TKI Urban Energy project:

INNO-PCM

<Innovative microencapsulated phase change materials for direct-absorption solar collectors>

Project number: 1407205 Date: 20-01-2019 **Public Report** on WP1 & 2 Confidentiality: reporting to TKI

Introduction:

The energy crisis and global warming have become serious concerns; thus attention in energy utilization efficiency and expansion of new renewable energy sources for a viable future have been increased. Solar energy utilization offers a promising sustainable solution to the energy crisis due to its free availability and least environmental effect [1]. The potential of solar-thermal radiation is bigger than all other forms of renewable energy combined. Solar thermal collectors are the most important and essential components of each solar thermal systems [2]. To simplify the typical solar thermal collectors, enhance the efficiency and overcome the corrosion and heating losses in existence types, a so-called Direct Absorption Solar Collector (DASC) has been proposed [3]. In a DASC, solar energy is directly absorbed and then transferred by the working fluid. The widespread adoption of solar thermal collectors in general, and of DASC in particular, is limited by the time mismatch between the availability of solar energy and the demand [4]. Therefore, an interesting concept to overcome the above-mentioned limitations is to add latent heat thermal storage materials to the heat carrier which can be exploited in combination with the sensible heat of the carrier itself. The technology of DASC is in the research phase but the previous experimental and numerical studies confirmed that it can be applied in broad application prospects in the building heating/cooling systems [5].

In this study two different slurries were introduced as the heat transfer fluids in DASC systems:

1) containing shaped stabilized palmitic acid combined with carbon black nanoparticles;

2) containing micro encapsulated PCM (provided with one of the partners) within Polyurea shell and Graphite nanoplatelet (GNP).

The following sections will explain the characteristic of some of the prepared slurries and their Photothermal performance. Due to the confidentiality, the results obtained with the second slurry will not be presented here.

Material characterization of shaped stabilized phase change materials (SSPCMs) :

The SSPCMs were prepared based on a sol-gel method (for further details please see [6]). The Scanning Electron Microscopy (SEM) photographs of PA/SiO₂ at different magnifications are shown in Fig. 1.a. The SEM photograph of the sample illustrates the spherical structure of material and also its smooth surface. The homogeneous and uniform size distributions of particles are obvious. The particles have diameter sizes of 200-300nm. HAADF-STEM (High Angle Annular Dark Field) image shows the presence of voids containing PA (darker spots) in the spheres (Fig. 1.b). The Differential Scanning Calorimetry (DSC) curves of melting and solidifying of palmitic acid and PA/SiO₂ are presented in Fig. 1.c. These curves show that the prepared sample starts melting at 63.1° C and freezing at 59.2° C, while pure PA starts melting at 64.6° C and solidifying at 60.4° C. The latent heat decreased significantly in the prepared sample compared to the pure palmitic acid which was predictable due to the synthesis and washing process (Table. 1). In addition, by testing the shape stabilization of the materials at 80 °C for almost 2 hours on a filter paper, very negligible leakage was observed (details are given in [6]).



Fig. 1 from left to right: a) SEM, b) HAADF-STEM and c) DSC outcomes of PA/SiO₂ SSPCMs

Characterization of the Slurry:

The slurry contains carbon black nanoparticles with particle size of less than 30 nm. The 45 ppm carbon black and different weigh concentrations of SSPCM particles were dispersed in water after being exposed to ultrasonic wavelengths (>20 kHz). The preparation differs in concentration, ultrasonication time and power to obtain the most stable slurry under different conditions. The prepared slurries are stable for at least 2 hours. For longer time some sedimentation were observed which could be easily re-dispersed by shaking; this shows the applicability of slurries for the stationary state test for up to 2 hours.

The optical transmittance spectra (wavelength: 200–2500 nm) of the slurries were measured at the room temperature using quartz cuvettes and a 10 mm beam path length. The results are shown in Fig. 2. To record the data with the spectrometer, the slurries were diluted to 45ppm. Water shows the well-known behavior with an

average transmittance of about 96% in the wavelength range of 200–900 nm, while typical absorption peaks exist at 900–1000 nm and again at 1200 nm. In the wavelength range of 200 to 900nm, the absorbance effect of carbon materials are illustrated in Fig. 2. The slurry has a full absorbance property in the visible area, which is all-important for collecting sunlight irradiation effectively. This confirms the direct absorption of solar radiation by slurries. The optical behavior of the materials also indicates that the carbon materials enhance the solar radiation absorption of the slurries.

Sample code	T _{m, peak} (°C)	$\Delta H_m (J/g)$	T _{c,peak} (°C)	$\Delta H_{c} (J/g)$	Encapsulation Ratio (%) ¹	Encapsulation Efficiency (%) ²	Thermal Storage Capacity (%) ³
PurePA	64.6	197	60.4	205.9	-	-	-
PA/SiO2	63.1	74.8	59.2	68.5	38.0	35.6	93.7

Table 1 The thermal properties of PA/SiO2 SSPCMs



Fig. 2 Transmittance spectra of PA/SiO2-carbon black slurries

Fig. 3 photothermal characterization set-up

Photo-Thermal behavior of the Slurry:

A static lab-scale Direct Absorption Solar Collector (DASC) set up was built to study the photo-thermal performance of slurries. To determine the overall efficiency, the effect of different parameters were studied. The experiments were carried under an artificial sunlight simulator as a light source with the capability of up to 7000 ± 0.1 W/m² irradiance that meets class AAA standard and an AM1.5 spectrum. The photo thermal slurries were kept in a 3D printed container (made of Polylactic acid (PLA)). This container was completely insulated to reduce heat losses from the collector walls and the quartz window covering the top of the cylinder. Six pt100 type thermocouples were installed in the center of the cylinder at different heights (y/h = 0, 0.2, 0.4, 0.6, 0.8 and 1) to measure the temperature distribution of the slurry during experiments.

The temperature profiles recorded by different thermocouples show a less uniform temperature distribution compared to those of observed for water (Fig. 4). The temperature distribution of the slurry is expected to become more uniform at the optimum concentration in a pumping system. The decrease in the slope of Temperature-Time graphs after reaching the melting temperature of PCM can be related to the thermal storage performance of the slurries. Moreover, it was found that as the particle concentration increases, the time required for slurries to reach to temperature of 75 °C does not decrease (Fig. 4); This indicates that the solar absorption and heat storage capacity of PA/Silica-carbon black slurry has a certain limiting value. However, analyzing the exact effect of concentration can be done only after testing a wider range of concentrations.

Receiver efficiency:

To further investigate the photo-thermal performance, the overall efficiency can then be calculated as:

$$\eta = \frac{m \int C(T) \, dT}{GAt} = \frac{m_{total} \cdot C_{slurry} \cdot \Delta T + (m_{melted \; SSPCM} \cdot \Delta H_{f,SSPCM})}{G.A.t}$$

$$_{3} \varphi = \frac{E}{R} \times 100\%$$

¹ Encapsulation ratio (**R**) describes the efficient encapsulation of core within the shells.

² Encapsulation efficiency (E) describes the effective performance of the PCMs inside the capsules.

$\Delta T = T(t) - T(initial)$

Where $T_{initial}$ (°C) is the initial temperature of the fluid, $G(W/m^2)$ is the heat flux of the incident light from the solar simulator, t(s) is the irradiation exposure time, and A (m²) is the illumination surface area. In our experiment, G was measured to be about 7000 W/m². The recorded temperature-time behavior of the samples indicated that after almost 4000s the temperature of the first two thermocouples goes above the melting temperature of the SSPCMs. This means that 40% of the slurry is acting as the thermal storage element. The receiver efficiency were calculated with the theoretical specific heat (see Fig. 5). Though the receiver efficiency for prepared slurry with 2 wt % does not show much improvement compared to the pure water, the slurry with 4 wt% presents a higher overall efficiency. This is due to the better optical absorption of slurry when the particle concentration increases. However, a further investigation is required to make a concrete conclusion. While it was expected to have a higher efficiency when the slurry reaches the melting temperature, the opposite was observed. This can be explained by the low encapsulation efficiency (Table 1) which results in a low latent heat. Regardless of the changes in the receiver efficiency, by introducing PCM into the system the bulk temperature of the receiver and therefore the heat losses was reduced which was one of our objectives.



Fig. 4 Photo-thermal performance of different concentrations of PA/SiO₂-Carbon black slurries

Conclusion:

Several PCM slurries for DASC's have been successfully prepared and some have promising properties. Initial investigations have given insight in the characterizations, however, future research is required to provide more information on the effect of these types of slurries on the energy density and efficiency of direct absorption solar collectors (DASC). The key point to improve the storage and therefore the photothermal performance of the prepared slurries is to enhance the encapsulation efficiency. The encapsulation efficiency achieved in this study is about 35%, which means there is a big room for improvement.



References:

- 1- Ge, T., et al., Solar heating and cooling: Present and future development. Renewable Energy, 2017.
- 2- Gorji, T.B. and A. Ranjbar, A review on optical properties and application of nanofluids in direct absorption solar collectors (DASCs). Renewable and Sustainable Energy Reviews, 2017. 72: p. 10-32
- 3- Qin, C., et al., Optimization of a direct absorption solar collector with blended plasmonic nanofluids. Solar Energy, 2017. 150: p. 512-520.
- 4- He, Q., et al., Experimental investigation on photothermal properties of nanofluids for direct absorption solar thermal energy systems. Energy Conversion and Management, 2013. 73: p. 150-157.
- 5- Chen, L., et al., Reduced graphene oxide dispersed nanofluids with improved photo-thermal conversion performance for direct absorption solar collectors. Solar Energy Materials and Solar Cells, 2017. 163: p. 125-133.
- 6- Tahan Latibari, S., et al., Preparation and Characterization of Heat Transfer Fluid for Application in Direct Absorption Solar Collectors, 13th SDEWES conference, October 2018, Palermo, Italy.