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Stearyl alcohol/palm triple pressed acid-graphite nanocomposites as phase change materials

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ABSTRACT

Mixtures of stearyl alcohol with palm triple pressed acid (essentially a mixture of palmitic and stearic acid derived from palm oil) were prepared and characterized to assess their phase change thermal energy storage utility. Unlike the other mixtures, the 35 mol% stearyl alcohol mixture showed a single crystallization exotherm peak, albeit with a small shoulder, in differential scanning calorimetry. The enthalpy associated with this phase change was 158 ± 5 kJ kg^{-1} and the crystallization peak temperature was 46 °C. Inclusion of 10 wt.% graphite nanoplatelets increased the solid state and melt state thermal conductivities by factors of approximately six and twelve respectively. This nanocomposite showed no deterioration in thermal properties after hundred heating and cooling cycles between the end-temperatures of 30 °C and 60 °C when scanned at a rate of 10 °C min^{-1}. There was also no evidence of graphite platelet sedimentation in the molten liquid after two months at 80 °C.

1. Introduction

Renewable energy sources, e.g. wind and sunlight, are only intermittently available. Energy storage is necessary to overcome the inevitable disparity between energy demand and supply [1–4]. Phase change materials (PCMs) are attractive options for solar energy storage [2]. They store thermal energy by absorbing and releasing latent heat during phase change transitions at a nearly constant temperature [1–3].

Fatty acids are potential energy storage PCMs [5]. They melt congruently and show negligible super cooling [2]. The latent heats of fusion and crystallization are relatively high [5] and the vapour pressure of the melt is low. They are non-toxic, have good chemical and thermal stability, and are relatively inexpensive [5]. However, fatty acids are mildly corrosive and have an unpleasant door [2,6]. Palm triple pressed acid is a bio-based product derived from palm oil that contains palmitic acid (ca. 54%) and stearic acid (ca. 43%).

Long-chain *n*-alkanols have also been considered as PCMs [7,8]. The fatty alcohols qualify as phase change materials for energy storage due to their high latent heats of fusion and non-corrosiveness [9,10]. However, they exhibit polymorphism which can affect heat storage and extraction [10]. The γ polymorph is the stable solid-state form for the higher *n*-alkanols with an even number of carbon atoms [10]. On heating, these ordered phases first transform into a rotator phase, the α form, which subsequently melts. The solid-solid γ → α phase transition overlaps with the melting α→ *liquid* phase transition so that, for the purpose of heat storage, the double transformation appears like a single transition. The *n*-alkanols first crystallize as the α form on cooling. Negligible super cooling has been observed for the *liquid* → α transition. However, significant super cooling can occur for the solid-solid α → γ transition [9]. This is undesirable and it may cause problems for heat extraction especially when the supercooling exceeds 5 °C [2].

The solid-solid transition on super cooling is not always detected for compositions near the eutectic point of *n*-alkanols + straight chain fatty acids mixtures [11,12]. Thus, it might be possible to find an appropriate mixture of palm triple pressed acid and stearyl alcohol, suitable for energy storage, which effectively exhibits an apparent single-phase transition. Mixing *n*-alkanols into fatty acids also lessens the odor and corrosion problems. However, only a few studies considered such mixtures for phase change energy storage materials [6,12–14].

The thermal conductivities of stearyl alcohol (0.38 W m^{-1} K^{-1} at room temperature) and of stearic acid (0.172 W m^{-1} K^{-1} at 70 °C) are relatively low [1,8]. These low values constrain the heat storage and extraction rates and therefore the utility of latent heat energy storage systems based on these compounds. Heat exchange can be enhanced by adding either highly thermally conductive particles, e.g. metal or graphite particulates [15], or by impregnation of the PCM into highly thermally conductive porous structures, e.g. graphite foams [16]. Finned configurations, metal matrices and metal insertions can also significantly enhance the heat transfer [15]. However, such approaches inevitably increase costs and compromise the weight of the system [17].

High loadings of conventional thermally conductive fillers are

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required for appreciable thermal conductivity enhancement [18]. Incorporation of nano-sized particles is a relatively new approach for enhancing the thermal conductivity of PCMs [19]. Dispersion of nanoscale carbons, e.g. nanofibers, nanotubes and graphene in PCMs is of special interest [4,8,20,21]. Theoretically, due to their very high thermal conductivities, low loadings should suffice to enhance the thermal conductivity by several orders of magnitude. Instead, the observed improvement in the thermal conductivity is usually rather marginal, for example less than 100%. Simulation studies suggest that the culprit is interfacial thermal resistance [22,23].

Graphite nanoplatelets (GNPs) are graphite flakes with thicknesses less than 100 nanometers but with lateral dimensions that may extend into the micrometer range [24]. GNPs are conveniently obtained by first thermally exfoliating expandable graphite into graphite nanoplatelet stacks [25] followed by ultrasonic treatment in a suitable liquid medium. This facilitates both flake delamination and the dispersion of the nanoplatelet stacks into the liquid [26]. The in-plane thermal conductivity of GNP flakes can be as high as 5.3 kW m^{-1} K^{-1} while in the perpendicular direction (c-axis of the crystal) it is only 6–30 W m^{-1} K^{-1} [27]. Due to the oxidative nature of the intercalation process used to prepare GNPs, oxygen containing functional groups are present on the surface. They enable hydrogen bonding with the alcohol and carboxylic acid groups present in fatty alcohols and fatty acids respectively. This may facilitate enhanced interfacial interaction between the graphite nanofiller and the PCM matrix.

The aims of this study were twofold. The first objective was to design a novel PCM based on a mixture of stearyl alcohol with palm triple pressed acid that exhibits a single apparent exotherm at the crystallization transition. The second aim was to find a facile preparation method for enhancing the thermal conductivity of PCMs with GNPs. This communication reports on the thermophysical properties (melting and crystallization enthalpies, thermal conductivity, thermal stability and thermal cyclability, etc.) of such mixtures and nanocomposites.

2. Experimental

2.1. Materials

Expandable graphite grade ES 250 B5 (exfoliation onset temperature 220 °C) was supplied by Qingdao Kropfmühl Graphite (China). Stearyl alcohol (designated R-OH hereafter) with purity ≥96% was obtained from Merck. Technical grade palm triple pressed acid (designated R-COOH hereafter) was obtained from Pan Century Oleochemical SND BHD, Malaysia. The fatty acid content of this bio-based, palm oil-derived carboxylic acid, as reported by the supplier, is listed in Table 1. Both the stearyl alcohol and the triple pressed acid were used as received, i.e. without further purification.

2.2. Sample preparation

2.2.1. Graphite exfoliation and delamination

About 3.5 g of the expandable graphite was exfoliated in a Samsung Model ME9144ST microwave oven at a power setting of 1 kW and a treatment time of 2 min. About 2 g exfoliated graphite was combined with 300 mL isopropanol in a 600 mL beaker and placed in an ice bath. Ultrasonication was performed for 2 h at a power setting of 300 W using a Vibracell VC375 ultrasonic generator with a 12.5 mm solid tip horn. During this time, the dispersion was agitated continuously with a magnetic stirrer.

Table 1
Fatty acid composition of the palm triple pressed acid (Palmac 55-16) reported by the supplier (Pan Century Oleochemical SND BHD, Malaysia).

Fatty acid	C12	C14	C16	C18	C18:1	Others
Content (wt.%)	< 1.0	< 2.0	52–56	42–47	< 0.5	< 1.0

Small portions of the colloidal dispersion of graphite nanoplatelets were deposited on a microscope glass slide and allowed to dry for observation with FESEM and for recording Raman spectra. Another small portion of the dispersion was used for particle size analysis. The dispersion was allowed to stand for two hours at ambient conditions. During this time, the GNPs settled in a uniform layer at the bottom of the beaker. The excess isopropanol was decanted from the beaker, taking care that the GNPs particles were retained. The dispersion was then ultrasonicated for a further five minutes with mild stirring before being dispersed into the molten PCM mixture.

A portion of the colloidal dispersion was fed into a rotary evaporator (Büchi Rotavapor R-114) set at 100 °C. The isopropanol was evaporated until a paste-like consistency was obtained. The paste was dried for 12 h in a convection oven set at 60 °C. A fluffy, highly friable graphite nanoplatelet aerogel was obtained for characterisation purposes.

2.2.2. R-OH/R-COOH mixtures

Mixtures of R-OH and R-COOH were prepared by accurately weighing out the relevant masses into a glass beaker. The mixtures (ca. 10 g) were melted on a hot plate controlled to a maximum temperature of 100 °C and simultaneously stirred with a magnetic stirrer for 5 min after melting. The mixtures were then allowed to cool and solidify before further analysis.

2.2.3. PCM-GNPs nanocomposite

A mixture of stearyl alcohol and palm triple pressed acid containing 35 mol% R-OH exhibited single crystallization peak (with a small shoulder) in DSC scans. Therefore, it was selected as the phase change material (PCM) matrix. This mixture was melted in a beaker placed on a hot plate with the temperature controlled at 80 °C. The melt was stirred with a magnetic stirrer for 5 min. The ultrasonicated GNPs dispersion was then poured into the molten R-OH + R-COOH mixture. Stirring was maintained, while the isopropanol evaporated, until the mixture turned into a thick paste. The residual isopropanol was removed from the PCM-GNPs by heating the nanocomposite for 12 h in a convection oven set at 60 °C. The PCM-GNPs nanocomposites were left to cool and solidify at ambient conditions before further analysis. The PCM-GNPs nanocomposites were prepared at compositions ranging from 0 to 10 wt.% GNPs.

2.3. Material characterization

2.3.1. Particle size, surface area and density

Graphite particle size distributions were determined with a Mastersizer Hydrosizer 2000 (Malvern Instruments, Malvern, UK). The specific surface areas of the graphite powders were measured with a Micrometrics TriStar BET in N_2 at 77 K.

A Micromeritics Accupyc II 1340 fully automated pycnometer was used to determine skeletal densities with helium as the operating gas. The instrument had a 10.00 cm^3 sample cup with a 1.00 cm^3 insert. Before measurement tests were conducted, a volume calibration was done using the 1.00 cm^3 insert. After the calibration, a weighted sample was placed in the sample cup together with the 1.00 cm^3 insert so that it was at least two-thirds full. The sample was placed in the instrument sample chamber and the volume of the sample was measured.

2.3.2. Imaging

Graphite particle morphologies were viewed on a Zeiss Ultra Plus 55 ultrahigh resolution field emission scanning electron microscope (FESEM) fitted with an InLens detector. The acceleration voltage was set at 1 kV to ensured maximum resolution of surface detail. No electroconductive coating was applied on the graphite particles. PCM-GNPs nanocomposites were cooled in liquid nitrogen and then fractured.

Optical microscope images of pristine stearyl alcohol, palm triple