

Graphite inserts for management of thermal conductivity in phase change materials – performances and limitations

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Abstract — Phase Change Materials (PCMs) have been used recently in applications where the supply is not synchronous with the demand in order to act as a buffer between the two and compensate the random variations of each. PCMs store and then release considerable amounts of heat without significant temperature variation. Their key property is the latent heat of fusion/solidification and the main point that has to be considered in the design of the application is the match between the melting point and operating temperature. Thus, the main mode in which heat is stored in the PCM is latent heat and a relatively small part is sensible heat. However, the main limitation in the applicability of PCMs is their value of the thermal conductivity coefficient. This rises various design constraints which eventually result in limited applications. Various methods exist to enhance the conduction heat transfer in PCMs. The paper presents a discussion on techniques, performances and limitations of graphite insertion to boost PCMs thermal conductivity. The main goals of the paper are (1) to demonstrate that although graphite inserts are beneficial in increasing the overall efficiency of a PCM – based thermal management system and (2) a number of limitations, side effects and factors that adversely influence the heat conductivity increase exist and must be accounted for by performing an overall optimization of the thermal management system under constraints dictated by functional requirements.

Keywords— Phase Change Materials, Graphite, Thermal conductivity.

ABBREVIATIONS:

DSC – Differential Scanning Calorimetry

EG – Expanded Graphite

FT-IR – Fourier Transform Infrared Spectroscopy

LA – Lauric Acid

MA – Myristic Acid

PCM – Phase Change Material

PED - Portable Electronic Devices

SA – Stearic Acid

SEM – Scanning Electron Microscope

I. INTRODUCTION AND STATE OF THE ART

Improvement of heat conductivity in Phase Change Materials is critical in achieving good thermal performance of the thermal management application. High heat conductivity of PCM heat storage/dissipation systems is important especially in PEDs due to the limited volume available, complex geometry and large ratio heat flux/surface area [1]. Various methods to improve heat conduction in PCMs especially in solid phase were developed: nano-graphene platelets [2], expanded graphite composite [3], a combination of nano-particles and fins [4], nano-particles – metal foam combination [5-6], fins (longitudinal, annular or helical) and metal matrixes [7-13].

One of the most efficient heat conductivity enhancement in PCM thermal management systems is graphite inserts, as reported by [14-19]. Different grain size and particle shape have been used in the works mentioned above but in all cases a significant improvement of the heat conduction coefficient has been found. The main factors that influence the gains in heat conduction coefficient were the graphite inserts/PCM ratio [15] and the graphite inserts – PCM heat transfer area – which is related to the graphite inserts grain size [17]. The finer the grain size the higher the heat conduction enhancement is obtained [17]. A factor that influences the increase of the heat conduction coefficient is the anisotropy of the graphite inserts [16]. A detrimental effect occurs when the graphite inserts grain size is decreased in order to increase the PCM – graphite inserts contact area, which is coagulation of the graphite particles. Coagulation occurs after a number of thermal cycles [17] and reduces significantly the positive effect obtained by addition of graphite inserts. Other unwanted side effects observed were the decrease of the specific heat of the composite [17] and especially the latent heat, which influences detrimentally the heat storage capacity of the composite.

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II. PHASE CHANGE MATERIALS (PCMs) – FUNDAMENTAL CONCEPTS

Any substance that – subject to a heat flow – undergoes a phase transition process at a temperature which is within the operating temperature range of the application can be used as a phase change material. PCMs are compounds that undergo a phase transition process – usually melting/solidification in a periodic way such as they absorb and then release significant amounts of heat with little temperature variation. Given the requirements to qualify as a PCM, in practice only a few compounds fulfill the conditions, amongst which the most important is the latent heat of fusion/solidification. Latent heat storage/release can be achieved through various phase transition processes: liquid – solid, liquid – gas or gas – solid. However, the only process of practical importance is liquid – solid.

PCMs classification. PCMs can be categorized in the following groups, depending on the substance chemical nature (Fig. 1):

Organic PCMs. Organic PCMs are usually paraffins, which are carbohydrate derived. Paraffins display negligible subcooling during solidification, melt congruently, possess self-nucleating properties – which favors solidification, are compatible with most materials (especially building materials), do not manifest segregation, are chemically stable, have a high value of the latent heat of melting/solidification. Among the main disadvantages: low thermal conductivity in the solid state especially, volumetric latent heat storage capacity can be low due to the low density in the liquid phase, some compounds can be highly flammable. Another major disadvantage is the fact that obtaining reliable melting point values, most manufacturers use technical grade paraffins which are essentially paraffin mixture(s) and are completely refined of oil, resulting in high costs.

Inorganic PCMs. Inorganic PCMs are usually salt hydrates, (MnH₂O), they have the following properties: High value of the volumetric latent heat storage capacity, low cost and widely available, very small deviation from the melting point, high value of the thermal conductivity, high value of the latent heat of solidification, not flammable. Salt hydrates have a number of disadvantages, such as: large volume change during the phase transition process, significant supercooling during liquid – solid transition, nucleation does not occur naturally requiring nucleating agents. The most important disadvantage is that after a number of cycles nucleating agents become inoperative.

Eutectics. Eutectics have very small deviations of the melting point similar to pure substance, volumetric storage density is slightly above organic compounds, extra water method can be used to avoid phase change degradation, involving dissolving the anhydrous salt during melting to result in a thickening of the liquid material so that it melts to a gel form. Eutectics have been introduced recently to heat storage applications.

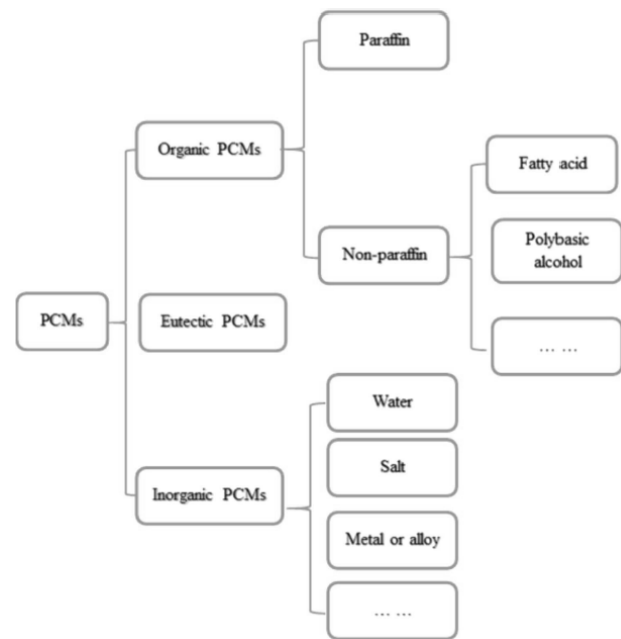


Fig. 1. Classification of PCMs [20]

From the application point of view, the key parameters of a PCM are the melting point and the latent heat of fusion. The applicability area is given mainly by these two parameters. In addition to the latent heat of fusion and melting point, other consideration must be taken into account before deciding the suitability of a given PCM for a heat storage application, such as: cost, chemical stability, chemical interaction with other heat storage system components and pipelines, fluid flow properties of the fluid phase, phase equilibrium, supercooling effects, non-sliding melting/solidification point, long term stability of the thermo- physical properties and the most important, thermal conductivity in both fluid and especially solid phase. In terms of the features mentioned above with the exception of the thermal conductivity, the best candidates to be used as PCMs are organic compounds, especially paraffins. However, paraffins have a low value of the thermal conductivity, as most organic compounds have. Therefore, it is important to identify solutions meant to improve the heat transfer through the PCM.

Modulation of thermal conductivity through various methods can increase the rate of charging and discharging heat, resulting in a higher efficiency of thermal energy storage systems [21]. The ways of enhancing thermal conductivity are divided into two types (Fig. 2): adding substances with high thermal conductivity and encapsulated phase change materials. The paper focuses in the first class of methods, analyzing the effects of graphite inserts on increasing the thermal conductivity of the PCMs.

Pure PCMs have the disadvantage of low thermal conductivity. Therefore, there are numerous studies about adding additives with high thermal conductivity to improve thermal conductivity of PCMs. This review paper focuses on the additives of carbon-based materials – graphite.

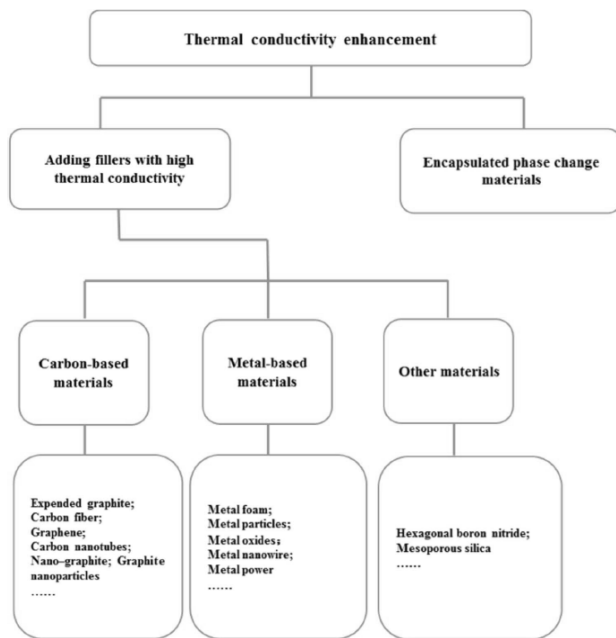


Fig. 2. PCM thermal management methods [20]

III. DISCUSSION

Carbon based materials are one of the most popular additives due to their high thermal conductivity, stable chemical nature, extensive usability and low density [23]. They have been extensively studied and applied. Carbon based materials have a variety of morphological structure, such as expanded graphite (EG), carbon fiber (CF), graphene, carbon nanotube (CNT).

Expanded graphite (EG) has a porous structure. Ling et al. [4] used the commercial PCM RT44HC and EG to develop RT44HC/EG composite, where RT44HC as organic PCM has phase transition temperature at 44 °C and latent heat capacity higher than 200 kJ/kg. The composites were developed using 25% and 35% (wt) EG, respectively. Experimental results show that the factors affecting thermal conductivity include the mass fraction of EG and packing density of composites. For the same density, the thermal conductivity of 35% EG loading in composites is 30% greater comparing with 25% EG loading. On the other hand, for the same mass fraction, the thermal conductivity of composites increases with density, and is 20–60 times the thermal conductivity of pure RT44HC corresponding to a lower density. A model has been developed to forecast the effective thermal conductivity of EG based compound material according to packing density and EG mass fraction at room temperature.

Jiang et. al [24] developed a PCM composite with high thermal conductivity by incorporating carbon bonded carbon fiber (CBCF) monolith into PCM to increase the thermal conductivity of the PCM. Paraffin wax was selected as the PCM because of its low cost, reasonable energy density, negligible supercooling and relatively chemical stability. The CBCF monolith was prepared by bonding random carbon

fibers with polymer binder to form a highly stable network after carbonization. The carbon fibers used have high thermal conductivity and are made from mesophase pitch. The PCM composites were obtained by soaking paraffin wax under vacuum. Because conductive carbon fibers can provide effective and stable conduction paths within the CBCF monolith, the thermal conductivity of the PCM composites was markedly increased by 18 to 57 times. Additionally, the PCM composites based on this CBCF monolith have advantages of light weight and dimensional stability. A significant increase of the thermal conductivity was found at the increase of the graphite inserts volumetric percentage.

Teng et al [25] used fully refined paraffin (Choneye Pure Chemicals, Taiwan) as the base materials and graphite (3.2 um, HOMYTECH, Taiwan). Fig.s 3(a) and (b) shows field-emission scanning electron microscope photographs of MWCNTs and graphite powder, respectively. The MWCNTs appear aggregated, and the outside diameter approximately met the specifications provided by the manufacturer.

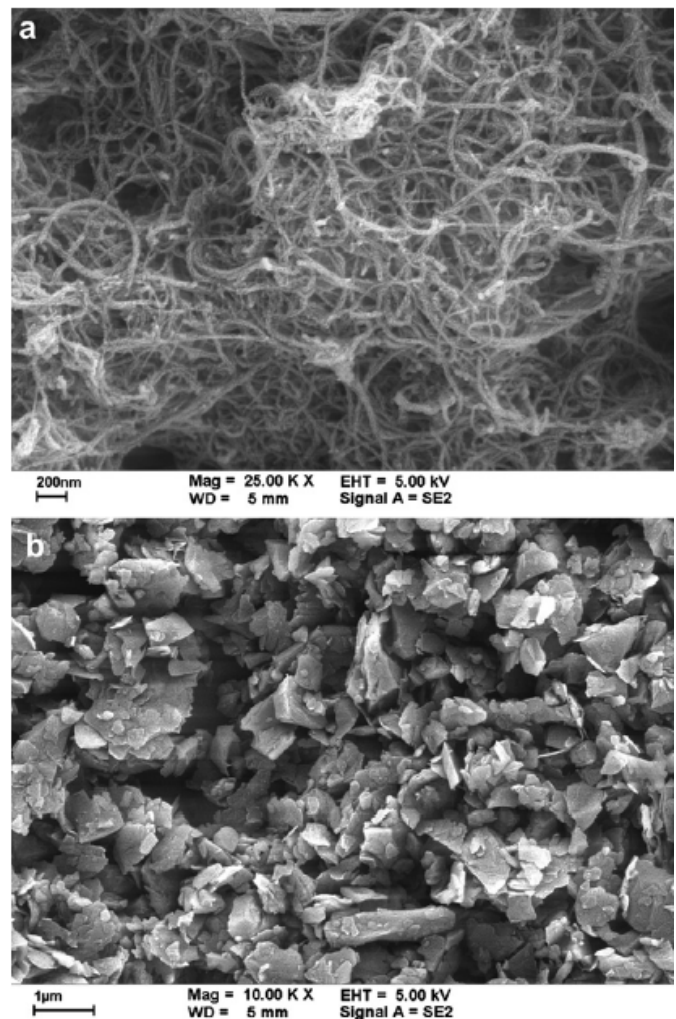


Fig. 3. Electron microscope image of MWCNT (a) and graphite (b) [25]

Uneven graphite particle size and aggregation phenomenon was observed. The overall particle size was generally lower

than the manufacturer's specifications. The MPCMs prepared by the direct-synthesis method were used to disperse the MWCNTs or graphite into three weight fractions (1.0, 2.0, 3.0 wt.%) in the paraffin, forming the experimental samples in this study. The main reason is to select the MWCNTs and graphite that are not easily oxidized and have excellent thermal conductivity. Paraffin was first melted to the liquid state by impermeable heating in water tank at 100 °C to successfully disperse the MWCNTs or graphite powder in the liquid paraffin. Then, the liquid paraffin was continuously stirred at 120 °C by an electromagnetic stirrer/hot plate. MWCNTs or graphite were divided into several times to add to the liquid paraffin until reaching the desired concentrations to complete the preliminary adding and dispersing procedures for MPCM. Secondly, the liquid MPCM was continuously dispersed for 40 min at 120 °C by a high-speed homogenizer at 6000 rpm to evenly disperse the MWCNTs or graphite in the liquid paraffin. The liquid MPCMs were then dispersed at 90 °C for 1 h using an ultrasonic vibrator to complete the modification procedures of PCMs. Finally, 40 g of paraffin and MPCMs was poured into a polypropylene (P.P.) test tube to complete a unit of sample for charging/discharging temperature experiment.

Adding higher concentrations of graphite to the paraffin did not help reduce the thermal resistance of the liquid paraffin. Graphite has a much higher thermal conductivity than paraffin, but adding a higher concentration of graphite did not help reduce the thermal resistance. This is because of the effect of poor dispersion performance, combination property, and the solid liquid interface layer. The reduction in heat transfer performance caused by the large thermal resistance of solid liquid interface is caused by the poor combination of graphite and liquid paraffin.

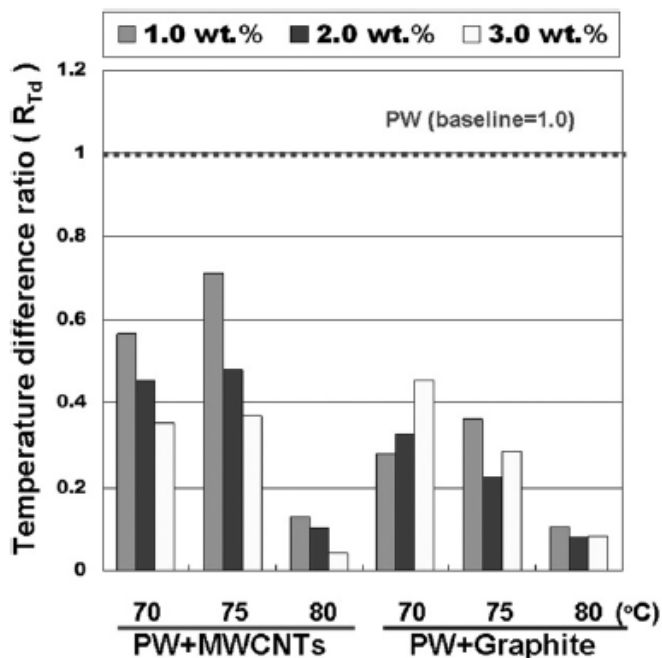


Fig. 4. The discharging temperature difference ratio of MPCMs [25]

Fig. 4 shows that adding MWCNTs and graphite to paraffin can significantly reduce the temperature difference between the sample temperature and cooling temperature at the same discharging time. The graphite can reduce the temperature difference ratio, but this does not vary with its concentration. A better combination of the graphite and solid paraffin can cause lower temperature difference and thermal resistance.

Commercial materials exist to be used as thermal conductivity enhancers in PCMs. SIGRATHERM GFG expanded graphite powder for enhancing thermal conductivity is shown in Fig. 5 [26].



Fig. 5. SIGRATHERM GFG expanded graphite powder for enhancing thermal conductivity [26]

Although significant increase of the heat conductivity has been reported in many studies some authors report effects such as a decrease of the latent heat. Fethi [14] elaborated a paraffin-graphite composite by dispersing graphite granules in molten paraffin and stirring until a homogenous mixture was obtained. Four different composites were elaborated with graphite mass fraction 5%, 10%, 15% and 20%. It was observed that the latent heat of the paraffin-graphite composite decreased from 142.16 J/g (pure paraffin) to 114.90 J/g (paraffin + 20% graphite). Nevertheless, the thermal conductivity increased continuously from 0.208 Wm⁻¹K⁻¹ (pure paraffin) to 0.874 Wm⁻¹K⁻¹ (paraffin + 20% graphite). These two contradictory trends suggest that an optimum can be identified depending on the constraints of the thermal management application (maximize heat flux, maximize ratio heat storage capacity/storage volume, etc.).

Jian Feng [16] observed that a paraffin – expanded graphite composite exhibits anisotropic thermal conductivity. This imposes supplementary design constraints in such way that the main heat flow direction is aligned with the direction with the highest thermal conductivity.

Agglomeration and coagulation of graphite particles forming macro-structures of irregular size and shape have a probability of occurrence inversely proportional to the graphite

grain size and directly proportional to the thermal cycling count. Agglomeration and coagulation occur with the PCM – graphite composite in liquid phase and are favored by the duration of time the composite is maintained in liquid phase [3]. These phenomena not only cancel out the benefit brought by addition of graphite inserts but can reduce the heat conductivity of the composite below that of the pure PCM. However, Liu et al [3] found that the PCM nature influences considerably its propensity to form macro-structures through agglomeration and coagulation. A novel composite phase change material (PCM) of LA–MA–SA/EG (12/1 w/w) was prepared [3]. The newly developed compound was tested by means of SEM, FT-IR and DSC. It was observed that EG is capable of absorbing the fat acid mixture into its porous structure until saturation threshold is reached. Saturation occurs when the porous structure is filled completely with molten acid mixture. A significant increase of the heat conduction coefficient was observed. It was also reported that the overall dynamics of heat storage/release was significantly improved compared to the pure PCM substances. The newly developed product was subject to 1000 thermal cycles showing no physical degradation or significant alteration of the thermos-physical properties.

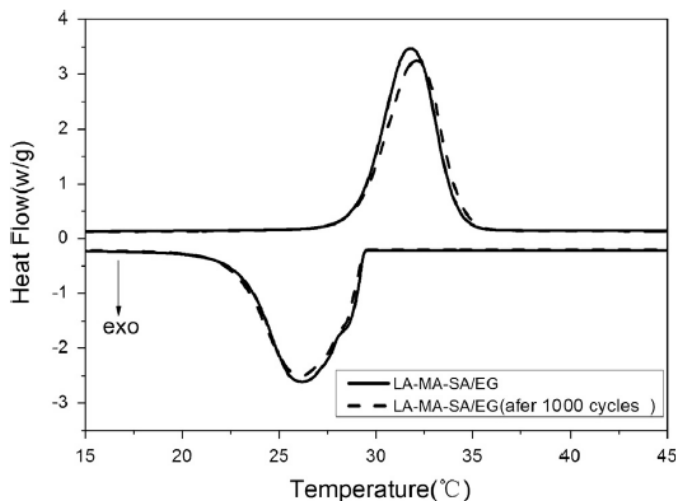


Fig. 6. DSC curves of LA–MA–SA/EG before and after thermal cycling [3]

DSC curves of LA–MA–SA/EG are presented in Fig. 6. It is noticeable that after 1000 cycles very little variation of the latent storage capacity is observed.

IV. CONCLUSIONS

Graphite insertions in various forms in PCMs offer a significant increase of the heat conduction, improving to a high degree the thermal performance of the PCM base thermal system. Graphite can be integrated into the PCMs as graphite foam or exfoliates. Graphite foam is more advantageous economically and offers better thermal performance. Exfoliates tend to migrate and form local agglomerations which is detrimental to the heat transfer. Foam is mechanically stable and preserves its thermal and mechanical properties

with thermal cycling. However, as shown in [6] the thermal conductivity of the treated PCM does not always increase as expected. This is not completely explained and it is thought to be caused by the large thermal resistance of solid liquid interface, which in turn has as main cause the poor combination of graphite and liquid paraffin. It is therefore essential to select adequately the PCM and the thermal conductivity enhancer. Increasing the heat conductivity by means of graphite inserts must be carefully considered and all side effects must be accounted for. The literature review presented above suggest that in each case an application-specific optimization approach must be conducted in order to identify the most appropriate graphite grain size, graphite particles mass ratio, heat storage system geometry and PCM nature.

The paper intends to point out that although graphite inserts are beneficial as thermal conductivity enhancers in thermal management PCM-based applications it is critical to consider all aspects resulting from the process of mixing graphite particles with PCM. To the authors' knowledge, it is for the first time when it has been shown that increasing thermal conductivity of PCMs by means of graphite inserts addition must be investigated and optimized to identify the key parameters of the graphite-PCM composite.

REFERENCES

- [1] S. Mahmoud, A. Tang, C. Toh, R. AL-Dadah, S. Leung Soo, Experimental investigation of inserts configurations and PCM type on the thermal performance of PCM based heat sinks, *Applied Energy* 112 (2013) 1349–1356
- [2] Rami M. Saeed, J.P. Schlegel, C. Castano, R. Sawafta, Preparation and enhanced thermal performance of novel (solid to gel) form-stable eutectic PCM modified by nano-graphene platelets, *Journal of Energy Storage* 15 (2018) 91–102
- [3] Cheng Liu, Yanping Yuan, Nan Zhang, Xiaoling Cao, Xiaojiao Yang, A novel PCM of lauric–myristic–stearic acid/expanded graphite composite for thermal energy storage, *Materials Letters* 120(2014)43–46
- [4] Jasim M. Mahdi, Emmanuel C. Nsofor, Solidification enhancement of PCM in a triplex-tube thermal energy storage system with nanoparticles and fins, *Applied Energy* 211 (2018) 975–986
- [5] Jasim M. Mahdi, Emmanuel C. Nsofor, Solidification enhancement in a triplex-tube latent heat energy storage system using nanoparticles-metal foam combination, *Energy* 126 (2017) 501e512
- [6] Peng Chen, Xuenong Gao, Yaqin Wang, Tao Xu, Yutang Fang, Zhengguo Zhang, Metal foam embedded in SEBS/paraffin/HDPE form-stable PCMs for thermal energy storage, *Solar Energy Materials & Solar Cells* 149 (2016) 60–65
- [7] Abduljalil A. Al-Abidi, Sohif Mat, K. Sopian, M.Y. Sulaiman, Abdulrahman. Th. Mohammad, Experimental study of melting and solidification of PCM in a triplex tube heat exchanger with fins, *Energy and Buildings* 68 (2014) 33–41
- [8] A. Sciacovelli, F. Gagliardi, V. Verda, Maximization of performance of a PCM latent heat storage system with innovative fins, *Applied Energy* 137 (2015) 707–715
- [9] Sohif Mat, Abduljalil A. Al-Abidi, K. Sopian, M.Y. Sulaiman, Abdulrahman Th Mohammad, Enhance heat transfer for PCM melting in triplex tube with internal–external fins, *Energy Conversion and Management* 74 (2013) 223–236
- [10] H. Eslamnezhad, Asghar B. Rahimi, Enhance heat transfer for phase-change materials in triplex tube heat exchanger with selected arrangements of fins, *Applied Thermal Engineering* 113 (2017) 813–821
- [11] Xiaohu Yang, Zhao Lu, Qingsong Bai, Qunli Zhang, Liwen Jin, Jinyue Yan, Thermal performance of a shell-and-tube latent heat thermal energy storage unit: Role of annular fins, *Applied Energy* 202 (2017) 558–570

- [12] M. Kazemi, M.J. Hosseini, A.A. Ranjbar, R. Bahrampoury, Improvement of longitudinal fins configuration in latent heat storage systems, *Renewable Energy* 116 (2018) 447-457
- [13] A. Rozenfeld, Y. Kozak, T. Rozenfeld, G. Ziskind, Experimental demonstration, modeling and analysis of a novel latent heat thermal energy storage unit with a helical fin, *International Journal of Heat and Mass Transfer* 110 (2017) 692–709
- [14] Albouchi Fethi, Lachheb Mohamed, Karkri Mustapha, Ben Ameur Tarek, Ben Nasrallah Sassi, Investigation of a graphite/paraffin phase change composite, *International Journal of Thermal Sciences* 88 (2015) 128-135
- [15] Yajun Lv, Weibing Zhou, Weizhun Jin, Experimental and numerical study on thermal energy storage of polyethylene glycol/expanded graphite composite phase change material, *Energy and Buildings* 111 (2016) 242–252
- [16] Luo Jian-Feng, Yin Hong-Wei, Li Wen-Yu, Xu Zhong-Jie, Shao Zheng-Zheng, Xu Xiao-Jun, Chang Sheng-Li, Numerical and experimental study on the heat transfer properties of the composite paraffin/expanded graphite phase change material, *International Journal of Heat and Mass Transfer* 84 (2015) 237–244
- [17] Ziye Ling, Jiajie Chen, Tao Xu, Xiaoming Fang, Xuenong Gao, Zhengguo Zhang, Thermal conductivity of an organic phase change material/expanded graphite composite across the phase change temperature range and a novel thermal conductivity model, *Energy Conversion and Management* 102 (2015) 202–208
- [18] Patrik Sobolciak, Mustapha Karkri, Mariam A. Al-Maadeed, Igor Krupa, Thermal characterization of phase change materials based on linear low-density polyethylene, paraffin wax and expanded graphite, *Renewable Energy* 88 (2016) 372e382
- [19] Benqiang Tian, Wenbin Yang, Lijuan Luo, Jing Wang, Kai Zhang, Jinghui Fan, Juying Wuc, Tao Xing, Synergistic enhancement of thermal conductivity for expanded graphite and carbon fiber in paraffin/EVA form-stable phase change materials, *Solar Energy* 127 (2016) 48–55
- [20] Yaxue Lin, Yuting Jia, Guruprasad Alva, Guiyin Fang, Review on thermal conductivity enhancement, thermal properties and applications of phase change materials in thermal energy storage, *Renewable and Sustainable Energy Reviews* 82 (2018) 2730-2742
- [21] Karaipekli A, Biçer A, Sarı A, Tyagi VV. Thermal characteristics of expanded perlite/paraffin composite phase change material with enhanced thermal conductivity using carbon nanotubes. *Energy Convers Manag* 2017;134:373–81
- [22] Wang CY, Feng LL, Li W, Zheng J, Tian WH, Li XG. Shape-stabilized phase change materials based on polyethylene glycol/porous carbon composite: the influence of the pore structure of the carbon materials. *Sol Energy Mater Sol Cells* 2012;105:21–6.
- [23] Ling ZY, Chen JJ, Xu T, Fang XM, Gao XN, Zhang ZG. Thermal conductivity of an organic phase change material/expanded graphite composite across the phase change temperature range and a novel thermal conductivity model. *Energy Convers Manag* 2015;102:202–8.
- [24] Zhao Jiang, Ting Ouyang, Yang Yan, Lei Chen, Xiaohua Fan, Yunbo Chen, Weiwei Li, Youqing Fei, Thermal conductivity enhancement of phase change materials with form-stable carbon bonded carbon fiber network, *Materials and Design* 143 (2018) 177–184
- [25] Tun-Ping Teng, Ching-Min Cheng, Chin-Pao Cheng, Performance assessment of heat storage by phase change materials containing MWCNTs and graphite, *Applied Thermal Engineering* 50 (2013) 637e644
- [26] www.sglgroup.com