieties, was found to be the second most effective. The coating with DEDMS, which features a smaller number of methyl groups than TEMS, was the least effective of the surface coatings at increasing water contact angle, although substantial improvement in the water contact angle compared to the original substrate was still achieved.

Thus, from the perspective of achieving the most hydrophobic possible surface, OTES based surface coatings are preferable.

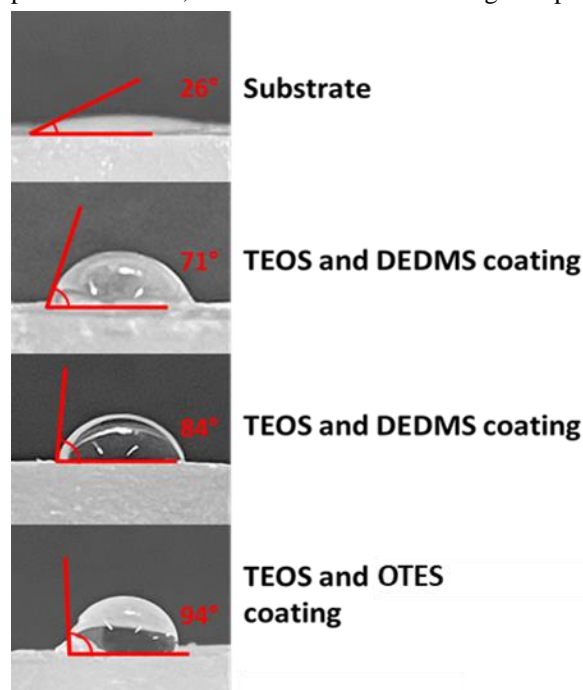


FIGURE 1: WATER CONTACT ANGLE MEASUREMENTS ON FOUR COATING TYPES. ALL WATER DROPLETS PICTURED WERE 15 μ L. COATINGS PICTURED WERE PREPARED BY ONE-STAGE DIP COATING METHOD.

However, for the TEMS and OTES based coatings, this method did not yield solid coatings. Rather, the coatings retained solution-like properties, resulting in a sticky surface.

We believe that the hydrophobic moieties present in these silanes interfere with the gelation process. They do not participate in the condensation reaction to form an extended network of bonds. Due to the molecular structure of these hydrophobic silanes, they can form fewer Si-O-Si bonds. In fact, in some cases, they may only be capable of forming one such bond, precluding them from participating in 3-dimensional gelation.

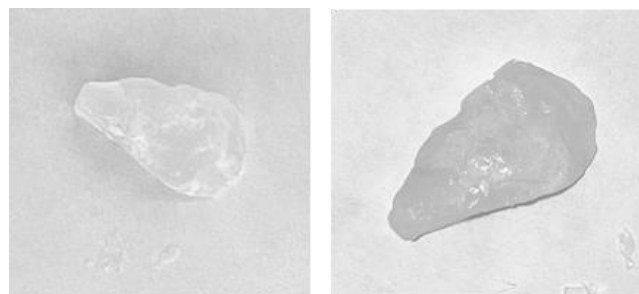


FIGURE 2: IMAGE OF TEOS AND DEDMS SAMPLE BEFORE (LEFT) AND AFTER (RIGHT) LEAKAGE TEST. ORIGINAL SHAPE OF MATERIAL IS RETAINED AND NO LEAKAGE IS OBSERVED.

Attempts to optimize the surface coatings by increasing the amount of TEOS relative to the hydrophobic silanes were unsuccessful. Thus, alternative methods of coating were explored.

Two-stage dip coating was attempted to achieve more control over the hydrolysis and condensation steps of the coating process. However, this method was unsuccessful, as the hydrolysis step of the dip-coating process led to partial dissolution of the substrate.

Therefore, vapor deposition techniques are being explored. This methodology, discussed above and illustrated in Figure 3, will yield much thinner coatings. The hydrophobic silanes, which may not be capable of forming 3-dimensional gels, will instead terminate the network of Si-O-Si bonds, forming a hydrophobic monolayer at the surface. Thus, we hope to maintain the favorable properties of hydrophobic silanes, while avoiding issues associated with thick, un-gelled surface layers. Optimization of furnace temperature for each silane is ongoing. Use of a vacuum chamber for deposition of less volatile silanes is also being explored.

Finally, fluorinated silanes are also being investigated using this method due to their extremely good hydrophobicity. While their high cost precluded their use in dip-coating methods, it may be feasible to utilize them as a monolayer.

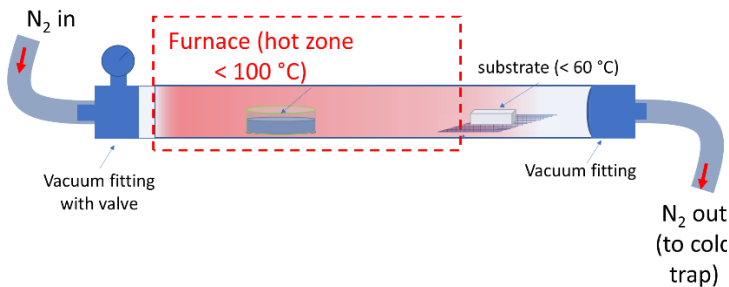


FIGURE 3: IMAGE OF VACUUM DEPOSITION CHAMBER THAT IS BEING DEVELOPED FOR OPTIMIZED SURFACE COATING.

4. CONCLUSION

A variety of hydrophobic silanes have been investigated to decrease the water uptake in increase the form stability of a novel sol-gel-based PCM material. These materials are effective at increasing hydrophobicity of the PCM substrates. They also decrease substrate leakage. However, incomplete gelation of the surface coatings is an ongoing problem, likely due to failure of the hydrophobic silanes to form extended networks of Si-O-Si bonds. Thus, methodologies for deposition of monolayer surface coatings are being examined.

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