ABSTRACT

The strong interaction between n-eicosane and silica nanoscale skeleton exhibits novel phase change temperature management and energy utilization. In this study, a sol-gel synthesized method to fabricate phase change nano-composites by impregnating silica nano-porous materials with n-eicosane is reported. Field emission scanning electron microscope (FE-SEM) results show that the sol-gel synthesized silica has an open network structure as a host for shape stabilization of molten n-eicosane. A combined thermodynamic/heat transfer analysis was carried out to determine the total mass, thickness, and temperature excursion as a function of the area fraction of n-eicosane at given maximum energy and thermal flux. The derived hyperbolic relations showed that increasing the n-eicosane area fraction resulted in a better thermal management in smoothing temperature fluctuation, lower total mass, and lower volume in the nano-composite.

Keywords: Nano-composite; Thermal properties; Modeling; Scanning electron microscopy (SEM); Sol-gel methods

1. Introduction

Phase change materials (PCMs), which store excess heat generated from the working components and release it reversibly when needed, provide a smart approach for efficient temperature management and energy utilization. Most practical applications, such as temperature regulating textiles [1], green house temperature-control [2], solar energy utilization [3,4], and heat management of electronics [5], require PCMs to have high density of latent heat and an appropriate phase change point. According to these requirements, n-eicosane is very promising for temperature controlling applications due to its comparative high fusion latent heat, suitable melting temperature, and chemical stability [6]. However, application of solid-liquid PCMs is limited due to leaking the liquid phase above the phase change point. Thus, accommodation of PCMs in an appropriate host material is essential to prevent the leakage of the liquid phase in temperature controlling applications using the solid-liquid phase change. The leakage is usually circumvented by introducing shape stabilization support [7,8]. Devoting to develop composites with a high PCMs load and heat storage density, research on silica nano-porous ceramics with high specific area has been steadily increasing as a potential shape stabilization matrix or supporting structural materials for PCMs' skeleton to avoid leakage in the solid-liquid transition [6,9]. As a host material, silica aerogels, i.e. sol-gel derived porous inorganic materials recognized for their low density (as low as 0.01-0.02 g/cm$^3$) [10], high porosity (>90%) [11], and high specific surface area (600-1000 m$^2$/g) [12], have been extensively used in many engineering applications. However, their structural properties result in a low thermal conductivity and high optical transparency [13]. Fragility and thermal radiation at high temperature due to the transparency of monolithic silica aerogels restrain their range of application. Mechanical strength and high transparency of silica aerogels have been improved using reinforced fibers [14] and pacifiers doped in the aerogels [15]. Composite silica aerogels are called silica nano-porous materials and they have a similar open network structure to that of monolithic silica with superior properties such as higher mechanical strength and excellent insulation at high temperatures [16, 17]. These properties enable silica nano-porous materials to be employed in a wider range of applications compared to monolithic aerogels, such as aeronautics and aerospace [18], transportation of off-shore oil and gas [19], and energy saving buildings [20], where strict limit of space, weight, or thermal insulation is required.

The concept of thermal design using PCM has been well established through various studies in recent decades, and is widely used in space and ground applications. The typical application is the cooling of the nose cone in a space shuttle or a manned spacecraft capsule upon its re-entry into the atmosphere. Recently, studies have been conducted on the use of PCM to cool computers to increase the calculation speed of CPU [21]. To apply PCMs as an alternating heat storage and discharge in space applications, the material is required to have particular thermo-physical properties such as conformance of phase change temperature to the design limits, high latent heat, and low density difference between liquid and solid phases. Structural and thermal considerations in the design are major concern in applying supporting materials. The structure of supporting materials is required to be leak-proof for the molten PCMs and be able to withstand imposed static and dynamic loads. In addition, it is necessary that the supporting materials to be integrated into the thermal protection package without degrading the system performance.

In this paper a combined thermodynamic/heat transfer analysis is developed for the n-eicosane in silica nano-porous materials to determine the relationship between the total mass, thickness, and temperature excursion as a function of area fraction of n-eicosane in the nano-composite at given maximum energy and thermal flux. The details on the preparation process of n-eicosane/silica nano-composite and the measured thermo-physical data are also reported.
2. Theory: modeling of combined thermodynamic/heat transfer

Fig.1. PCM thermal control system and model of PCM/silica nano-composite

![PCM thermal control system and model of PCM/silica nano-composite](image1)

3. Experimental

3.1. N-eicosane

The n-eicosane (C20H42) used in this study were supplied by Nanyang Chemicals Company, China. The thermo-physical properties of the PCM are given in Table 1. The melting temperature ranges and the fusion heat of the n-eicosane were measured using a DSC (NETZSCH STA449C) with a heating rate of 10 °C/min within the temperature range of 20-80°C.

Table 1 Thermo-physical properties of n-eicosane and silica nanoporous material

<table>
<thead>
<tr>
<th>Name</th>
<th>n-Eicosane, C20H42</th>
<th>Silica porous material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point, °C</td>
<td>36.7*</td>
<td>-</td>
</tr>
<tr>
<td>Latent heat of fusion, J/kgx10(^{-3})</td>
<td>247*</td>
<td>-</td>
</tr>
<tr>
<td>Specific heat, J/kg K</td>
<td>2210 at 308 K**</td>
<td>549**</td>
</tr>
<tr>
<td>Thermal conductivity, W/m.K</td>
<td>0.15**</td>
<td>0.37**</td>
</tr>
<tr>
<td>Density, kg/m(^3)</td>
<td>856 at 308 K***</td>
<td>280***</td>
</tr>
</tbody>
</table>

Note: *measured by DSC, ** measured by LFA 1000 Laserflash (thermal conductivity/diffusivity), *** calculated by experiment

3.2. Preparation of n-eicosane/silica nano-composite

The preparation process of n-eicosane/silica nanoporous composite is shown in Fig.3. Initially, Silica sols were synthesized by a two-step sol-gel process using TEOS as the precursor and the co-precursor diluted in EtOH solvent. The hydrolysis and condensation were carried out

Fig.2. Stored maximum energy from PCM and pulse power generated by the component during one thermal cycle

![Fig.2. Stored maximum energy from PCM and pulse power generated by the component during one thermal cycle](image2)

Fig.3. Experimental preparation process of n-eicosane/silica nano-composite

![Fig.3. Experimental preparation process of n-eicosane/silica nano-composite](image3)
under the acidic (nitric acid (HNO₃)) and basic (ammonium hydroxide (NH₄OH)) catalyzed conditions using the molar ratio of HNO₃: NH₄OH set as 1:2. Acid or base catalyzed hydrolysis and condensation reactions of the sol-gel process were prerequisite to the formation of silica gels.

Then, reinforced fibers (main compositions: SiO₂ > 99.95%) were exploited as the structural reinforcement matrix. The fibrous materials were uniformly pre-shaped in a mold; then, the sol-gel mixtures were poured into the mold, as shown in Fig. 1. Then, ethanol was added into the mold. After gelation and aging for 24 hr, the whole mixture was dried in an autoclave above the critical temperature (T=270 °C) and critical pressure (7.5 MPa) of ethanol to obtain the final bulk silica nano-porous material. Fig.3. also illustrates the supercritical fluid drying equipment used in this process.

(The Rest Part is Omitted)

4. Results and discussion

4.1. Thermo-physical properties

The phase change temperature of PCM should be within the maximum/minimum operating temperature range of the electronic component. Also it would be better if the latent heat of fusion is higher. Furthermore, silica nano-material as the PCM support must remain chemically stable within the maximum/minimum operating temperature range. In addition, according to the design constraints, there must be a small density difference between the solid and liquid phases. According to the above criteria n-eicosane with 20 carbon atoms is the primary choice compared to the other PCM materials tabulated in Table 1. The phase change temperature of n-eicosane is 37°C. Its latent and specific heat are 247 kJ/kg, 2.21 kJ/kg·K respectively. The density is 856 kg/m³, which decreases about 5% in the liquid phase. The thermal conductivity is very low in both the liquid and solid phases with an average value of 0.15 W/m·K.

4.2. Structure and modeling

Fig.4 shows the FE-SEM images of the silica nano-material and n-eicosane/silica nano-composite. The silica open network structure with supporting fibers distributed uniformly within the silica nano-material is shown in Fig. 4 (a). The large surface area and low density of porous material enhance the shape stabilization capability and thus, maximize the surface area per unit volume of PCM. Furthermore, the high porosity and high surface area facilitates the impregnation of the reinforced silica structure with liquid n-eicosane, yielding an integrated thermal control system, as shown in Fig. 4 (b). This can be further used in the applications where small size and light weight are demanded. Silica nano-material serves not only as a reinforced skeleton of the composite, but as a heat conducting medium to transfer heat between the component and the low thermal conductive PCM to melt or solidify it during the service.

The PCM thermal control system and the cross-section of the designed structure, where the PCM is embedded in silica nano-material, are depicted in Fig.1. The cross-section of the n-eicosane/silica nano-composite is 100mm x 100mm. The performance of the thermal control device was investigated by a numerical analysis using MATLAB. The main purpose of the study was to determine the effect of n-eicosane’s weight fraction on the mass, thickness, and temperature excursion, employing a combined thermodynamic/heat transfer analysis. The outputs were used to smooth the temperature fluctuations by assimilating heat and releasing it though phase change of PCM according to the thermal cycle (Fig.2).

![Fig.4 FE-SEM images of the silica nano-material (a) and n-eicosane/silica nano-composite (b)](Image)

The heat in the component is generated periodically during the service. The maximum energy stored by the PCM/silica nano-composite, Emin, is input as 3.6x10⁶kJ and then, a 100 W warming up step, Qpulse, started during the service cycle, as shown in Fig.1 and Fig.2. The thermodynamic/heat transfer analysis as per given in Eq. (1)-(5) were programmed into MATLAB to solve for the excursion temperature, Tcomp-Tmei, the total mass, Mtot, and the thickness, t, of the nano-composite as a function of PCM area fraction, Apcm/Atot. The thermo-physical data of the PCM and silica nano-material given in Table were the inputs to the program. The derived hyperbolic curves for temperature excursion and the total mass and thickness as a function of n-eicosane area fraction are shown in Fig. 5 and 6, respectively.

When Apcm/Atot = 0, i.e. there is only solid silica nano-material, the temperature excursion is maximum and decreases drastically with the addition of n-eicosane, as shown in Fig. 5. In our previous study [22], the SEM microstructure analysis and the experimental calculations showed that 75 weight% PCM charged into the silica nano-material can completely fill the voids in the matrix [22]. PCM 75 wt% is where the temperature excursion reaches a minimum value, as shown in Fig. 5. When the heat generated by the components reaches the maximum value the PCM changes to the liquid phase. However, when the component generated heat is minimum, a liquid to solid transition occurs in the PCM. These results show that the high latent heat of n-eicosane enables better controlling of temperature fluctuations compared to silica nano-material without PCM.
5. Conclusion

A sol-gel synthesized method to fabricate silica nanoporous material was introduced to prepare phase change nano-composite through impregnating silica nano-porous network structure with n-eicosane. FE-SEM results showed that impregnation of n-eicosane into the open network structure of silica nano-material improved the structural integrity of the nano-composite. A combined thermodynamic/heat transfer analysis revealed a hyperbolic relationship between the n-eicosane area fraction in with the temperature excursion and the total mass and thickness. These curves indicated that increasing the n-eicosane area fraction within the nano-composite decreased the temperature excursion (smoothing the temperature fluctuations) at a given maximum energy and thermal flux. It was also shown that the increase in the area fraction of n-eicosane resulted in a lower mass and volume for the nano-composite. These results exhibit that the interaction between n-eicosane and silica skeleton leads to a novel temperature management for a lighter and smaller nano-composite.

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REFERENCES