Solar Energy Materials & Solar Cells 147 (2016) 101–107

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Graphite nanoparticles-dispersed paraffin/water emulsion with enhanced thermal-physical property and photo-thermal performance

Fangxian Wang, Jian Liu, Xiaoming Fang*, Zhengguo Zhang**

Key Laboratory of Enhanced Heat Transfer and Energy Conservation, the Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

ARTICLE INFO

Article history:
Received 24 September 2015
Received in revised form
24 November 2015
Accepted 13 December 2015

Keywords:
Phase change material
Paraffin/water emulsion
Graphite
Heat transfer fluid
Photo-thermal performance

ABSTRACT

In this paper, graphite nanoparticles have been dispersed into a paraffin/water emulsion with the purpose of improving the thermal conductivity and photothermal conversion performance of the emulsion. The melting enthalpy and apparent specific heat of 20 wt% paraffin/water emulsion is 39.2 J g^{-1} and 9.105 J g^{-1} K^{-1} and its melting and freezing temperatures are very close to those of paraffin. Moreover, the 300 heating–cooling cycles test indicates that the paraffin/water emulsions containing 0.1 wt% graphite exhibits good thermal reliability. The viscosities of all samples are lower than 0.0750 Pa s, meeting the transportablilty requirements in pump systems for applications. In addition, the thermal conductivity of the emulsion containing 0.1 wt% graphite increases by 20.0% as compared to the base fluid and its receiver efficiency is higher than 86.0% as the temperature ranges from room temperature to 80 °C. As a result, the paraffin/water emulsion containing graphite with high energy storage capacity, enhanced thermal conductivity and excellent photo-thermal performance, good thermal reliability and good fluidity shows great potential for use as advanced heat transfer fluid (HTF) in the low temperature applications of direct absorption solar collector (DASCs).

1. Introduction

Solar energy is the most abundant and sustainable natural energy source, with one hour sunlight strikes on the Earth's surface being greater than all of the human consumption of energy in an entire year. The challenge lies in efficiently capturing, converting, and storing solar energy for applications [1]. Solar collector is a crucial component of any solar utilization systems, which absorbs the solar radiation and then transfers to a useful fluid medium [2]. The performance of solar collectors directly determines the efficiency of the solar thermal utilization systems. The flat-plate black-surface absorber is the most common type of solar collector that absorbs solar energy by a black surface and then transfers heat to a running fluid in tubes [3]. However, the absorber and the heat transfer fluid (HTF) exist thermal resistance, leading to a large temperature difference between the surface and the fluid and thus decreases the overall conversion efficiency of solar energy [4]. To overcome this shortcoming, the direct absorption solar collector (DASC) was first proposed in the 1970s [5]. In a DASC, solar energy was absorbed by a black liquid directly, which makes solar receiver gain more heat flow and thus improves the outlet temperature [6]. However, the traditional black liquid, based on typical fluids like water, ethylene glycol, etc., show serious shortcomings such as the light-induced degradation and poor thermal stability as well as low thermal conductivity, demonstrating the necessity to develop a new kind of fluid with high energy storage capacity and excellent photo-thermal performance for high-efficiency DASCs [7].

Phase change materials (PCMs) are used in many fields as thermal energy storage media, since they can store and release a large amount of latent heat during their phase transition at a defined temperature range [8–10]. It has been found that the specific heat of a fluid can be improved by incorporating some amount of PCMs into it, which has been considered as an effective route for heat transfer enhancement of fluids [11–13]. The fluids containing PCMs are generally classified into two kinds: microencapsulated PCM slurry and PCM emulsion [14]. Although microencapsulated PCM slurries exhibit enhanced specific heat and good fluidity, they suffer from the complex process for preparing PCM microcapsules [15,16], the damage of the capsule walls during transportation by pumps or other machine, and the

* Corresponding author. Tel.: +86 20 8711 2997; fax: +86 20 8711 3870.
** Corresponding author. Tel.: +86 20 8711 2845; fax: +86 20 8711 3870.
E-mail addresses: cexmfang@scut.edu.cn (X. Fang), cezhang@scut.edu.cn (Z. Zhang).

http://dx.doi.org/10.1016/j.solmat.2015.12.013
0927-0248/

significant thermal resistance resulted from the thick capsule walls [17]. Comparatively, PCM emulsions have several advantages such as simple process for emulsifying [18], negligible thermal resistance of the protective surfactant layer, and good operation stability [8]. Consequently, PCM emulsions have attracted an increasingly interest in recent years, which researches mainly focus on preparing stable PCM emulsions by selecting suitable emulsifiers [8,19–21], reducing the supercooling of the PCM emulsions with low phase change temperatures by adding higher melting temperature PCM [22,23], suitable surfactants [24] as well as nanoparticles [25,26], together with investigations on the rheological properties of PCM emulsions [27,28]. It has been found that the viscosity of a PCM emulsion increases with the mass fraction of the PCM, and the PCM emulsions with a mass fraction of the PCM lower than 50 wt% is more suitable for practical application [27]. Apparently, no work has been done on PCM emulsions for use as the working fluids for DASCs yet.

In the current work, aiming at developing a novel working fluid with excellent energy storage capacity, good optical absorption property, and high thermal conductivity for DASCs, graphite nanoparticles have been dispersed into a PCM emulsion, in which a paraffin with a melting point of 58–60 °C has been chosen as the PCM. The droplet sizes and the size distribution of the obtained PCM emulsions have been characterized. Furthermore, the thermophysical properties of the graphite nanoparticles-dispersed paraffin/water emulsions, including phase change enthalpy, apparent specific heat, apparent thermal conductivity, and rheological behavior have been investigated using appropriate experimental techniques. In addition, the thermal reliability of the paraffin/water emulsion containing 0.1 wt% graphite has been estimated by 300 heating–cooling cycles. Finally, the photo-thermal performance of the graphite nanoparticles-dispersed paraffin/water emulsions were evaluated under simulative conditions.

2. Experimental

2.1. Materials

Paraffin (melting point 58–60 °C) was purchased from Huayong Paraffin Co, Ltd. Polyvinyl alcohol (PVA, AH-26, degree of alcoholysis ≈ 97.0–98.8%) was supplied by Sinopharm Chemical Reagent Co., Ltd. Polyethylene glycol 600 (PEG-600) were purchased from Shanghai Chemical Reagent Co., Ltd. Graphite nanoparticles with an average diameter of less than 30 nm were purchased from Nanjing XFNano Material Tech Co., Ltd.

2.2. Preparation of graphite nanoparticles-dispersed paraffin/water emulsions

60 g of the paraffin/water emulsion was prepared by emulsifing 12 g of paraffin and 1.7 g of a mixed surfactant, which consists of PVA and PEG-600 (the mass ratio of PVA to PEG-600 is 0.76 to 0.24), into water using a rotor-stator homogenizer (model FJ200-SH, purchased from Shanghai Specimen Model Factory) at a rotation speed of 12,000 rpm for 5 min. For preparing the graphite nanoparticles-dispersed paraffin/water emulsions, a certain amount of the graphite nanoparticles was added into the mixed system followed by emulsifying under the same conditions, in which the mass fraction of the graphite nanoparticles was set at 0.05% and 0.1%, respectively.

2.3. Characterization and measurements

The morphology of the graphite nanoparticles-dispersed paraffin/water emulsions with different mass fractions of graphite nanoparticles were examined with an optical microscope (Observer. A1, Carl Zeiss, Shanghai) under a magnification of 400. The size distribution of all as-prepared emulsions were measured by Zetasizer Nano (Nano-ZS90, Malvern Instruments, England), and all samples were diluted 30 times. The analyzer has a large measuring rang from 0.01 nm to 10,000 nm and its accuracy is within ± 1%. The average particle size was analyzed by Zetasizer PCS Software.

The phase transition enthalpy and apparent specific heat of the samples were measured by a differential scanning calorimeter (DSC, Q20, TA Instruments, USA) under N_2 atmosphere at a flow rate of 50 ml min^{-1}. The temperature was kept at 30 °C for 5 min, and then ramped to 90 °C at the scanning rate of 5 °C min^{-1}. To test the thermal reliability of the emulsions, the paraffin/water emulsions were heated to 80 °C and kept for 5 min and then cooled to 20 °C and kept for 5 min with the aid of a temperature-controlled instrument (C50p, HAAKE). This process was repeated for 300 heating–cooling cycles. The DSC meausrements were conducted on the samples after experiencing the heating–cooling cycles.

The viscosity of the emulsions were measured using a Rheometer (ARG2, TA-Instriment.Inc, USA) with accuracy within ± 1%. In order to analyze the viscosity of emulsions during phase transition, each sample was measured at the temperature ranging from 30 °C to 80 °C.

The apparent thermal conductivity of the samples was measured at temperatures ranging from 30 to 80 °C using a thermal constants analyzer(Hot Disk TPS 2500 s, Hot Disk AB, Sweden), and the accuracy was within ± 3%. In order to control the temperature precisely, all samples were equilibrated for at least 5 min before tested. The apparent thermal conductivity of every sample was measured for three times, and an average value was obtained.

2.4. Evaluation of photo-thermal performance

An experimental apparatus for evaluating the photo-thermal conversion performance of the emulsion is illustrated in Fig. 1, which consists of a data collection system and a photo-thermal conversion system. The data collecting system consists of a computer and three thermocouples. The photo-thermal conversion system is composed of a light source, a quartz beaker, and a foam insulation system. A 150 W solar simulator (SOLAREDGE 700, Perfectlight, China) was used as the irradiation source, and its light intensity was measured to be 1800 ± 20 W m^{-2} with an irradiatometer (ST-80C, Photoeletric Instrument Factory of Beijing Normal University, China). The temperatures of the emulsion at different depths in the beaker were recorded by the three thermocouples. The average value for muti-measurement was used in this paper.

The receiver efficiency of the DASC was calculated by Formula (1).

$$\eta = \frac{m \int C_P(T) dT}{G_s A t} \times 100\% \quad (1)$$

Where η is the receiver efficiency, m represents the mass of the PCM emulsions, $C_p(T)$ is the apparent specific heat of the PCM emulsions, T is the temperature of the PCM emulsions, G_s is the irradiance of the solar simulator, A is the surface area of the receiver, t is the time. In this study, the mass of the emulsion is 20 g and the surface area of the receiver is 19.6 cm^2.

3. Results and discussion

3.1. Droplet sizes and size distribution of emulsions

Fig. 2 shows the micrographs of the emulsions after 30:1 dilution at 30 °C. The paraffin is found to be dispersed in water in the form of subglobose droplets, and its distribution is inhomogeneous (Fig. 2a). The diameter of particle decreases after adding