Development of Flame Retardant Stearic Acid Doped Graphite Powder and Magnesium Hydroxide Nanoparticles, Material for Thermal Energy Storage Applications

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Abstract. Nano-enhanced organic phase change material (PCM) composite consists of stearic acid (SA, act as the thermal storage media), graphite powder (GP, function as thermal conductor), and magnesium hydroxide nanoparticles (nMH), micro-sized (MMH), function as the flame retarder), were formulated and investigated for their thermophysical properties and flammability. The flame-retardant properties of nano-enhanced composite PCM were evaluated by using the burning test. Phase change temperature, phase change latent heat, and thermal conductivity were obtained by the T-history method. To reduce the flammability, 5wt% of MH with 0.8µm and 200nm were added to PCMs. 1wt% of GP improved thermal conductivity of stearic acid from 0.245 to 0.4887 W/mk, and doping of flame-retardant nanoparticles to PCM showed the reduction of flammability and slightly effecting on latent heat of PCM. nMH were found to work better for stearic acid flammability than MMH, where combustion time of 0.1g pure stearic acid (SA) was decreased from 41s to 17s and 23s. For nano-sized(SA/nMH) and micron-sized(SA/MMH)composites, the latent heat of pure PCM dropped from 171.26 to 124.85KJ/kg, but micron-sized addition negatively affects latent heat values by reducing from 171.26 to 88.87 KJ/kg. The results confirmed that nMH/GP/SA composite could reduce flammability without showing a negative impact on storage capacity.

1. Introduction

PCMs are classified into organic and inorganic materials. Both types of organic PCM present advantages and disadvantages, which makes them suitable for a specific application[1][2]. Organic PCMs have lower thermal conductivity and suffer from flammability, but organic PCM has many advantages
including, lower segregation and corrosion and long-term stability, and not suffer from supercooling during phase changing[3][4]. Organic PCMs are known to suffer from two major effects, which are poor thermal conductivity and flammability.

Heat transfer and thermal conductivity of PCMs can be improved by incorporating a high thermal conductivity material such as metal particles or graphite. Cheng et al.[5] showed that the thermal conductivity of composite PCM could be increased around 6.2 times by adding 9 wt% expandable graphite. However, the higher mass fraction of graphite leads to a reduction of the latent heat of composites. Therefore, a compromise between an increase in thermal conductivity and a reduction of heat storage capacity must be explored to find the optimized loading[11].

The flammability can be improved by doping the material with flame retardants. It is known that not all flame retardants will be compatible with the PCMs. Therefore, a selection must be performed to identify the proper combination. Magnesium hydroxide is an effective flame retardant additive for polymers[7]. When heated, magnesium hydroxide decomposes to magnesium oxide and release water. Materials will adsorb a great deal of heat to lessen the temperature on the surface of materials, retard the decomposition of material, and reduce the formation of combustible compounds. It was reported that the fire-retarding effectiveness of MH relies on particle size[9]. The Limiting Oxygen Index (LOI) of EVA containing 50% (w/w) of magnesium di-hydroxide was improved from 24% to 38.3% when micrometric magnesium di-hydroxide (2–5 μm) is replaced by nanometric Mg(OH)2. The enhancement of EVA flame retardancy by nanosized Mg(OH)2 was attributed to a superior dispersion of the nanoparticles, which leads to the formation of a more compact and cohesive char during the combustion test. Song et al. [8] found that doping of flame retardant nanoparticles in organic PCMs(paraffin) can improve fire performance significantly where LOI was increased and did not show an adverse effect on its latent heat.

The main objective of this study is to investigate the possibility of using stearic acid as PCMs with improved thermal conductivity and flammability. The graphite was used to enhance the thermal conductivity, and MH was used to improve the flammability.

2. Materials and Methods

2.1. Materials
Stearic acid with a melting point of 63°C, was obtained from Peerapat Technology Public Company Limited. Magnesium hydroxide(MH) powder(99.5%,10×40 nm, Nanostructured & Amorphous Materials Inc, USA), GP, ANHUI ELITE Industrial. Co. Ltd, China), Graphite powder was used.

2.2. Preparation of nano-enhanced PCMs
Nano MH was prepared by using the bead milling technique(Minicer, NETZSCH GmbH & Co. Holding K G., Germany). 13wt% of micron size MH was dispersed 500mL ethanol and undergone bead milling. 3g of MH particles with micron and nanosized were dispersed in 10mL of APTES in 200mL of ethanol solution for the surface treatment. The reaction was stirred overnight at room temperature. The precipitate was separated by centrifuge and washed four times with ethanol to remove an unreacted silane. The product was dried at 40°C for 24 hrs. In a separate container, 1.3 g of stearic acid was dissolved in 300 mL of ethanol. 0.2 g of MH treated particle was placed into the stearic acid in ethanol. The mixture was stirred for 1 hr ethanol was slowly removed by gentle evaporation and heat treatment. Finally, nano-enhanced PCMs samples were made ready to be tested for flammability and thermal performance. Samples with different compositions were studied as tabulated in Table 1.
Table 1. PCM composites with different additives

| PCM Composites | Stearic Acid. (wt%) | 800nm-Mg(OH)_2 (wt%) | 200nm-Mg(OH)_2 (wt%) | Graphite (wt%) |
|----------------|--------------------|----------------------|----------------------|---------------|
| PCM A          | 100                | -                    | -                    | -             |
| PCM-B          | 99                 | -                    | -                    | 1             |
| PCM-C          | 95                 | 5                    | -                    |               |
| PCM-D          | 95                 | -                    | 5                    |               |
| PCM-E          | 94                 | 5                    | 1                    |               |

2.3. PCM Composite Characterization

2.3.1. Burning Test
The composite powder was placed on aluminium foil. The incident flame from the gas torch was placed 0.75 inches away from the sample. The ignition time is defined as the time at which the first flame appears on the surface of the sample. The combustion time is related to the length of the combustion and, therefore, to the ability of the material to self-extinguish. A combination of short combustion times together with a longer ignition time is a sign of a flammable material that can extinguish the flame upon heating[6].

2.3.2. T-history Method
The T-history method was introduced by Yinping et al. [11]. It was proposed as a simple and effective method to analyse almost all the thermophysical properties associated with phase change materials from their cooling curves. Lumped capacitance method is used to analyse the liquid region, the phase change region and the solid region of the PCM. A hot plate magnetic stirrer (Shanghai Bilon Instrument Co. Ltd, China), and thermocouple Type-K stainless steel in the dimension of 5mm diameter and 200 mm length (Warf Corporation Co. Ltd, Thailand), data logger, glass test tubes and a borosilicate beaker were used in these experiments. The 250ml water was heated to 90 °C. Samples were heated to 90°C, held for 7.5 mins and cooled down to room temperature. The temperature of samples was recorded by the data logger. From the data, cooling curves were drawn to investigate the thermophysical properties. The thermophysical properties are computed from time-temperature curves (t–T curves), respectively. All of the experiments were conducted at least three heating and cooling cycles.

3. Results & Discussions

3.1. Flammability analysis of PCM composites
Figure 1 is the graph of ignition time(red) and the combustion time(blue) of five PCM composites. MH flame retardants cause a significant improvement in the fire performance of PCM. The ignition time and combustion time of PCM-A(pure SA) are 3s and 41s. Upon the addition of 5% micron-size MH (0.8µm) and nano-size MH(200nm), there is an increase of ignition time to 4s and a reduction of combustion time to 23s and 16s, respectively. Graphite was found to be an effective material for reducing the combustion time, as evidenced from PCM-B and PCM-E. In the presence of both graphite and MH, ignition time was increased to 5s, and the combustion time was reduced to 15s.
3.2. Evaluation of Thermal properties of PCM composites

Graphite was found to be an effective enhancer for thermal conductivity, as shown in figure 2. The nano-size MH causes a poorer thermal conductivity. A synergetic effect was observed in the presence of graphite and nano-size MH, where the thermal conductivity is higher than those of stearic acid.
A reduction of latent heat was observed in all the doped samples. Micrometre size MH showed the highest reduction of latent heat of fusion, as evidence in figure 3. A drop of latent heat was observed in all samples as the additive was added to the stearic acid. Both micron size MH and graphite showed a reduction in latent heat and an increase in the melting point of material. To weigh all the effects, PCM-E was found to be the most suitable composition.

4. Conclusion

In summary, a novel flame retardant phase change material (PCM) based on stearic acid, nMH, MMH and Graphite Powder (GP) were prepared and studied using the burning test and T-history method. The burning test results showed that the addition of the nano-MH and GP have significantly improved over 60% reducing the flammability of stearic acid PCM, while GP enhances 20% of thermal conduction of the blends. The T-history analysis indicated that the introduction of nMH and GP into the PCM composites has significantly increased the phase transition. Therefore, it can be concluded that these satisfactory compositions of additives into blends is comparable to the organic stearic acid PCM.

Acknowledgements

This research was supported by Mahidol University and National Nanotechnology Center (NANOTEC) through the Research Network of NANOTEC (RNN). The authors would like to thank Peerapat Technology Public Company Limited for partially finance support.

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