

EXPERIMENTAL INVESTIGATION OF SOLIDIFICATION AND MELTING CHARACTERISTICS OF NANOFLUID AS PCM FOR SOLAR WATER HEATING SYSTEMS

S. Harikrishnan¹, S. Kalaiselvam^{1,2*}

¹Centre for Nanoscience and Technology, Anna University, Chennai, India.

²Department of Mechanical Engineering, Anna University, Chennai, India.

Corresponding author email address: kalai@annauniv.edu

ABSTRACT

In this study, thermal and heat transfer characteristics of nano based PCM during energy storage and release processes were investigated. This work also presented the preparation of nanofluid, which is solid-liquid composite material consisting of TiO₂ nanoparticles (NPs) embedded into melting palmitic acid. Size of the TiO₂ nanoparticles synthesized by sol-gel method was measured by using transmission electron microscope (TEM). Differential scanning calorimetry (DSC) measurements were used to determine the phase change temperatures and latent heats of nanofluids for melting and solidification processes. From the experimental results, it was observed that complete melting times of nanofluids with 0.1, 0.2 and 0.3 wt% of TiO₂ nanoparticles were reduced by 6.43, 14.62 and 21.05% respectively, than the palmitic acid. Similarly, complete solidification times of nanofluids with 0.1, 0.2 and 0.3 wt% of TiO₂ nanoparticles were reduced by 6.18, 12.37 and 20.11% respectively, than the palmitic acid. Based on all results, it was clearly understood that the dispersed nanoparticles into palmitic acid had enhanced the heat-transfer characteristics of palmitic acid in a better way, which in turn would accelerate the energy storage and release rates faster as compared to that of palmitic acid. Thus, the newly prepared nanofluids could be considered as a promising candidate for solar water heating system.

Keywords: Phase change material, Nanofluids, TiO₂ nanoparticles, Energy storage and release.

1. INTRODUCTION

Latent thermal energy storage (LTES) system is the most popular technique due to its salient features like high storage density for given volume and storing the thermal energy almost at constant temperature [1-4]. But, phase change materials (PCMs) employing in LTES system have low thermal conductivity, which hinders their utility for large scale applications as low thermal conductivity decelerates the energy storage and release rates [5-7]. Although many methods for improving the thermal conductivity of PCMs are prevailing in practices, enhancement of the thermal conductivity is able to achieve minimum level only and not as expected level.

Nanotechnology introduced the new method known as nanofluids, comprising of solid nanoparticles and melted PCM as composite materials, which would improve the thermal and heat transfer characteristics of the PCM. As far as thermal conductivity enhancement is concerned metal and metal oxide nanoparticles, graphene and carbon nanotubes (CNTs) are usually preferred. Size and shape of the particles make significant effect on the thermal conductivity enhancement of the nanofluids [8, 9]. Kalaiselvam et al. reported that concentration of nanoparticles dispersed into PCMs should be optimal for better thermal and heat transfer characteristics of PCMs [10]. Zeng et al. prepared the Ag nanoparticles and added with 1-tetradecanol for improving the thermal conductivity and the result showed that as the concentration of Ag nanoparticles

increased the thermal conductivity of the composite PCM also increased [11].

Liu et al. demonstrated that TiO₂ nanoparticles embedded into BaCl₂ solution enhanced thermal conductivity significantly while comparing to pure BaCl₂ and in succession the cool storage and supply rate and the cool storage and supply capacity were increased greatly [12].

Wu et al. investigated the melting and freezing characteristics of Cu-Paraffin nanofluids for solar energy storage system and the result suggested that the dispersion of Cu nanoparticles to paraffin was able to achieve good thermal properties, thermal and chemical reliability and heat transfer rate [13]. Hong et al. reported that as volume fraction of Fe nanoparticles in ethylene glycol increased thermal conductivity of nanofluids also increased nonlinearly [14]. Also, in another study, volume fraction of alumina nanoparticles in the de-ionized water increased dynamic viscosity also increased along with thermal conductivity [15]. Further, an increase in operating temperature caused an increase in thermal conductivity of the alumina nanofluids whereas dynamic viscosity of alumina nanofluids decreased. In the present study, thermal and heat transfer characteristics of palmitic acid based TiO₂ nanofluids during melting and solidification processes have been investigated. Phase change temperatures and latent heats of nanofluids have been determined by DSC measurements. The complete melting and solidification processes of composite PCMs and palmitic acid have also been accomplished in order to observe the energy storage and release rates.

2. MATERIALS AND METHOD

2.1 Preparation of nanoparticles

Titanium butoxide and ethanol were mixed in the volume ratio of 1:4 for synthesis of TiO₂ nanoparticles by adopting sol-gel method. The mixed solution was kept on the magnetic stirring for 10 min at the speed of 700 rpm. During stirring action, NaOH pellets were gradually added with the above solution until the pH value of the solution attained at 7. After sometimes, the large amount of TiO₂ white precipitation was observed. Then, it was centrifuged and washed with 2D water for 3 times to derive the

purified nanoparticles. It was dried in oven at 100°C for 24 h and then, grinded by using agate mortar, to obtain powder. In this synthesis process, Titanium butoxide and NaOH were acting as main precursor and reducing agent, respectively. Besides, the addition of NaOH during the reaction had made significant impact on the size and shape of the nanoparticles.

2.2 Preparation of composite PCMs

Palmitic acid (melting point of 60-62°C) of 80g was considered as base material and TiO₂ nanoparticles as supporting material. A two-step method was preferred to prepare the composite PCMs of 0.1, 0.2, and 0.3 wt% TiO₂ nanoparticles. During the preparation of nanofluids, it was important to keep in mind certain parameters like stable dispersion, low agglomeration of particles and no chemical change of the fluid. SDBS was selected as capping agent for uniform dispersion of nanoparticles into palmitic acid. Furthermore, to improve the particles dispersion stably and minimum aggregation of the nanofluids, preparation processes were performed using an ultrasonic vibrator [16] at a frequency of 40 kHz. Residing times of nanofluids in the vibrator were varied for different mass fractions and they were 35, 40 and 45 min for 0.1, 0.2, and 0.3 wt%, respectively. A longer residing time in the vibrator would lead to introduce the defects in the composites. The vibrator temperature during the preparation processes was kept at above the melting point of the palmitic acid as it was sufficient to keep the palmitic acid in melted state.

2.3 Analysis methods

Philips CM120 series transmission electron microscope (TEM) model was employed for measuring the size of the synthesized TiO₂ particles. Samples were prepared by dispersing drop of colloid on copper grid, covered with the carbon film and the solvent was dried. The TEM image for TiO₂ nanoparticles is illustrated in Fig.1 and sizes of the particles observed were ranging from 17 to 69 nm. Differential scanning calorimetry (DSC) measurements were carried out to determine the latent heats and phase change temperatures of palmitic acid and composite PCMs using DSC 6220 series instrument (SII, Japan). Nitrogen was used as

cooling medium and the samples were tested at the heating and cooling rates of 10 and 5 K/min, respectively. The maximum deviations in the measurements of phase change temperatures and latent heats were found to be 0.018 °C and 0.02 kJ / kg, respectively. Samples were kept in a sealed aluminium pan with a mass of about 6.08 mg.

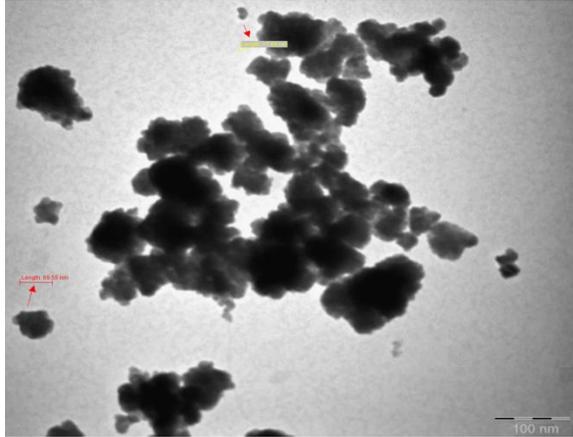


Fig.1. TEM image of TiO₂ nanoparticles

Besides, melting and solidification points were determined by drawing a line at the point of maximum slope of the peaks. The latent heats were calculated by numerical integration of the peak using software of DSC instrument.

2.4 Experimental set up

The schematic diagram of the experimental set up used for analysing the melting and solidification characteristics of composite PCMs during heating and cooling processes is shown in Fig. 2. Experimental setup consisted of the insulated thermal energy storage (TES) tank including the PCM encapsulation and constant temperature tank containing heating and cooling units for providing heat and cold energy to the circulating heat transfer fluid (HTF) during energy storage and release processes. Palmitic acid and composite PCMs with 0.1, 0.2, 0.3 wt% TiO nanoparticles were tested with the help of spherical encapsulation kept in the TES tank, separately. Water was used as the circulating heat transfer fluid, whose temperature can be varied from 30°C to 90°C. Temperature controllers with electrical stirrer and pressure sensors were used to

ensure the uniformity of the temperature and pressure conditions inside the TES tank as well as the constant temperature tank. The estimated uncertainty in the temperature measurement was 1.2% and the resolution of digital temperature controller was 0.1°C. Digital camera was used to observe the progress of the solidification and melting of the composites during both the processes. All the sensors/transducers were interfaced to the 80 channel data logger (Agilent 34972A, USA) for ensuring better operational features of the LTES system under varying thermal load conditions.

For studying the solidification process of base material and composite PCMs, the refrigerating system was operated to cool the circulating HTF to the required temperature level. The temperature of the HTF was kept at 40°C for the entire cooling process and pumped to the TES tank using the circulating pump. This cold energy from HTF was transferred to the PCMs until the PCMs reached the complete solidification. Similarly, for analyzing the melting process of base material and composite PCMs, the heating system was switched on in order to increase the circulating HTF temperature at the required condition. In the melting process, the temperature of the HTF was set at 80°C and supplied to the TES tank using the circulating pump. This heat energy from HTF was then transferred to the PCMs until the PCMs attained the complete melting. In this way, melting and solidification processes for the base material and the composite PCMs were repeated for assessing as latent heat storage material suitable for thermal energy storage system.

3. RESULTS AND DISCUSSION

3.1 Thermal properties of composite PCMs

Phase change temperatures and latent heats of base material and composite PCMs with 0.1, 0.2, and 0.3wt% TiO₂ nanoparticles during melting and solidification were determined by means of DSC measurements. Phase change temperatures and latent heats obtained from DSC measurements are furnished in Figs. 3 and 4, respectively. Small changes were observed in between phase change temperatures of base material and composite PCMs. Similar changes were found in between latent heats of base material and composite PCMs.

These little changes may be due to physiochemical changes caused by the dispersed TiO₂ nanoparticles in the base material. From the Fig. 3, the maximum

deviations of phase change temperatures for both melting and solidification were found to be -0.19 and -0.26%, respectively. For latent heats, maximum

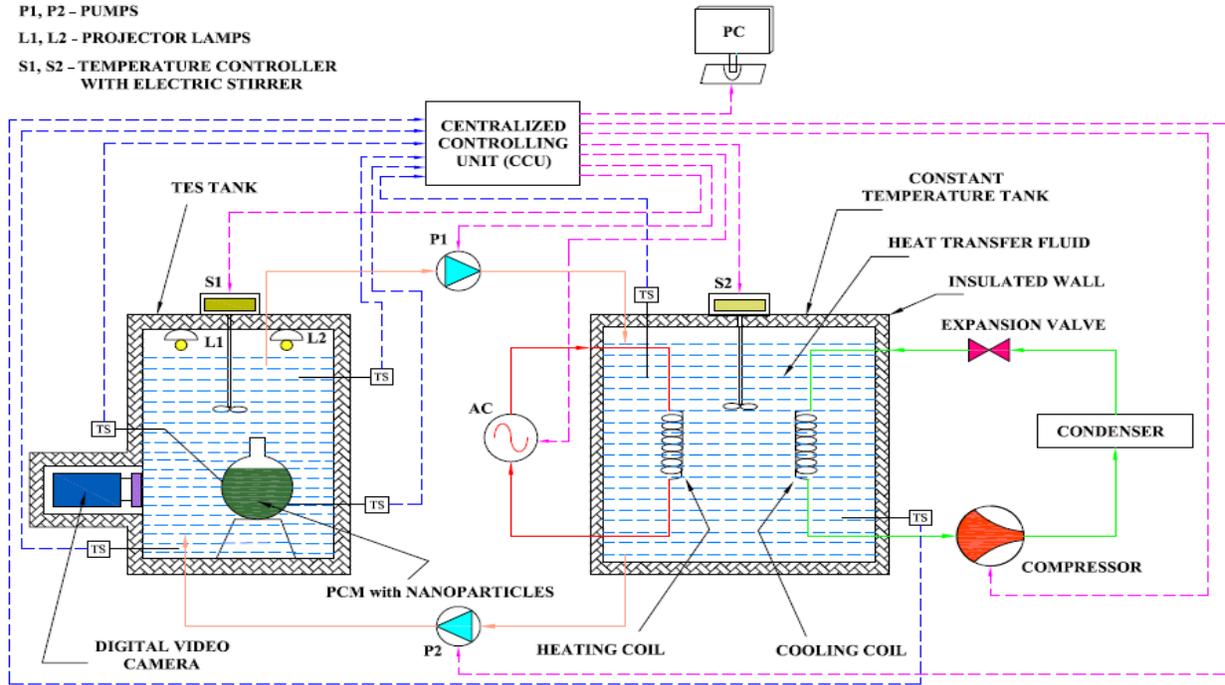


Fig.2. Experimental set up for testing the phase change behavior of PCMs

reduction during melting and solidification were determined as 0.48 and 0.51%, respectively, as shown in Fig. 4. In spite of these small deviations in thermal properties of the composite PCMs, energy storage and release processes would never cause any

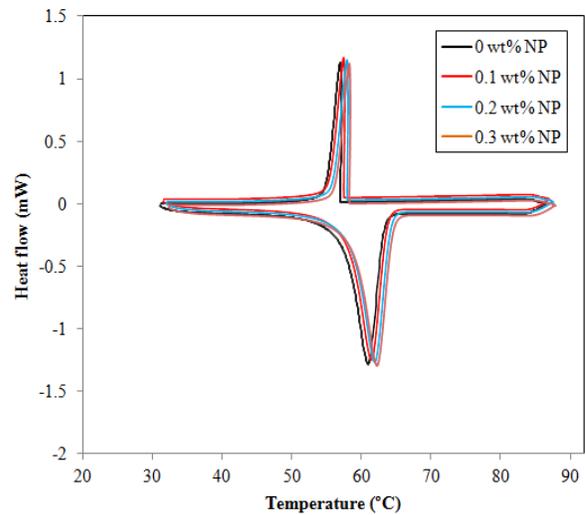


Fig.3. DSC measurements of palmitic acid and composite PCMs

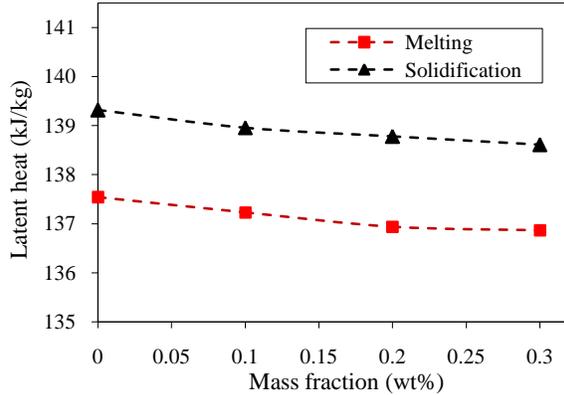


Fig.4. Effect of concentration of nanoparticles on latent heat of PCM

unfavorable effect towards the performance of the LTES system. Conversely, these changes accelerated the energy storage and release rates of the composite PCMs better as compared to base material. As far as solar energy storage for heating application is concerned, PCMs of 120 kJ/kg latent heat capacity of PCM are preferred [17]. Hence, the small reduction of latent heats of each composite in this study could be neglected.

3.2 Thermal reliability of composite PCMs

For long-run utility, phase change temperatures and latent heats of PCMs should not be altered noticeably after undergoing more number of thermal cycles. Because, these changes would cause adverse effect on the energy storage and release rates, which in turn would make the LTES system perform poorly. The composite PCM with 0.3 wt% TiO₂ nanoparticles was tested for ascertaining the long-term thermal stability. The variation of phase change temperature with respect to thermal cycles for composite PCM is illustrated in Fig. 5. The maximum shift of solidification temperature and melting temperature was found to be -1.34 and -1.59%, respectively. The variation of latent heat with respect to thermal cycles for composite PCM is shown in Fig. 6. The maximum shift of latent heats for solidification and melting was observed as 0.61 and 0.56%, respectively. These shifts might be due to thermo-physical changes within the composite PCM.

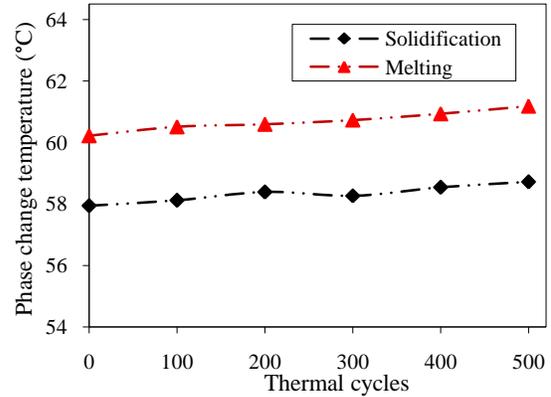


Fig.5. Variation of phase change temperatures of composite PCM with respect to thermal cycles

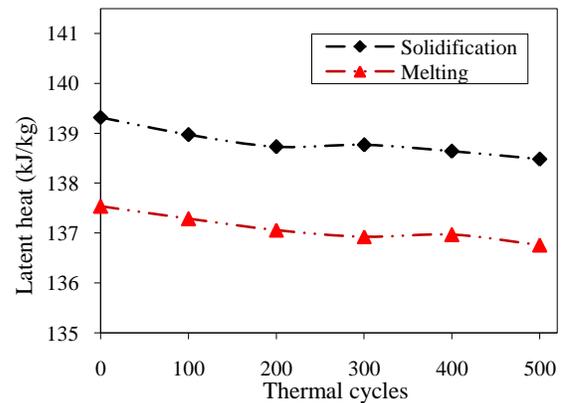


Fig.6. Variation of latent heats of composite PCM with respect to thermal cycles

These changes would neither cause any adverse effect on the energy storage and release rates of composite PCM greatly nor affect the performance of the solar LTES system distinctly. Hence, these shifts can be acceptable as far as latent heat storage for solar heating application is concerned. Thus, palmitic acid based TiO₂ nanofluid as composite PCM had exhibited good thermal reliability characteristics.

3.3 Melting and solidification characteristics of composite PCMs

The heat transfer rates of palmitic acid and composite PCMs were investigated during the melting and solidification processes. Temperature profiles of the palmitic acid and composite PCMs for both the processes are represented in Figs. 7 and 8.

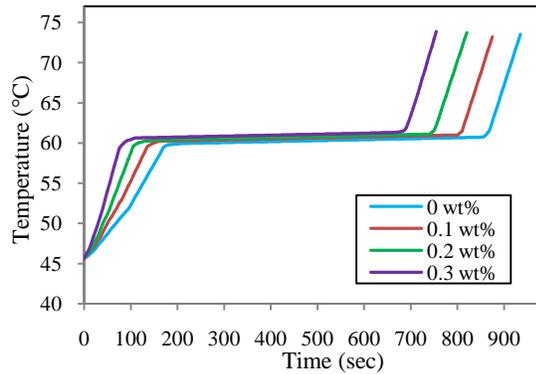


Fig.7. Melting curves of the base material and composite PCMs

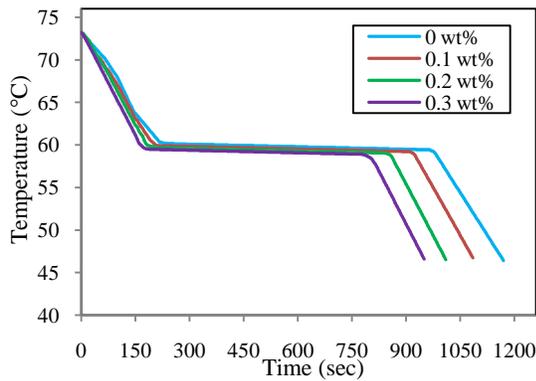


Fig.8. Solidification curves of the base material and composite PCMs

As seen in Fig. 7, temperatures of palmitic acid and composite PCMs were observed as 40°C at the beginning of melting process. As time progresses, temperatures of the base material and composite PCMs got increased and it continued until the base material and composite PCMs reached their melting point. Once reaching the melting point, base material and composite PCMs had started to change their phase from solid to liquid. The time taken by base material for complete melting from the starting was 855s and composite PCMs with 0.1, 0.2 and 0.3 wt% nanoparticles were 800, 730 and 675s, respectively. It was clearly indicated that the dispersed nanoparticles into base material had introduced the conductive heat transfer along with convective heat transfer during the melting process.

As seen in Fig. 8, temperatures of base material and composite PCMs were found as 80°C at the start of solidification process. As time progresses, temperatures of the base material and composite PCMs got decreased and it continued until the base material and composite PCMs attained their freezing point. The moment they reached the freezing point, base material and composite PCMs had begun to change their phase from liquid to solid. The time taken by base material for complete solidification from the starting was 970s and composite PCMs with 0.1, 0.2 and 0.3 wt% nanoparticles were 910, 850 and 775s, respectively. It was clearly elucidated that these results had made good agreement with computational simulation work accomplished on thermal conductivity enhancement of nanofluids for thermal energy storage system by Khodadadi and Hosseinizadeh [18]. Dispersed effective nanoparticles into base material accelerated the conductive heat transfer further during the solidification process. Results obtained from the experiment revealed that mass fraction of TiO₂ nanoparticles into base material increased, melting and solidification rates of composite PCMs also increased. Furthermore, faster rates of melting and solidification of composite PCMs would be evident to the thermal conductivity enhancement of base material.

4. CONCLUSIONS

Experimental study was conducted on the newly prepared palmitic acid based TiO₂ nanofluids with capping agent as composite PCMs. The TEM image for TiO₂ nanoparticles confirmed the size of the synthesized particles in nano range. The little deviation was observed for the phase change temperatures and latent heats between composite PCMs and palmitic acid from DSC measurements. These little deviations would not affect the heat transfer performance of the LTES system significantly. From the experimental results, it was observed that time reduction of composite PCMs with 0.1, 0.2, 0.3 wt% nanoparticles for complete melting and solidification processes were 76.43, 14.62, 21.05% and 6.18, 12.37, 20.11% respectively, than palmitic acid. With these results, the newly prepared nanofluids could be considered to be efficient PCMs for solar water heating system due to



its enhanced heat transfer characteristics, good thermal stability and thermal reliability.

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REFERENCES

1. L. M. Jiji, S. Gaye., 2006, "Analysis of solidification and melting of PCM with energy generation", *Applied Thermal Engineering*, 26: 568–575.
2. A. Kaizawa, H. Kamano, A. Kawai, T. Jozuka, T. Senda, N. Maruoka, T. Akiyama., 2008, "Thermal and flow behaviors in heat transportation container using phase change material", *Energy Conversion and Management*, 49: 698-706.
3. N. Yuksel, A. Avci, M. Kilic., 2006, "A model for latent heat energy storage systems", *International Journal of Energy Research*, 30: 1146-1157.
4. H. Yin, X. Gao, J. Ding, Z. Zhng., 2008, "Experimental research on heat transfer mechanism of heat sink with composite phase change materials", *Energy Conversion and Management*, 49: 1740–1746.
5. A. Sari, A. Karaipekli., 2007, "Thermal conductivity and latent heat thermal energy storage characteristics of paraffin/expanded graphite composite as phase change material", *Applied Thermal Engineering*, 27: 1271–1277.
6. R. Parameshwaran, S. Harikrishnan, and S. Kalaiselvam., 2010, "Energy efficient PCM based variable air volume air conditioning system for modern buildings", *Energy and Buildings*, 42: 1353–1360.
7. Kalaiselvam. S, Marcel Xavier. L, Kumares. G. R, Parameshwaran .R and Harikrishnan .S., 2010, "Experimental and numerical investigation of PCMs with finned encapsulation for energy efficient buildings", *Journal of Building Performance Simulation*, 1–10.
8. S. Harikrishnan, S. Kalaiselvam., 2012, "Preparation and thermal characteristics of CuO–oleic acid nanofluids as a phase change material", *Thermochimica Acta*, 533: 46–55.
9. S. Ozerinc, S. Kakac, A.G. Yazicioglu., 2010, "Enhanced thermal conductivity of nanofluids: a state-of-the-art review", *Microfluidics and Nanofluidics* 8: 145–170.
10. S. Kalaiselvam, R. Parameshwaran, S. Harikrishnan., 2012, "Analytical and experimental investigations of nanoparticles embedded phase change materials for cooling application in modern buildings", *Renewable Energy*, 39: 375-387.
11. J.L. Zeng, L.X. Sun, F. Xu, Z.C. Tan, Z.H. Zhang, J. Zhang, T. Zhang., 2007, "Study of a PCM based energy storage system containing Ag nanoparticles", *Journal of Thermal Analysis and Calorimetry*, 87: 369–373.
12. Y.D. Liu, Y.G. Zhou, M.W. Tong, X.S. Zhou., 2009, "Experimental study of thermal conductivity and phase change performance of nanofluids PCMs", *Microfluidics and Nanofluidics*, 7: 579–584.
13. S. Wu, D. Zhu, X. Zhang, J. Huang., 2010, "Preparation and melting/freezing characteristics of Cu/Paraffin nanofluids as phase-change material (PCM)", *Energy and Fuels*, 24: 1894-1898.
14. T. Hong, H.S. Yanga, C.J. Choi., 2005, "Study of the enhanced thermal conductivity of Fe nanofluids", *Journal of Applied Physics*, 97: 064311.
15. C-Y. Lin, J-C. Wang, T-C. Chen., 2011, "Analysis of suspension and heat transfer characteristics of Al₂O₃ nanofluids prepared through ultrasonic vibration", *Applied Energy*, 88: 4527-4533.
16. D.H. Kim, H.W. Ryu, J.H. Moon, J. Kim., 2006, "Effect of ultrasonic treatment and temperature on nanocrystalline TiO₂", *Journal of Power Sources*, 163: 196–200.
17. M. Kenisarin, K. Mahkamov., 2007, "Solar energy storage using phase

- change materials”, Renewable and Sustainable Energy Reviews, 11: 1913-1965.
18. J.M. Khodadadi, S.F. Hosseinizadeh., 2007, “Nanoparticle-enhanced phase change materials (NEPCM) with great potential for improved thermal energy storage”, International Communications in Heat and Mass Transfer, 34: 534–543.

AUTHOR BIOGRAPHY



Mr. S. Harikrishnan is currently doing Ph.D work on nano based phase change materials for HVAC applications, for Nanoscience and Technology, Anna University, India. He has obtained two fellowship awards namely, Anna centenary research fellowship (ACRF) and National renewable energy fellowship (NREF). He has 7 years of teaching experience and 1 year of industry experience. He has published 4 and 3 papers in refereed international journals and conferences, respectively.



Dr. S. Kalaiselvam is an Associate Professor at Department of Mechanical Engineering in College of Engineering, Guindy, Anna University, India.

He has 10 years of teaching experience. He was awarded as Young Scientist 2009, by Department of Science and Technology, India and Young Engineer 2010, by Institute of Engineers (India). He has research interest in nano heat transfer, nano composite, nano based PCM and HVAC systems. He has more than 25 publications in national and international journals. He has got an Indian patent on nano based PCM.