Thermal performance evaluation of energy efficient paraffinic PCMs/expanded vermiculite and perlite composites for energy saving

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Abstract

This paper deals with the preparation, characterization, thermal properties and thermal reliability of form-stable composite phase change materials (PCMs), composed of n-octadecane, expanded vermiculite, and perlite for thermal energy storage. The composite PCMs were prepared by incorporation of liquid n-octadecane within the expanded vermiculite (eVMT) and expanded perlite (ePLT), using a vacuum impregnation method. The microstructures of n-octadecane/expanded vermiculite and pearlite were characterized by scanning electron microscopy (SEM). Analysis of Fourier transform infrared spectroscopy (FT-IR) of the prepared composite PCMs showed good compatibility between n-octadecane and the expanded vermiculite and pearlite. The thermal conductivities of composites were reduced, based on the TCi results. Differential scanning calorimetry (DSC) analysis indicated that the n-octadecane/eVMT and n-odtadecane/ePLT composites maintained their large latent heat capacity and original phase change temperatures, due to large surface area and good dispersion of the eVMT and ePLT. TGA analysis revealed that the prepared composite PCMs had good thermal durability in the working temperature ranges. Therefore, n-octadecane based composite PCMs can be considered as suitable candidates for latent heat thermal energy storage, with high thermal performance.

1 Introduction

Phase change materials (PCMs) are a kind of latent heat energy storage material, and can be applied to store substantial thermal energy, which is collected from solar radiation. PCMs can play an important role in an energy storage device, by utilizing their high storage density and latent heat property. The latent heat property is the amount of heat released or stored by a substance during a change of state, without much change in temperature. This can be used to shift the cooling or heating load from the peak period, to the off-peak period [1]. Vermiculite is a hydrous silicate mineral that is classified as a phyllosilicate, and when heated, it can greatly expand. Exfoliation occurs when the mineral is sufficiently heated, and the effect is routinely produced in commercial furnaces. Vermiculite is formed by the weathering or hydrothermal alteration of biotite or phlogopite. The exfoliated (expanded) vermiculite is light, and clean to handle. Also, it has high insulation value, acoustic insulation properties, and is absorbent to a wide range of liquids. The expanded vermiculite is a lightweight material that is porous, inexpensive, ecologically harmless, and non-toxic. Perlite is a volcanic glass

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containing 65-75 % of SiO_2, and 2-5 % of H_2O. The characteristic property of perlite is that if it is exposed to rapid heating temperature of 900 to 1.200°C, it increases its volume by 4 to 20 times. This happens because perlite includes bound water, which expands during heating, according to the well-known popcorn effect, and adopts the form of a porous swollen material. The size of swollen pellets varies between 1 and 10 mm, with an apparent density of 75 to 150 kg/m^3. Thanks to these numerous tiny voids, the volcanic rock becomes light, and acquires unique thermal and sound proofing properties. In this paper, form-stable composites consisting of n-octadecane with expanded vermiculite (eVMT) and expanded perlite (ePLT) were prepared as novel potential PCMs for high thermal energy storage in building applications. Their thermal properties and reliability were analyzed by differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). The thermal conductivity of composites was measured by TCi thermal conductivity analyzer. Their morphologies and structures were investigated by scanning electronic microscopy (SEM), and Fourier transformation infrared spectroscopy (FTIR).

2 Experimental

For preparation of samples, n-octadecane purchased from Sigma-Aldrich company was used for the experiment as heat storage material. The n-octadecane has a latent heat capacity of 256.5 J/g, and melting phase change range of 26.9 °C~28.7 °C. The eVMT and ePLT were supplied from Misung Corporation in South Korea. In this study, the composite n-octadecane was prepared by a vacuum impregnation method to solve the leakage problem, keeping their efficient thermal storage quantity. [2]. The morphology of the eVMT, ePLT, and composite PCMs were observed by JEOL scanning electron microscopy (SEM, JSM-6360A), at room temperature. Fourier transformed infrared spectroscopy (FT-IR, 300E Jasco) was used to confirm the change of chemical groups of composite PCMs at room temperature, by analyzing FT-IR spectra of the n-octadecane and composite PCMs [3]. The thermal conductivity of the composites was measured by TCi thermal conductivity analyzer (C-Therm Technologies Ltd). Thermal durability tests of the thermal stability composite PCMs were carried out using thermo gravimetric analysis (TGA, TA Instruments, TGA Q5000) on approximately 2 - 4 mg samples, in the range of 0-600 °C, at a heating rate of 10 °C /min, in a nitrogen atmosphere (99.5 % nitrogen, 0.5 % oxygen content) to prevent unwanted oxidation [4]. The thermal properties of n-octadecane and composite PCMs, i.e. the melting and crystallizing points and phase change enthalpies of shape-stabilized composite PCMs, were measured using differential scanning calorimetry (DSC Q 1000, TA instrument, USA), in the range of 0 ◦C – 80 ◦C, at a melting and freezing rate of 10 ◦C/min, in an nitrogen atmosphere, with a flow rate of 60 ml/min [5].

3 Results and discussion

3.1 Characterization of composite PCMs

The morphology of the eVMT, ePLT, n-octadecane/eVMT, and n-octadecane/ePLT were studied by scanning electron microscopy observation. SEM images of the porous building materials and composite PCMs are shown in Fig. 1. As seen from Figs. 1 (a) and (b), eVMT and ePLT have irregular layers, and uneven pores in the layers. The eVMT and ePLT have rough and random microstructures. The image in Fig. 1 of the composite PCMs also shows that the n-octadecane is dispersed into the porous network of eVMT and ePLT, which are used as supporting materials. Chemical compatibility between the components of the composites was examined by FT-IR spectroscopy. Fig. 2 shows the FTIR spectrum of base materials and composite PCMs [6]. This experiment was carried out to determine the chemical properties of the composite PCMs. The n-octadecane has the molecular formula of

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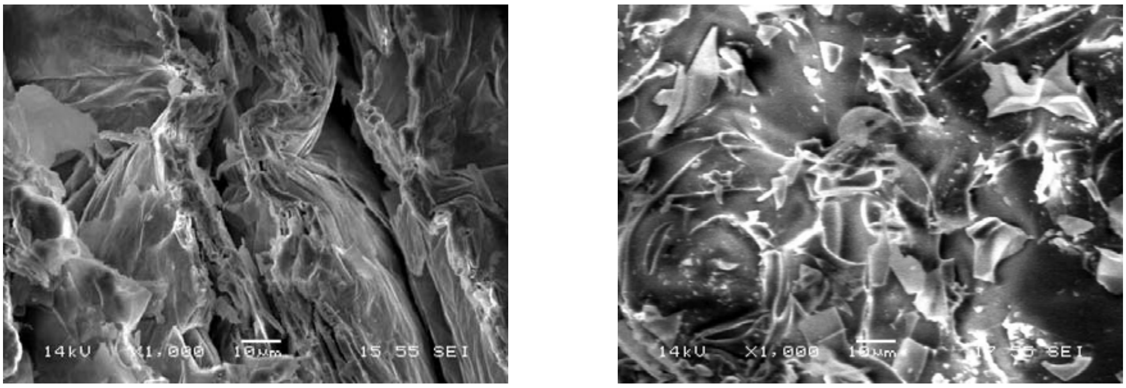
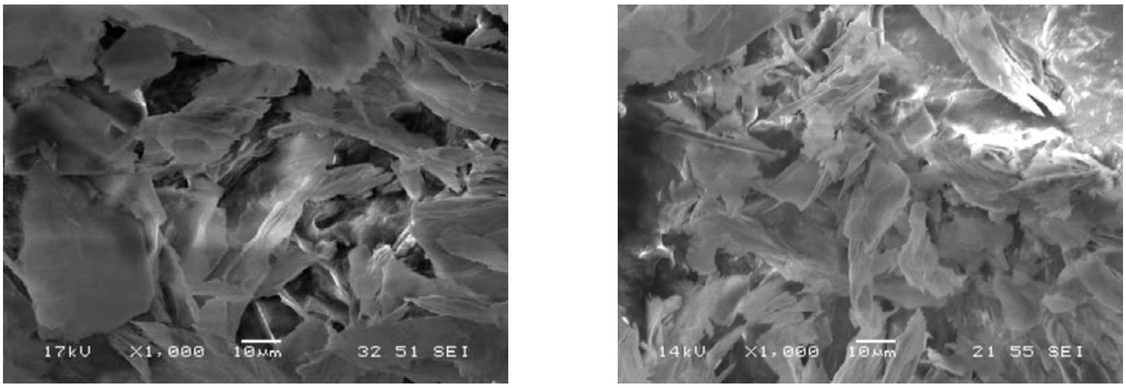


(a) Expanded VMT (b) Expanded PLT



(c) Octadecane/Expanded VMT (d) Octadecane/Expanded PLT

Figure 1. SEM images of the (a) Expanded VMT, (b) Expanded PLT, (c) Octadecane/Expanded VMT, and (d) Octadecane/Expanded PLT.

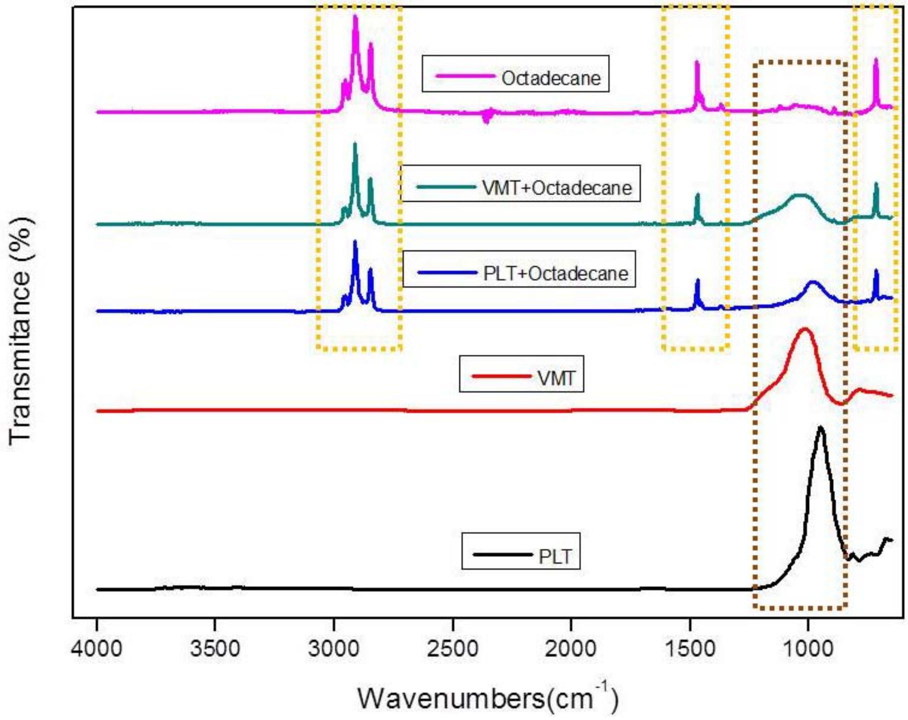


Figure 2. FTIR spectra of the octadecane, VMT+Octadecane, PLT+Octadecane, VMT, and PLT.

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$C_{18}H_{38}$, and is composed of $-CH_2$ bonding and $-CH_3$ bonding. FT-IR absorption peaks of 2918, 2850, 1470 and 715 cm^{-1} are caused by stretching vibration of the functional groups of $-CH_2$ and $-CH_3$. FTIR spectra confirmed that these bondings were not broken or changed during the incorporation process, as seen in the n-octadecane/eVMT and n-octadecane/ePLT composites peaks. In FTIR spectra of the eVMT and ePLT, the peaks usually appear between 1100 and 950 cm^{-1}. In addition, the FITR peaks range of composite PCMs shows stretching vibration of the Si–O group of building materials. The eVMT shows a main absorption band at 948 cm^{-1}. The ePLT shows a main absorption band at 1014 cm^{-1}. This means that there is no chemical interaction between n-octadecane and the porous materials used. As shown in Fig. 2, for n-octadecane/eVMT and n-octadecane/ePLT, no new characteristic peak was observed in the spectra of the n-octadecane, eVMT, or ePLT. This means that no chemical interaction occurred between the components of the composites [7].

3.2. Thermal conductivity of the composites

The thermal conductivity is crucial to the applicability of phase change materials. Low thermal conductivity severely reduces the rate of heat storage and extraction during the melting and solidification cycles. The thermal conductivity was studied by TCi analysis. The results are the average of five measurements, for each carbon nanomaterials loading and the coefficient of those correlation (R^2) is 0.99. Fig. 3 shows the thermal conductivity of n-octadecane, n-octadecane/ePLT and n-octadecane/eVMT. The thermal conductivities of composites decreased, compared to that of pure n-octadecane. The thermal conductivity of n-octadecane/ePLT is 0.2310 W/mK, which is 87.3% that of the pure n-octadecane. The thermal conductivity of n-octadecane/eVMT is 0.1569 W/mK, which is 59.3% that of the pure n-octadecane. This is due to the low thermal conductivity of vermiculite and perlite of 0.03-0.05 W/mK, which resulted in the low thermal conductivity of the composite.

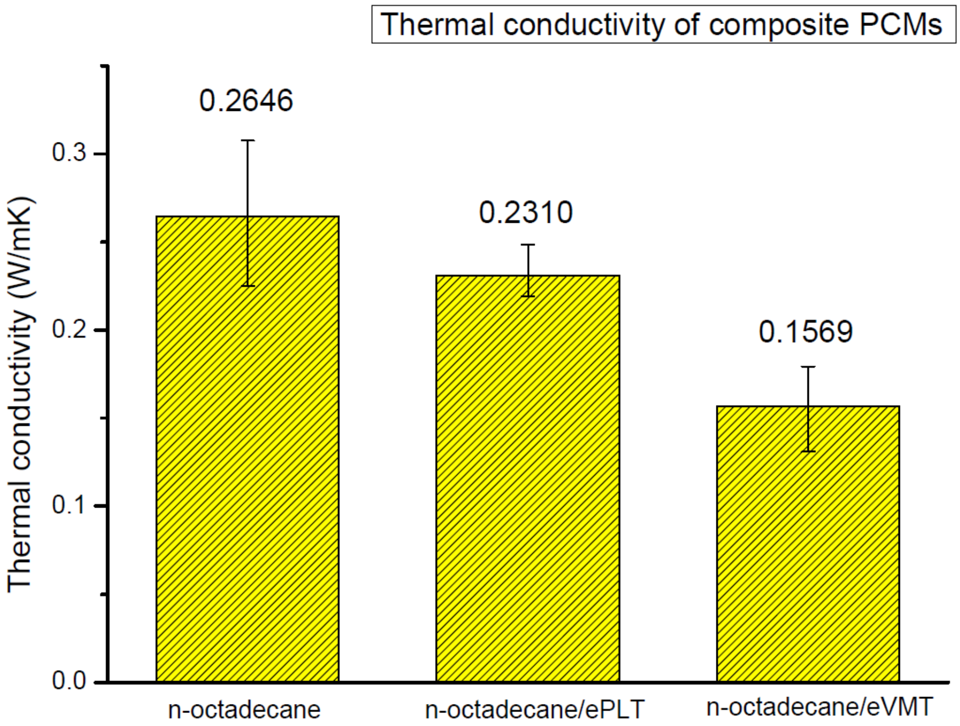

Figure 3. Thermal conductivity of the PCMs.

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3.3. Thermal properties of the composites

DSC analysis is the most valid method to determine the thermal energy storage properties of PCMs, since it gives reliable results for the phase change temperatures range and latent heat. Fig. 4 shows the DSC curves of the n-octadecane, n-octadecane/eVMT and n-octadecane/ePLT that were obtained. Table 3 presents the DSC data of the phase transition temperature (Tt), phase change temperature (Tm), latent heat, and incorporated rate. DSC thermograms determined the melting and freezing temperature ranges to be 28.7 °C and 26.9 °C for the n-octadecane, 26.1 °C and 24.9 °C for the n-octadecane/eVMT, and 26.2 °C and 25.3 °C for the n-octadecane/rPLT, respectively. Although there are small decreases in the phase change temperatures of the composite PCMs, the phase change temperatures of the composite PCMs are very close to those of n-octadecane. The n-octadecane, n-octadecane/eVMT and n-octadecane/ePLT showed latent heats of melting of 226.0 J/g, 142.0 J/g, and 132.2 J/g, respectively, and latent heats of freezing of 242.6J/g, 125.5 J/g and 174.3 J/g, respectively. The values for latent heat capacity of the n-octadecane/eVMT and n-octadecane/ePLT were nearly 80.65 % and 59.35 % that of the n-octadecane, respectively. The measured latent heats of melting and freezing of the composite PCMs were close to the values calculated by multiplying the mass ratio of the n-octadecane in the composites, and their phase change enthalpies. These results were probably caused by abnormal interactions between the PCM, and the inner surface of pores of the eVMT and ePLT.

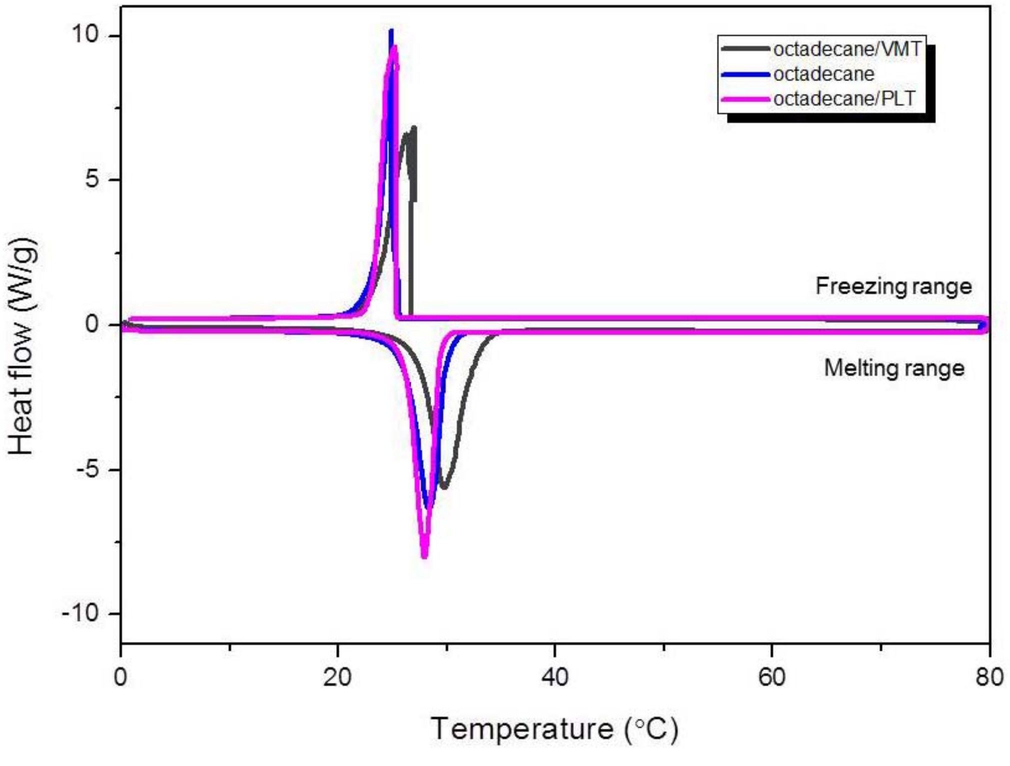

Figure 4. DSC curves of the PCMs.

3.4. Thermo gravimetric analyses

The thermo gravimetric analysis curves show the weight of n-octadecane and its composite PCMs, and derivative weight of n-octadecane and its composite PCMs. As shown in Fig 5, the n-octadecane has one curve of thermal oxidation degradation, and the peak occurred at

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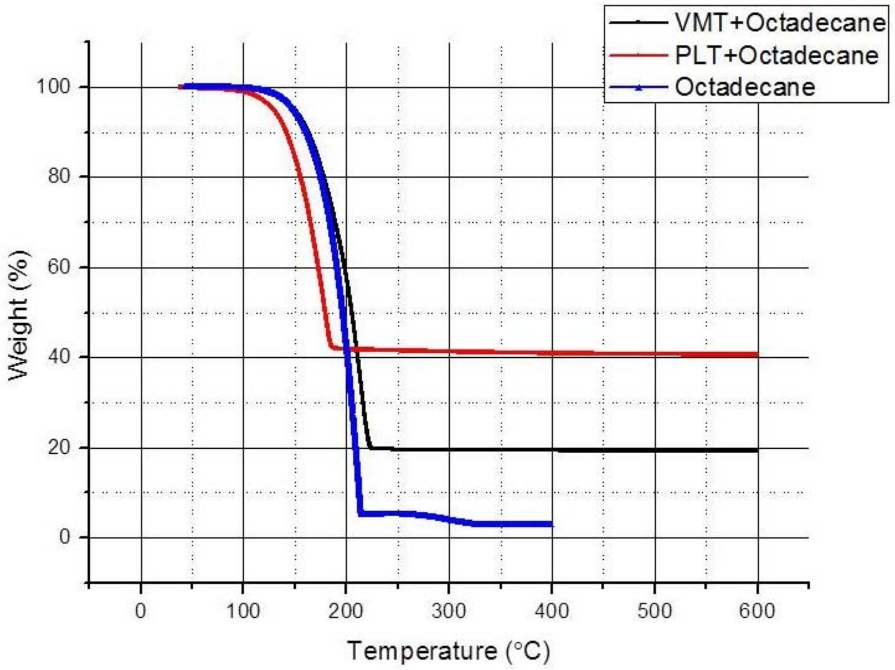
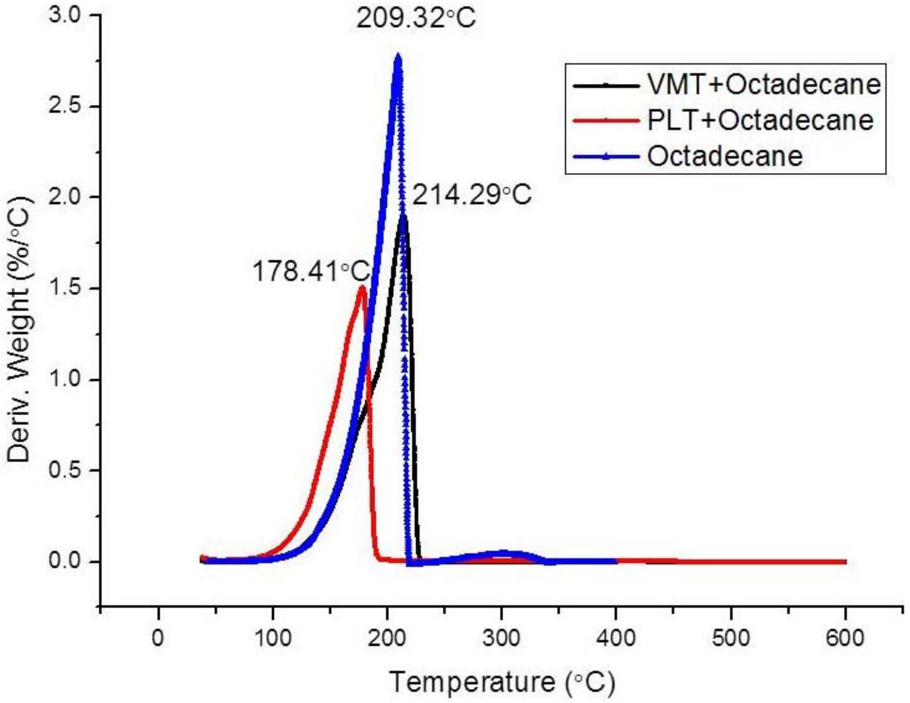


(a) The weight of pure PCM and the composite PCMs



(b) The derivative weight of pure PCM and the composite PCMs

Figure 5. Thermo gravimetric analysis of pure PCM and the composite PCMs: (a) The weight of pure PCM and the composite PCMs, and (b) the derivative weight of pure PCM and the composite PCMs.

209.32 ℃. Also, the derivative weight of n-octadecane/eVMT shows a peak of 214.29 ℃, and n-octadecane/ePLT shows a peak of 178.41 ℃. In these graphs, we found the derivative weight peaks of shape-stabilized composite PCMs are higher than that of pure PCM. Also, TGA analysis showed the prepared composite PCM left a more plentiful combustion residue, because of loading contents of the porous material with the properties of flame retardancy.

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This result also showed plenty of the n-octadecane incorporated into the structure of the porous material. As a result, eVMT and ePLT led to thermal resistance of the n-octadecane. After thermal decomposition, composite PCMs with weight percent remained, after about 250 ℃. Also, weight loss did not happen in all composite PCMs below 100 ℃, so it can be concluded that the prepared composite PCMs exhibit available thermal stability at room temperature.

Conclusion

In this study, novel form-stable composite PCMs were prepared, by a vacuum impregnation method. We determined the characteristics of n-octadecane based composite PCMs that contained eVMT and ePLT, by using FT-IR, SEM, DSC, and TGA analysis techniques. Because of the effect of capillary force and surface tension force, n-octadecane was confined in mass fractions of 80% and 59% in the eVMT and ePLT, respectively, without any liquid n-octadecane leakage from the porous material of the composites. DSC results showed that the melting and freezing temperatures and latent heats of composite PCMs are suitable for low temperature thermal energy storage applications.

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