



Pentaerythritol with alumina nano additives for thermal energy storage applications



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ABSTRACT

Pentaerythritol is a poly alcohol with high solid–solid phase change enthalpy that makes it suited for thermal energy storage applications. At solid–solid phase transition temperature, pentaerythritol change from body centered tetrahedral molecular structure into a homogeneous face-centered cubic crystalline structure accompanied with the absorption of the hydrogen bond energy. The present work investigates the effect of adding alumina (Al_2O_3) nanoparticles to pentaerythritol on thermal and chemical stability by performing thermal cycling test. Dispersion stability and aggregation of nanoparticles during thermal cycling were studied with FESEM and EDX analysis. The thermal and chemical stability of pentaerythritol samples added with alumina nanoparticles in the weight proportions 0.1%, 0.5% and 1% were tested using the characterization methods such as TGA, DSC and FTIR. The change in the specific heat and thermal conductivity of pentaerythritol was studied by the T-history method. The experimental results showed good thermal and chemical stability for alumina enhanced pentaerythritol subjected to 100 thermal cycles along with a negligible change in specific heat and thermal conductivity values. Non-isothermal crystallization kinetics of the PE added with alumina nanoparticles were also studied in this experimental work.

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1. Introduction

Thermal energy storage (TES) systems store thermal energy by heating or cooling a storage medium and permit the stored energy to be used for heating and cooling applications and power generation. Phase Change Materials (PCMs) are latent heat storage materials, which provide much higher thermal energy storage density than sensible thermal storage materials. PCMs allow large amounts of energy to be stored in relatively small volumes, resulting in some of the lowest storage media costs of any storage concepts [1–3]. The phase change materials are classified as organic, inorganic and eutectic PCMs. Organic PCMs are constituted by a wide range of materials including paraffins, fatty acids and their eutectic mixtures, esters and other organic compounds where as the inorganic materials are generally hydrated salts and

metallics. The organic materials are more chemically stable than inorganic substances, they melt congruently and supercooling does not pose as a significant problem [4]. A PCM is reliable if it is thermally, chemically and physically stable after a number of repeated heating and cooling cycles. So it is very important to carry out cycling stability test in order to ensure the long-term performance of a thermal energy storage system [5]. PCMs those involve phase transition from solid to liquid and back to the solid state are the most commonly used latent heat storage materials [6]. Most PCMs have a limitation of very low thermal conductivity [7] that leads to poor thermal energy storage performance of the PCM-based TES systems. Sharma et al. [8] reviewed the developments in the organic solid–liquid phase change materials and their applications in thermal energy storage. They have found that organic PCMs have inherent characteristic of low thermal

Abbreviations: PCM, phase change material; PE, pentaerythritol; PG, pentaglycerine; NPG, neopentylglycol; TES, thermal energy storage; LHTES, latent heat thermal energy storage; TGA, thermogravimetric analysis; DSC, differential scanning calorimetry; DTA, differential thermal analysis; FTIR, Fourier transforms infrared spectroscopy; XRD, X-ray diffraction; SEM, scanning electron microscopy; FESEM, field emission scanning electron microscopy; EDX, energy dispersive X-ray spectroscopy; CNT, carbon nano tubes; CNF, carbon nano fibers; RT, room temperature; RSS, root sum squares.

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Nomenclature

C_p	Specific heat
k	Thermal conductivity
m	Mass
T	Temperature
R	Radius of test tube
H	Enthalpy of fusion
t	Time
ρ	Density
A	Area
X_t	Relative crystallinity
dT	Temperature difference ($^{\circ}\text{C}$)
dH	Enthalpy change (kJ/kg)
φ	Cooling rate
T_o	Onset temperature

Subscripts

p	Pcm
t	Tube material
f	Fusion
R	Reference
m	Melting
∞	Ambient

conductivity (0.15–0.35 W/mK), hence, a larger surface area is required to enhance the heat transfer rate. Therefore, attention is needed for the thermal conductivity enhancement of the materials, which helps to keep the area of the system to a minimum. Paraffin and fatty acids are organic PCMs that have been investigated by numerous researchers for lower thermal energy storage applications because of their desirable characteristics like good heat storage density with little or no sub cooling, chemical stability and low cost [9,10]. But the main disadvantages with these PCMs are again their lower thermal conductivity. Molten salts are very good inorganic phase change materials which have been widely used for medium- and high-temperatures thermal energy storage applications. But their usage as PCMs is also limited by several reasons like chemical incompatibility and low thermal conductivities [11,12]. Improving the thermal conductivity of PCM by dispersing thermally conductive particles is one of the ways to improve the effectiveness of the PCM-based TES systems. Many such research works that investigated the thermal energy storage performance of organic as well as inorganic PCMs with different nano particles additives have been reported in literature. Though the addition of nano particles enhances the conductivity of PCMs, it was also reported in literature that phase change properties were affected due to the presence of nanoparticles [13]. Among the different nanoparticles, carbon nano tubes (CNT) and carbon nano fibers (CNF) have exhibited very good thermo-physical properties that make them suited in the field of PCM based LHTES. Elgafy and Lafdi [14] analytically and experimentally investigated the performance enhancement of Paraffin wax based LHS system by adding carbon nanofibres (CNF) with mass fraction of CNF ranging from 1 to 4%. Their study showed an almost linear increase in thermal conductivity with increase in mass ratio of carbon nanofibres. Wang et al. [15] conducted an experimental study of enhancement of thermal conductivity of palmitic acid based phase change materials with carbon nanotubes as fillers. Sadegh Motahar et al. [16] developed a novel phase change material for thermal storage by dispersing mesoporous silica (MPSiO₂) nanoparticles in *n*-octadecane. A maximum thermal conductivity enhancement of 5% for 3 wt.% MPSiO₂ at 5 $^{\circ}\text{C}$, and 6% for 5 wt.% MPSiO₂ at 55 $^{\circ}\text{C}$ was

reported by them. A composite phase change material comprised of organic montmorillonite (OMMT)/paraffin/grafted multi-walled nanotube (MWNT) was tested by Min Li et al. [17]. They reported that the thermal conductivity of the OMMT/paraffin/grafted MWNT composites was 34% higher than that of the OMMT/paraffin composites and 65% higher than that of paraffin. Changzhong Chen et al. [18] proposed the composites of polyethylene glycol (PEG)/the synthesized polymeric as a novel form stable phase change material (FSPCM) for thermal energy storage. Their results indicated that the proposed FSPCMs with different PEG contents have high thermal storage density and the enthalpy efficiency than that of the traditional FSPCMs. Duan et al. [19] conducted an experimental investigation on thermal conductivity enhancement of CaCl₂·6H₂O and expanded graphite composite. Their results showed that composite sample with less mass fraction of expanded graphite exhibited comparatively higher latent heat of fusion than the composite sample with greater mass fraction of expanded graphite. Tun-Ping Teng and Chao-Chieh Yu [20] reported the production of nanocomposite-enhanced phase-change materials using the direct-synthesis method by mixing paraffin with alumina (Al₂O₃), titania (TiO₂), silica (SiO₂), and zinc oxide (ZnO) in three concentrations of 1.0, 2.0, and 3.0 wt.%. Their experimental results demonstrated that TiO₂ was more effective than the other additives in enhancing both the heat conduction and thermal storage performance of paraffin for most of the experimental parameters. Mettawee and Assassa [21] conducted an experimental study on thermal conductivity enhancement of paraffin wax by incorporating with 0.1, 0.3, 0.4 and 0.5% mass fractions aluminum particles. Their study showed a 60% reduction in charging time with aluminum mass fraction of 0.5% compared to pure paraffin wax. Zhiwei Ge et al. [22] have studied the carbonate-salt-based composite materials for medium- and high-temperature thermal energy storage applications. Advanced nanocomposite phase change material based on calcium chloride hexahydrate with aluminum oxide nanoparticles for thermal energy storage was proposed and studied by Xiang Li et al. [23]. They conducted thermal cycling test of the composite PCM with 1% weight fraction of alumina particles and observed from the characterisation study that the chloride hexahydrate/aluminum nanocomposite PCM possesses acceptable thermal reliability, chemical stability, and heat transfer characteristics which makes them suited for low-temperature solar thermal energy storage applications. D K Singh et al. [24] have conducted an experimental study on Myo-Inositol based nano PCMs for solar thermal energy storage. In their experimental study, they have reported the thermal cycling characterisation of Myo-Inositol added with CuO and Al₂O₃ (mass fractions of 1%, 2% and 3%) nanoparticles using DSC, TGA and FTIR methods. Based on the results obtained they have concluded that, myo-inositol based nano-PCMs could be recommended as a potential material for solar thermal energy storage applications at 160 $^{\circ}\text{C}$ –260 $^{\circ}\text{C}$.

Even though Solid–liquid PCMs are mostly used in the field of thermal energy storage and heat transfer applications, they suffer from major issues like volume change and liquid leakage when they are in their liquid phases. A simpler solution that solves the issues of leakage and volume change is to use a PCM that undergoes a solid–solid phase transition. Solid-solid PCMs undergo a solid/solid phase transition with the associated absorption and release of large amounts of heat. These materials change their crystalline structure from one lattice configuration to another at a fixed and well-defined temperature, and the transformation can involve latent heats comparable to the most effective solid/liquid PCMs [25]. Polyalcohols such as pentaerythritol [PE], pentaglycerine [PG], and neopentylglycol [NPG] are known to have solid–solid transition enthalpies which are comparable to the fusion enthalpies of many types of paraffin

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