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Development and characterization of paraffin-based shape stabilized energy storage materials

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ABSTRACT

The passive nature of energy storage through phase transition makes phase change materials (PCMs) a reliable choice for many applications. Shape-stabilized phase change materials (PCMs) mix liquid PCM with a molten polymer to create a material in which the PCM is fully contained even above the melt temperature of the PCM. Since the energy storage in the material will be a function of the amount of PCM, it is desirable to shape stabilize the material with as little polymer as possible. It is also important to understand the physical strength of these materials if they are to be used without a containment structure. Therefore, this study experimentally characterizes the structural and thermal properties of SS-PCM, identifies the effects of changing polymer loading level, provides guideline to determine at what point the material becomes shape-stabilized, and determines the heating and cooling curves. Based on these tests, it can be concluded that a sample of PCM can be considered to be shape-stabilized when the loading level of polymer creates a sample with structural integrity above the melting point, with geometric stability including elimination of contraction upon solidification and a sample with no circulation of the PCM during the melt phase, as well as full containment of the melt. For the samples investigated here, shape stabilization occurs in paraffin/HDPE mixtures above 25–30% HDPE.

1. Introduction

The term “phase change material (PCM)” is often used to describe materials which are used to store energy internally through the latent heat of fusion. These materials are typically solid at ambient temperatures but have melting points below the operating point of the application. As the system heats up, the PCM melts and stores energy with little change in overall system temperature. The use of PCMs for transient thermal management is well documented with applications in solar power, aviation and electronics [1–10]. The passive nature of energy storage through phase transition makes them a reliable choice for many situations.

PCMs are generally classified into three distinct categories: organic materials such as paraffin; inorganic materials, such salt hydrates and metallic materials; and eutectic materials, containing various combinations of inorganic and organic materials. One of the most widely studied organic phase change materials is paraffin wax, as it is chemically stable and does not degrade after repeated cycling. Paraffin is highly compatible with a wide variety of materials and has a latent heat of fusion of 200–250 kJ/kg depending on the particular paraffin selected.

Most PCMs must be used in a containment module, which prevents loss due to leakage when the PCM is in its liquid phase. This containment module is located adjacent to the heat source. The module represents an additional thermal resistance in a system, and adds weight and cost. Thus there has been interest in eliminating the containment module. Some studies have considered plastic encapsulants in which very small spheres of PCM are coated with a plastic shell. However, the thermal conductivity of the plastic shell is lower than that of the paraffin [11], and creates a thermal resistance in series between the heat source and the PCM. A second technique involves mixing liquid phase PCM with a molten polymer to create a supporting polymer matrix similar to a foam matrix within the PCM itself [12–15]. In this case the resistance of the polymer structure is in parallel with the PCM rather than in series between the PCM and the heat source which should improve thermal response. The polymer matrix fixes the shape of the PCM in a compact form and as the PCM melts, the liquid phase is fully contained within the matrix due to capillary forces. This thus removes the need for an additional containment module. Depending on the shape and size of the containment module, which is often made of aluminum, its elimination can save a significant amount of cost and weight per unit when compared to the low cost, lightweight HDPE that replaces it. This design is referred to as shape-stabilized phase change material (SS-PCM) and is well-suited for many applications including solar energy storage and passive thermal energy storage in energy efficient buildings.

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Table 1
HDPE and paraffin material properties.

Material	Specific heat, C_p (kJ/kg K)	Thermal conductivity, k (W/m K)	Kinematic viscosity, υ (m^2/s)	Density, ρ (kg/m^3)	Latent heat h_f (kJ/kg)	Melt temp. (°C)
Paraffin IGA-1230A	2.7	0.25	3.7×10^{-6}	880 solid 645 liquid	197	57
HDPE	1.8	0.46		940	154	130

Different polymer stabilizing agents can be used to create SS-PCM. Xiao et al. [12] mixed paraffin with styrene–butadiene–styrene (SBS) and noted that shape stabilization occurred at 20% by weight loading level of SBS. The latent heat of the sample was found to be 80% of that of paraffin, and the heating curves showed slight improvement with the SBS addition due to its slightly higher conductivity. Iniba and Tu [13] stabilized paraffin with high density polyethylene (HDPE) at 26% HDPE by weight. The density, specific heat, latent heat and thermal conductivity of the samples were reported, but no heating curves and no structural properties were provided. Krupa et al. [14] mixed low density polyethylene (LDPE) with hard (high density) and soft (low density) paraffin and found that that the high density wax and LDPE were miscible whereas LDPE and the low density wax were not. Furthermore, the lower density wax was more easily separated from the polymer matrix. Results from property testing in a DSC were presented, but the temperature response during thermal cycling was not. Wirtz et al. [15] created a shape stabilized matrix using styrene–ethylene–butadiene–styrene (SEBS) polymer and n-eisocane paraffin wax. The latent heat of the sample for 75% paraffin and 25% SEBS by weight was 75% of the latent heat of paraffin and the thermal conductivity of the sample increased slightly from 0.20 W/m K to 0.25 W/m K once the PCM fully melted due to better wetting at the polymer/PCM interface. Storage modulus and loss modulus were also presented.

While these papers present some of the basics of creation of SS-PCM, there exists little data on either the physical properties of the shape stabilized materials or the transient response of SS-PCM to thermal cycles. Additionally, none of these reference papers define the criteria under which the material is considered to be shape-stabilized, and do not present any data on the effect of changing the percentage of polymer in the samples.

Many of the applications which lend themselves to the standard use of PCMs are also candidates for the use of SS-PCM. Since the energy storage in the material will be a function of the amount of paraffin, it is desirable to shape stabilize the material with as little polymer as possible. It is also important to understand the physical strength of these materials if they are to be molded and used without a containment structure. Finally, as the SS-PCM will be used in thermal cycling, the heating and cooling curves of the materials must be quantified.

Therefore, this study will experimentally characterize the structural and thermal properties of SS-PCM, identify the effects of changing polymer loading level, provide guideline to determine at what point the material becomes shape-stabilized, and determine the effects of sample size, and applied power on the heating and cooling curves.

2. Materials development and experimental methods

A series of samples consisting of varying concentrations of paraffin and HDPE were prepared for testing. Three different material property experiments were performed in this project: (1) impact testing to determine sample hardness at ambient and elevated temperatures, (2) volume displacement to measure volume contraction during solidification and (3) differential scanning calorimetry (DSC) to determine sample melting points and latent heat. Once it is it is confirmed that shape stabilization occurs within the sample, transient thermal testing is performed to determine the heating and cooling curves.

2.1. Materials

The present work employs the use of organic paraffin as the phase change material. Paraffin is a commonly used energy storage material since it is stable, non-corrosive, and non-toxic. The paraffin (type IGI-1230A) is purchased in bulk from The International Group (IGI), an industrial supplier, is a fully refined paraffin wax and is used without any modifications. Its thermal properties are listed in Table 1.

The stabilizing polymer used in this study is high density polyethylene (HDPE) a common and commercially available product purchased in pellet form from Sigma-Aldrich chemical supply. HDPE, much like paraffin, is stable, non-corrosive, and non-toxic. HDPE has a latent heat of 154 kJ/kg and a melting point of 130 °C, well above the normal operating range of the paraffin (melt temperature of 57 °C). Its thermal properties are listed in Table 1. In this experiment, increasing concentrations of HDPE are added to the paraffin to identify the conditions under which the HDPE will form a stabilizing polymeric matrix and create a shape-stabilized phase change material.

2.2. Sample preparation

The paraffin is melted in a beaker over a hot plate and once the paraffin is completely melted the stabilizing polymer is added at rates from 10% to 50% by weight of the paraffin, depending on the sample being prepared. The liquid HDPE is evenly distributed into the liquid PCM using a magnetic stir bar. The temperature of the mixture is monitored and maintained at 180–200 °C for the duration of the mixing. During the mixing process it is clear from observation that the two materials are miscible and mix readily. The mixing occurs over a 30–60 min time period depending on the sample. No further testing is done to assure uniformity. The mixture is poured into a mold and allowed to solidify. The samples are referred to by their weight percentage of paraffin followed by the weight percentage of polymer. Thus, a 100/0 sample is paraffin only and a 0/100 sample is HDPE only. The samples tested include 100/0, 90/10, 80/20, 70/30, 60/40, 50/50 and 0/100.

2.3. Property testing

2.3.1. Shape stabilization testing

A key aspect of this work is the determination of criteria under which the sample can be considered to be shape-stabilized. In addition to the criteria that no PCM leak from the edges of the sample during melting, the sample should also hold its shape during thermal cycling. Paraffin typically exhibits a significant contraction during solidification, as evidenced by the difference in density between the liquid and solid phase (see Table 1). This contraction creates a conical divot at the top surface of the sample, referred to as the ullage space. A shape-stabilized sample should not change