Characterization of shape-stabilized phase change material using beeswax and functionalized multi-walled carbon nanotubes

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Abstract. One of the promising solutions for energy management is thermal energy storage. Beeswax is a type of wax from beehive which can also be performed as thermal storage with high latent heat but it has low thermal conductivity. On the other hand, multi-walled carbon nanotubes (MWCNTs) are known as an advanced nanoparticle which has high thermal conductivity. In this research, modification of Beeswax/Acid-treated CNTs (A-CNTs) composite was conducted in order to determine shifting on its structure and thermal performance. MWCNTs were functionalized with strong acidic mixture by ratio 3:1 of H2SO4 and HNO3 becoming A-CNTs. Impregnation method was being used to shape the composite with mass ratio of 5% A-CNTs. Several tests were conducted, functional group formation was determined by Fourier Transform Infrared (FTIR) test and thermal performance was observed by Differential Scanning Calorimetry (DSC) test, and thermal conductivity test. Test results show that modification of stable Beeswax/A-CNT composite was successfully formed and indicate that with addition of 5 wt.% A-CNTs, the latent heat of Beeswax decreases 25% and significantly escalate the Beeswax’s thermal conductivity by up to 84%. It supports that Beeswax is a promising solution for energy management system near in the future that is available abundantly and affordably.

1. Introduction
Today we are facing two major challenges in this world which are reducing gas emissions from fossil fuels and finding alternative energy source to fulfil our needs. This condition forces people to utilize the energy usage and it also drives researcher to develop a new solution. One of the most significant advancement for energy efficiency is Thermal Energy Storage (TES). A large number of Phase Change Materials (PCM) such as organic, inorganic compound, paraffin, and non-paraffin organic acids have been considered to be applied for latent heat thermal energy storage (LHTES) applications [1-4]. It has been recently studied that the PCMs organic, inorganic and their mixtures are prospective LHTES materials that can be used for...
building materials impregnation [3]. Organic PCMs have been attracted more than the others due to its good characteristics [5, 6].

In Indonesia, one of the most popular organic PCMs is Beeswax. Beeswax is comprised of esters of fatty acids and long chain alcohols. Beeswax belongs to category of organic non-paraffin PCMs. Its development as PCM described by Sinaringati, et al. 2016 for infant incubator heat source [5]. Amin, et al. 2017 tested the modification of nano-PCM using Beeswax and graphene with variative mass ratio to determine its thermal characteristics and the result is thermal conductivity of this nano-PCM increased by 12% [6]. Nevertheless, Beeswax as organic PCM possess some drawbacks that it has low thermal conductivity, and possesses leakage during phase transition. In order to eliminate these disadvantages, there are several methods to advance the process, for instance, encapsulation and formation of Shape Stabilized Phase Change Material (SSPCM) [7]. Type of material that is frequently prepared and characterized as SSPCM are porous and carbon-based materials. This method is an effective way to resolve the leaking and low thermal conductivity problems of PCMs because carbon has high thermal conductivity of 2000–6000 W/m K [4].

The objective of this paper is to prepare a novel form-stable PCM utilizing Beeswax as PCM and Multi-walled Carbon Nanotubes (MWCNTs) as supporting material. Characterization of the composite was conducted with FTIR test, and DSC test to capture the thermal properties and thermal reliability of the SSPCM. It was discovered that the thermal conductivity of SSPCM is increased by the addition of MWCNTs.

2. Methodology
2.1. Materials
The pristine MWCNTs were procured from Chengdu Organic Chemical Co., Ltd in diameter of 10-30 nm and length of 10-30 μm with surface area of 60 m²/g and purity: 95 wt.%. Beeswax as PCM has melting temperature of 60–62 °C [6], and the chemical compounds of nitric acid (HNO₃, 65 wt.%), sulfuric acid (H₂SO₄, 98 wt.%), and absolute ethanol were purchased from Merck Millipore Co.Ltd.

2.2. Preparation of MWCNTs
To begin the acid oxidation, two grams of Pristine CNTs and 400 ml of acid mixture which consisted of nitric (6M) and acids (6M) with volume ratio of 1:3 were stirred altogether in a beaker for 1 hour at temperature of 50 °C. Then the sample in beaker was diluted with aquadest for several times until the solution show no acidity (pH = 6.5), next it was filtrated by using a polycarbonate membrane filter with pore diameter of 45 nm. The neutral MWCNTs were put in a stainless steel container covered by alumunium foil and heated in an oven to remove the attached water at 100 °C for 24 h. The MWCNTs that were treated by the aforestated method of acid oxidation as shown in figure 1 named as A-CNTs.

![Figure 1. Oxidation of carbon nanotubes using acidic mixture.](image-url)
2.3. Preparation of Beeswax/MWCNTs composite shape-stabilized PCMs
As shown in figure 2, the preparation of Beeswax/MWCNTs composite implemented by using impregnation method [8]. A fixed proportion of A-CNTs/ethanol (1 gr/150 mL) suspensions was blended with Beeswax/ethanol solution with weight ratio of Beeswax/A-CNTs is 5%. Then the mixture was treated in an ultrasonic bath for 30 minutes and stirred for 4 h at 70°C by using magnetic stirrer [9]. Sonication is important in order to make a well dispersed and homogeneous Beeswax/A-CNTs composite. In order to evaporate the attached ethanol, the mixture was heated in an oven at 80 °C for 24 h and finally the sample of Beeswax/A-CNT 5 wt.% was successfully prepared for properties identification.

Figure 2. Composite preparation by impregnation method.

2.4. Characterization
Fourier Transform Infrared Spectroscopy (FTIR) was occupied to identify the shifting and formation of chemical groups in MWCNTs after treated by axid oxidation. Differential Scanning Calorimetry (DSC) ASTM D3418:15 was occupied to measure the thermal properties of SSPCM including its melting temperature, freezing temperature and latent heat capacity. The DSC assessments was completed at a 5 °C/min heating and cooling rate and temperature ranges of 0 to 100 °C and 100 to 0 °C. Physical phase stabilization of SSPCMs was potrayed by using a hot stage-digital camera at temperature of 100 °C [8]. Finally, thermal conductivity of SSPCMs were measured by comparative cut-bar method [10].

3. Results and discussion
3.1. Physical, Chemical and Morphological properties
Based on the observation of each sample that had been heated at 80°C for 5 different time variations: 0 minute and 15 minutes as seen in table 1, it was shown that Beeswax/A-CNTs composite is able to maintain its shape without any lamination better than pure Beeswax. Composite using A-CNT 5 wt% was able to maintain its shape until the tenth minute without leakage. Oxidized carbon nanotubes using strong-acid resulted to the most optimal CNT that could be used for SSPCM formation. This type of CNT traps beeswax inside the A-CNT cavity, therefore the beeswax did not leak out during the heating process.

Table 1. Phase changing process for period of 15 minutes.

|                  | 1 minute | 5 minutes | 10 minutes | 15 minutes |
|------------------|----------|-----------|------------|------------|
| Pure Beeswax     |          |           |            |            |
| Beeswax/A-CNTs 5 wt.% |          |           |            |            |
Based on the physical examination, Beeswax/A-CNTs composite tends to maintain its form due to its chemical structure changes. Oxidizing CNT using strong acid allows the CNT to form certain functional groups. Therefore, the success of CNT oxidation could be observed using Fourier Transform Infrared (FTIR) Spectrophotometer, Shimadzu IR Prestige 21. The FTIR test graph shows waves’ crests that can be used to identify the functional groups of samples. Figure 3 shows the FTIR test results of CNT and A-CNT that were used as the base materials for SSPCM. The FTIR spectrum of pure CNT does not show peak on the characteristic band, meanwhile A-CNT result shows several peaks.

Carboxylic acid C=O is shown from 1535 cm\(^{-1}\) wave, which is a specific carbonyl of CNTs. If there is >3200 cm\(^{-1}\) wave, there is a high chance that the CNT contains carboxyl functional group (-COOH), as 3442 cm\(^{-1}\) indicates the existence of O-H bond. Between 1750 – 1550 cm\(^{-1}\) wave, there are C=O functional group which has alkanoic acid and C=C bond. Wavenumber shown between 3300 – 2700 cm\(^{-1}\) introduces C-H bond as the sample has at 2915 cm\(^{-1}\). Lastly, 1300 – 950 cm\(^{-1}\) wave proves C-O bond does exist [11]. The peak formations on the FTIR graph indicate that A-CNTs, which was used as supporting material for composite, has new functional groups after being oxidized with strong acid. The desired result is for the bond between A-CNTs and Beeswax to become stronger and still be able to maintain its form although has reached its melting point to meet the desired characteristics of SSPCM.

3.2. Thermal properties
The thermal properties of pure Beeswax and Beeswax/MWCNTs composite were identified for the further analysis by using Differential Scanning Calorimetry (DSC). These samples’ freezing points, melting points, characteristics temperatures and phase change enthalpies were examined and compared in order to distinguish the thermal performance of Beeswax with and without the addition of MWCNTs.

The cooling and heating rate of DSC was set at a constant rate of 5 ºC per minute and at the beginning of DSC analysis, both of pure Beeswax and Beeswax/A-CNTs composite were at an initial temperature of 10 ºC. These samples experience the phase transition processes through melting – freezing cycles within temperature range of 10-100 ºC. Occupied calorimeter has accuracy within 0.2% and temperature error measurement within 0.05 ºC. The working principle of DSC shows that the heat flow signal of a DSC curve could demonstrate characteristic temperatures of the inserted sample which are melting point, freezing point, onset heating temperature and onset cooling temperature. Figure 4 shows the comparison of DSC analysis for pure Beeswax and Beeswax/A-CNTs 5 wt.% during the melting and cooling process, and the value of characteristic temperatures are shown in table 2.
Table 2. Phase change temperature and latent heat of the Beeswax and the Beeswax/CNTs composite.

| Sample                  | Heating |            |            | Cooling |            |            |
|-------------------------|---------|------------|------------|---------|------------|------------|
|                         | Tm (°C) | Onset (°C) | ΔH (J/g)   | Tc (°C) | Onset (°C) | ΔH (J/g)   |
| Beeswax (Bwx)           | 60.59   | 51.36      | 153.21     | 57.00   | 58.71      | -154.01    |
| Beeswax / A-CNT 5 wt.%  | 60.18   | 49.38      | 115.54     | 56.39   | 58.46      | -126.20    |

From the result, there is no substantial temperature change between sample with and without addition of A-CNTs. The melting and freezing temperatures are determined as 60.59 °C and 57 °C for the pure Beeswax whereas Beeswax/MWCNTs composite exhibited modest changes in the phase transition temperatures because there is a confinement of the Beeswax molecules into the pores of MWCNTs. Form stable composite with impregnation of A-CNTs have melting point and cooling point of 60.18 °C and 56.39 °C for Beeswax/A-CNTs composite. The melting and freezing temperatures of the Beeswax/A-CNTs composite are suitable for TES applications in buildings [12]. However, the slight variation during this phase change process due to MWCNTs addition could be affected by the heat transfer enhancement and crystallization effect [13].

Moreover, DSC results show the latent heat for melting and freezing are found to be 153.21 J/g and 154.01 J/g for the pure Beeswax, 115.54 J/g and 126.2 J/g for the Beeswax/A-CNTs 5 wt.% composite. Latent heat is decreasing by addition of MWCNTs. This thermal performance is appropriate to the initial hypothesis that in order to enhance the thermal conductivity of PCM, addition of nanoparticle MWCNTs is required.

One of important parameters that must be considered in the selection of a composite PCM is thermal conductivity, especially for TES system application. Therefore, improvement of this parameter is efficient on enhancing the storage and release performance and designing of TES system [1]. Knowing this fact, this research is also considering on increasing the thermal conductivity of the fabricated Beeswax/A-CNTs composite. The thermal conductivity performance of SSPCM was measured by thermal conductivity meter Ogawa Seiki OSK 4565-A.

Thermal conductivity of samples are shown in table 3 which the thermal conductivity of Beeswax is approximately 0.25 W/m·K at temperature 40°C as reported from literature [6]. Increaseamnt of MWCNTs into Beeswax improve the thermal conductivity of the composite. Based on test result, thermal conductivity of form-stable Beeswax/A-CNTs 5 % wt is 0.46 W/m·K, meaning that the thermal conductivity of composite is increased by 84% compared to the pure Beeswax. This shows that the MWCNTs affects the enhancement of the thermal conductivity of Beeswax. Through the thermal conductivity analysis, it is confirmed that the modified composite in this research is useful for TES applications.

Table 3. Thermal conductivity of samples at T = 40°C.

| Material          | K (W/mK) |
|-------------------|----------|
| Beeswax [6]       | 0.25     |
| 5 wt.% A-CNT      | 0.46     |

4. Conclusion
The preparation and characterization of physical/chemical/morphological properties of Beeswax/A-CNTs as SSPCM with enhanced thermal conductivity were presented in this paper. Two samples were utilized which are pure Beeswax and Beeswax/MWCNTs composite. MWCNTs were modified, tested, and added in order to form a shape-stable composite. From experiments conducted, it is known that the SSPCM was successfully fabricated by the impregnation of A-CNTs into Beeswax. Thermal conductivity of composite is increased by the addition of 5 wt.% A-CNTs. Based on FTIR test, it is proven that A-CNT has a good physicochemical compatibility as supporting material for composite. The DSC results confirm that the prepared Beeswax/A-CNTs composite has melting temperatures of 59.79 °C, and latent heat value of 91.64
J/g. The composite possess a good realibility as well as shape stability for TES material. Moreover, thermal conductivity of Beeswax is increased considerably as 84% by the addition of 5 wt.% A-CNTs. In conclusion, Beeswax/A-CNTs 5 wt.% composite is a promising TES material that could reduce energy usage in buildings that unintentionally could lessen the climatic catastrophe. However, the large-scale TES performance of this Beeswax/A-CNTs composite is necessary for further consideration.

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