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# ORGANIC-ORGANIC EUTECTIC PHASE CHANGE MATERIALS WITH ENHANCED THERMAL CONDUCTIVITY USING GRAPHENE NANOPLATELETS AND ALUMINIUM NITRIDE WITH LOW-LOADING NANOADDITIVES

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*Modern high-performance compact electronic devices generate a lot of heat during operation; thus, researchers are investigating more advanced thermal management strategies. Operating electronics in extremely high or low temperatures might cause malfunctions. Consequently, phase change materials (PCM) employ phase transition via latent heat to maintain isothermal temperature. Using a straightforward solution blending method, nano additives such as 2D graphene nanoplatelets (GN) and aluminum nitride (AlN)-loaded palmitic stearic acid-based organic-organic eutectic PCM (PSGx) were made in order to increase thermal conductivity and ascertain the phase transition temperature of novel eutectic PCM. To observe the effects of addition of nano additives on PSGx's melting thermogenetic, thermal transport, and thermal heat storage properties, the amount of GN was varied. 326 % increase in thermal conductivity and 5.07 % decrease in latent heat is noticed with the addition of 3 weight percent GN. Outstanding thermal conductivity was attained by the formation of thermally conductive scaffolds enhanced with synergistic AlN and GN. The phase transition peak temperature, as determined by differential scanning calorimetry, is between 55 and 60 degrees Celsius, suggesting that it could be a viable option for high-power electronics thermal control.*

**Keywords**: Graphene; Nanoplatelets; Eutectics; Phase Change Material; Thermal conductivity; Calorimetry.

## 1. INTRODUCTION

Highly-powerful and densely packed compact appliances have drawn a lot of attention recently from high-end electronic applications. The chip and other components of the device generate expensive thermal energy when they are operating continuously. Electronic devices need to be properly drained of this extremely high heat rate to avoid malfunctioning immediately away [1]-[2]. The design and operation of contemporary electronic components have advanced significantly, yet managed cooling and heat management are still a big challenge. Although active cooling based on liquid, air, or hybrid is widely used for cooling,

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phase change material (PCM)-based passive cooling is better suited to handle thermal management due to its higher cooling efficiency.

Even though the choice of cooling method depends on several aspects, such as operating temperature, heating power rate, available space, and cost, the PCM-based cooling system seems to be the best option when considering all of the aforementioned parameters [3]-[4]. Modern cooling technologies, such air and liquid cooling, are rather ineffective at cooling, have a significant chance of leaks, and are difficult to install. It is desirable to use a new and efficient cooling technique based on PCM to handle the increased heat load. It is highly recommended that alternative energy-based thermal management systems use PCM composites with high latent heat and thermal conductivity [5]. It's interesting to note that PCMs can release or store thermal energy during the phase transition. Heat is released as the phase changes from liquid to solid at lower temperatures. The practical applications of perfect PCM are restricted by some features, such as low heat conductivity, leakage during melting, and an improper phase transition temperature [6]. These drawbacks can be overcome by employing the appropriate methods, such as the addition of nano additives, and PCM's thermal transport characteristics are improved by the addition of high-thermal conductivity nano additives. Thermally conductive additives such as graphene nanoplatelets (GN), carbon nanotubes, carbon fiber, expanded graphite, CuO, Al2O3, SiO2, hexagonal boron nitride (hBN), and AlN are widely employed to boost thermal conductivity because of their exceptional intrinsic thermal characteristics [7]-[8].

Graphene is considered one of the most promising nanoadditives because to its superior thermal conductivity and chemical inertness, which may promote improved heat transmission [9]-[10]. A practical phase transition temperature adjustment technique involving the combination of two or three fatty acids is adapted, especially for the proper choice of PCM [11]-[12]. It is a known fact that the melting and freezing points of the eutectic mixture are comparatively lower than those of the two or three corresponding individual fatty acids [13]. Moreover, a sufficient phase transition temperature characterizes the ideal eutectic composition for creating an effective heat management system [14]-[17]. By adding sheet-like structured additives, nanofillers with porous architectures, and other additives, PCM composites can benefit from the synergistic effect of several additives [18]-[22].

This study created an organic-organic eutectic phase change material (PSGx) based on palmitic stearic acid and aluminum nitride (AlN) loading to prepare PCM nanocomposites with compatible melting behavior. We looked into the melting behavior, melting enthalpy, and thermal transport of GN and AlN-loaded PSGx. The study revealed that as the loading of GN increased, the thermal conductivity of the nanocomposites increased gradually.

## 2. Proposed materials and methods

We employed analytical-grade reagents; no additional purification was performed on them. Commercial-grade fatty acids, such as stearic and palmitic acid (M/s SRL, India), were used without additional processing. After co-solvent mixture-mediated liquid-phase exfoliation of exfoliated porous graphite (EP), GN was produced utilizing a mechanical mixer and sonication (Sonics, Vibracell, 750 W). During the GN preparation procedure, bulk EP was dispersed in an isopropanol-water combination using a mechanical mixer and sonication for one hour and one hour in sequential order, respectively. With a few minor modifications, the comprehensive preparation process is covered elsewhere [17]. Solution-phase fragmentation assisted by complicated fluid dynamics could be used to delaminate the bulk into 2D-structured GN. The fine powder was collected by vacuum-assisted filtering, and it was subsequently dried for 12 hours. Later, PSGx was produced utilizing a brand-new melt-mixing technique. After the eutectic combination of stearic acid and palmitic acid (63:37 weight percent) was fully melted, GN (0, 0.5, 1, and 3 weight %) and AlN (1 wt. % in all composites except PSG0) were added to each PSGx in the prescribed amounts). The composition of PSG0, PSG1, PSG2, PSG3, and PSG4 are shown in Table1.

*Table 1*:

**Different compositions with concentration (Wt. %) of Nanocomposites**

| S.NO | NANO MATERIAL | PALMITIC ACID (Wt. %) | STEARIC ACID (Wt. %) | AIN (Wt. %) | GN (Wt. %) |
|---|---|---|---|---|---|
| 1 | **PSG0** | **63** | **37** | **0** | **0** |
| 2 | **PSG1** | **62.37** | **36.63** | **1** | **0** |
| 3 | **PSG2** | **61.05** | **36.445** | **1** | **0.5** |
| 4 | **PSG3** | **61.74** | **36.26** | **1** | **1** |
| 5 | **PSG4** | **60.48** | **35.52** | **1** | **3** |

The slurry was homogeneously dispersed for an hour before being placed into a 10 x 10 x 60 mm mold to solidify it. For the purpose of clarity, the PCM material with GN contents of 0, 0.5, 1, and 3 were referred to as PSG1, PSG2, PSG3, and PSG4.The acronyms PS, and PSGx refer to the eutectic mixture of stearic-palmitic acid and nanocomposites are depicted (Photos of the samples) in Fig. 1.

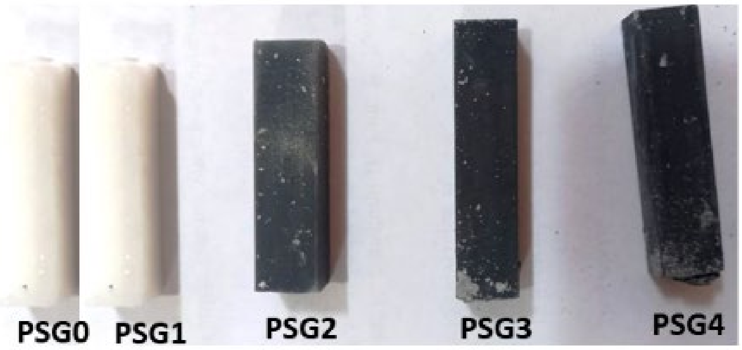

Fig. 1: Photos of PSGx nanocomposite samples

Differential scanning calorimetry (DSC) was used to determine thermal properties such as phase transition temperature and latent heat. A simultaneous thermal analyzer (Netzsch, STA 449 F3, Jupiter, Germany) was used to take measurements at 2 °C/min in an argon atmosphere while maintaining an adequate flow rate of 50 ml/min. The thermal conductivity of PSGx was measured using a laser flash analyzer system (Netzsch, LFA 427). For consistent results, the average of three thermal conductivity readings has been noted. Research methodology have been maintained in Fig. 2.

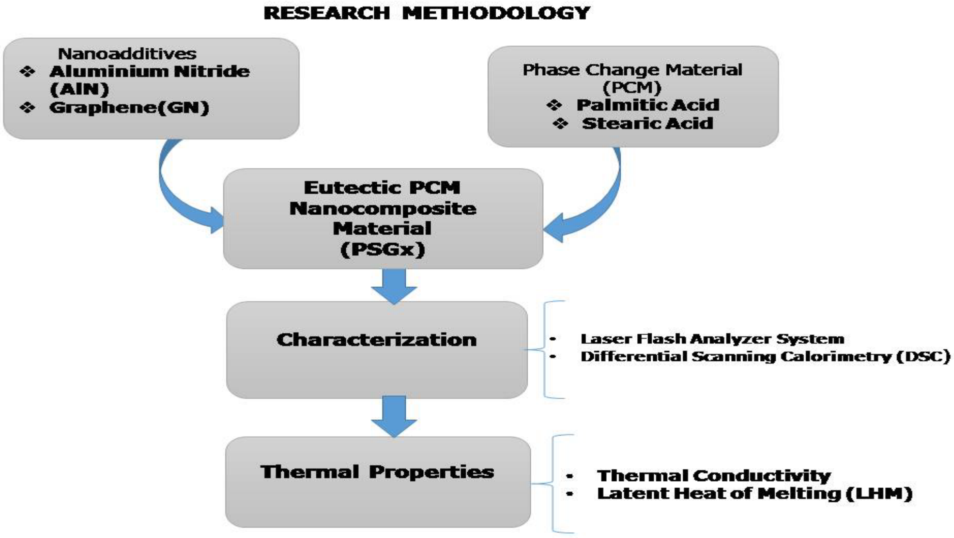

Fig. 2. Schematic representing research methodology

The commercial characteristics of GN (e.g., Particle Size is ~30 nm, Purity 99%, surface Area: 35-50 m²/g, GN is thin-structured platelets with size in the range of

0.38-1.5 μm$^2$).

## 3. Results and discussion

GN's is generated through cosolvent-mediated liquid-phase exfoliation with complex fluid dynamics-assisted vertical diffusion (VD) in a mechanical mixer possessing equally spaced sharp blades. An appropriate co-solvent mixture with minimal mixing enthalpy assisted in forming 2D-structured GN from the bulk EP. The bulk EP particles repeatedly rotated along the eddy direction, and the combination of fine and large eddy could fragment the bulk into fine-structured nanoplatelets [18]. Thus, the combination of intense mechanical agitation and sonication could create GN from the bulk EP. To derive suitable phase transition temperatures for PCM composites, a eutectic binary mixture comprising palmitic and stearic acid was developed, as it is more convenient for thermal energy storage systems applied for electronics thermal management than those of pristine palmitic and stearic acids. A eutectic composition based on the mass fraction of palmitic acid and stearic acid was considered in the work reported by H. Ke et al. using the Schrader equation (an eutectic mixture with a ratio of 63:37 wt.%) [13]. After melting the palmitic acid and stearic acid with eutectic composition, a predetermined quantity of GN (0, 0.5, 1, and 3 wt.%) and AlN (for 1 wt.%) in all PSGx was incorporated. A custom-designed vacuum-assisted infiltration module was deployed for evacuation and to remove the air. The preparation procedure for the development of PSGx is illustrated in Fig. 3.

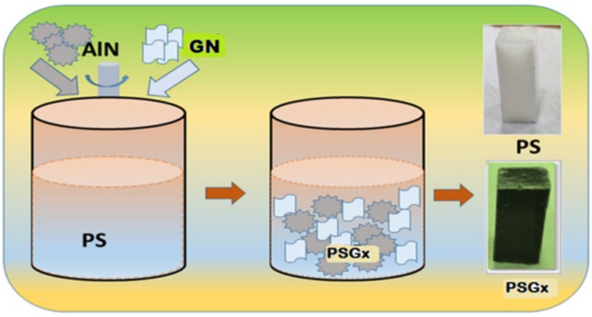

Fig. 3: Schematic diagram presenting the procedure for preparation of PSGx

The phase transition temperature, latent heat storage, and melting behavior of PSGx were comprehensively studied by applying the DSC technique.

The melting behavior of PSGx is illustrated in Fig. 4. Heat flow curves precisely locate the phase transition temperature, such as the onset (To), peak (Tp), and end (Te) of the phase transition temperature, as shown in Table 2.

Fig. 4 indicated that the measured phase transition peak temperatures of PSG0, PSG1, PSG2, PSG3, and PSG4 composites were around 60.1, 56.05, 55.82, 55.48, and 55.37 ºC, respectively. It demonstrated that the lowering in phase transition peak temperature was noticed with the increase in the addition of GN loading. An increase in the quantity of nano additives resulted in a slight decrease in $T_0$, $T_p$, and $T_e$. The aforementioned criteria could account for the high thermal conductivity of GN and AlN, which might have led to the creation of thermally conducting scaffolds to impart an efficient heat transfer pathway.

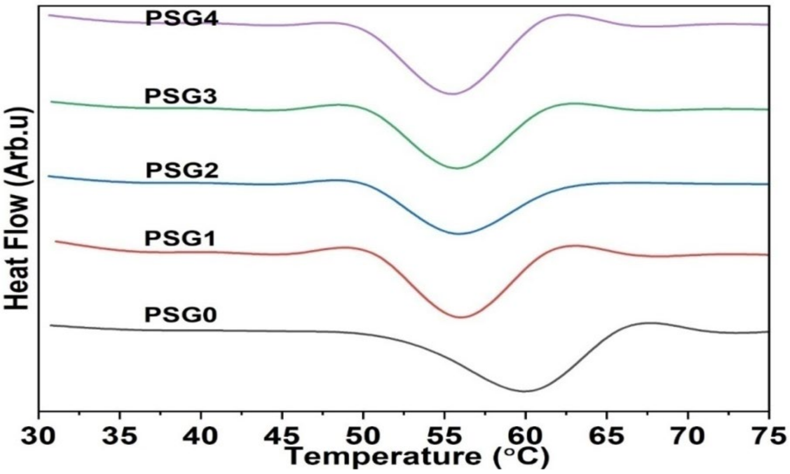

Fig. 4: DSC curves of PSGx Nanocomposites

*Table 2:*

**Phase Transition Temperatures of Nanocomposites (PSGx)**

| S.NO | NANO MATERIAL | ONSET TEMP. (To) °C | PEAK TEMP. (Tp) °C | END TEMP. (Te) °C |
|---|---|---|---|---|
| 1 | **PSG0** | **54.2** | **60.1** | **62.1** |
| 2 | **PSG1** | **52.2** | **56.05** | **59.8** |
| 3 | **PSG2** | **49.7** | **55.82** | **64.05** |
| 4 | **PSG3** | **49.4** | **55.48** | **62.62** |
| 5 | **PSG4** | **48.7** | **55.37** | **62.06** |

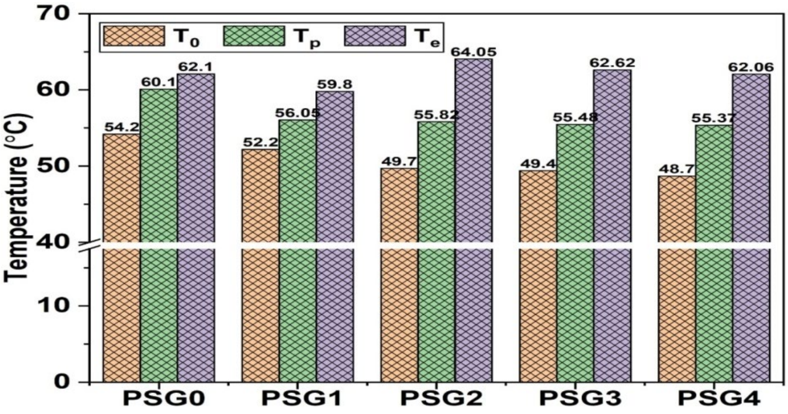

Fig. 5: Phase Transition temperatures of PSGx: $T_0$, $T_p$ and $T_e$

*Table 3:*

**Latent Heat Enthalpy of Melting of Nanocomposites**

| S.NO | NANO MATERIAL | ENERGY STORED-LHM (J/g) | HEAT FLOW STATUS IN LHM (%) | THEORETICAL VOLUME FRACTION NANOADDITIVES (%) |
|---|---|---|---|---|
| 1 | **PSG0** | **173.5** | **-----** | **-----** |
| 2 | **PSG1** | **169.9** | **2.075** | **1** |
| 3 | **PSG2** | **168.6** | **2.824** | **1.5** |
| 4 | **PSG3** | **167.5** | **3.458** | **2** |
| 5 | **PSG4** | **164.7** | **5.07** | **4** |

Fig. 5 shows the GN loading-induced variation in the latent heat of enthalpy of melting (LHM) of PSGx nanocomposites. The latent heat of PSGx was measured to be around 173.5, 169.9, 168.6, 167.5, and 164.7 J/g for PSG0, PSG1, PSG2, PSG3, and PSG4, respectively. It is clear from Fig. 5 that the LHM of the PSGx nanocomposites has decreased with an increase in GN addition. As GN or AlN are not active at the phase transition temperature during melting, their addition reduces the latent heat storage capacity proportionately. Thus, LHM decreases delightfully and was found to be inversely proportional to the amount of GN loading in PSGx. The sharp heat flow curves demonstrated the decrease in LHM by 2.075, 2.824, 3.458, and 5.072% for PSG1, PSG2, PSG3, and PSG4, respectively.

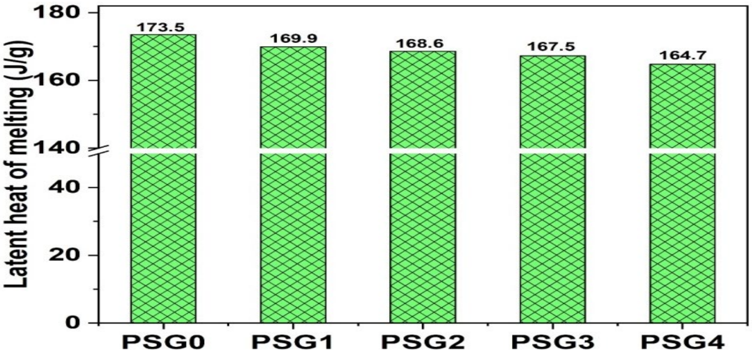

Fig. 6: Latent heat of melting of Nanocomposites(PSGx)

*Table 4:*

**Thermal Conductivity of Nanocomposites**

| S.NO | NANO MATERIAL | THERMAL CONDUCTIVITY (K) W/m K | ENHANCED THERMAL CONDUCTIVITY (%) |
|---|---|---|---|
| 1 | **PSG0** | **0.19** | **----** |
| 2 | **PSG1** | **0.31** | **63** |
| 3 | **PSG2** | **0.49** | **162.6** |
| 4 | **PSG3** | **0.67** | **256.8** |
| 5 | **PSG4** | **0.81** | ***326** |

Fig. 6 depicts the thermal conductivity of PSGx. At room temperature measurements, PSG0, PSG1, PSG2, PSG3, and PSG4 exhibited a thermal conductivity of 0.19, 0.31, 0.499, 0.678, and 0.81 W/mK, respectively. It infers that the higher the GN loading, the higher the thermal conductivity. The addition of GN enhanced thermal conductivity by 63, 162.6, 256.8, and 326% for PSG1, PSG2, PSG3, and PSG4, respectively.

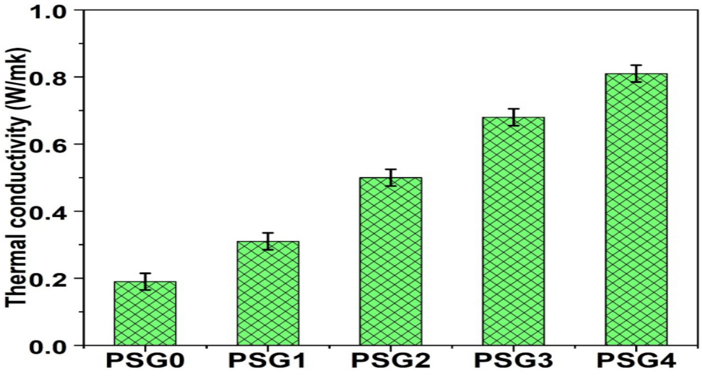

Fig. 6: Thermal conductivity of Nanocomposites(PSGx)

The thermal conductivity of PSGx nanocomposites increased significantly, although GN is loaded at a smaller amount (3 wt.%), which could be attributed to the synergistic effect, robust interface, and high thermal conductivity of GN and AlN. The nanoplatelet-like 2D-planar structure with exceptionally high thermal conductivity and crystallinity of GN ensured minimal phonon scattering at the PS and GN interfaces. GN translated its conductivity into the improved thermal conductivity of PSGx nanocomposites. The thermal conductivity measurements confirmed that the inherent thermal conductivity and the tailored interface between the nanofiller and the matrix helped in increasing the thermal transport characteristics of PSGx. GN acted as an efficient nano additive owing to its superior thermal conductivity and 2D planar structure, which could be able to manage the reduced phonon scattering and, as a result, the minimal interface thermal resistance. In nonmetallic composite PCMs, phonon scattering caused by the mismatch between additives and supporting materials induces large interfacial thermal resistance and reduces the thermal conductivity.

However, the addition of nanoadditives (GN and AlN) with high thermal conductivity and a minimum loading threshold could aid in efficient thermal transfer pathways for phonon propagation. Moreover, the firm interface between the nanoadditive and PCMs can reduce the interfacial thermal resistance. “firm interface" suggests a strong interface. The results demonstrated that the GN’s 2D structure, crystallinity, and planar sheet-like structure helped in augmenting the thermal conductivity. Interestingly, the clustering of nanoadditives in solid-phase PCM enhances the thermal conductivity as the aggregation of nanoadditives occurs through physical interactions like adhesion forces between the neighboring particles in the matrix. The phenomenon of clustering plays a key role in improving thermal transport. However, the tendency to form clusters at higher loadings may create severe sedimentation. Preferably, low loading of nanoadditives aids in boosting the higher thermal transfer than the sedimentation. Overall, the penalty of slightly decreased latent heat storage may be accepted compared to the remarkable intensification in thermal conductivity required to apply PSGx composites in practical applications for electronic heat management.

Various nanoadditives are explored to enhance the thermal conductivity of pristine PCM materials (19). A few studies revealed the effect of the addition of nanofiller on the thermal transport of PCM as follows: MASA+CNT (9 wt.%, 23.2 % (20)), PASA+EG (865.3%, (21)), stearic-lauric+TiO2 (1 wt.%, 34.85, (22)), stearic-lauric+ZnO (1 wt.%, 46.97, (22)), stearic-lauric+CuO (1 wt.%, 62.1, (22)). In this work, the PSGx exhibited a remarkable thermal conductivity increase of 326% and a peak phase transition of 55.37 °C. Interestingly, PSGx has shown exceptional thermal transport on par with the previous reports with an appropriate peak phase transition, which is a probable candidate for electronic appliances’ thermal management. Here, MASA (Myristic Acid-Stearic Acid), PASA (Palmitic

Acid-Stearic Acid) and EG (Expanded Graphite).

## 4 Conclusions

In this paper a straightforward solution-blending method was used to produce PSGx nanocomposites with remarkable thermal transport and thermophysical properties. For 3 weight percent GN loading, PSG4 quadrupled thermal conductivity while reducing latent heat by 5.07% less than PS. The creation of thermally conductive scaffolds enhanced with complementary AlN and GN increases thermal conductivity (326%). PSGx nanocomposites may offer a special route for use in thermal energy storage for electronics thermal management due to their good thermal conductivity and minimal latent heat.

## REFERENCES

[1] *Tang Y, Jia Y, Alva G, Huang X, Fang G.* Synthesis, characterization and properties of palmitic acid/high density polyethylene/graphene nanoplatelets composites as form-stable phase change materials. Sol. Energy Mater. Sol. Cells. 2016, 155, 421–429.

[2] *Siyabi IA, Khanna S, Mallick T, Sundaram S.* Multiple Phase change material (PCM) configuration for PCM-based heat sinks-An experimental study. Energies. 2018, 11, 1629, pp.14.

[3] *Fang X, Fan, L W, Ding Q, Wang X, Yao XL, Hou J.F, Yu ZT, Cheng GH, Hu YC, Cen KF.* Increased Thermal Conductivity of Eicosane-Based Composite Phase Change Materials in the Presence of Graphene Nanoplatelets. Energy Fuels. 2013, 27, 4041–4047.

[4] *Jaworski M.* Thermal performance of heat spreader for electronics cooling with incorporated phase change material. Appl. Therm. Eng. 2012, 35, 212-219 .

[5] *Bianco V, Rosa MD, Vafai K.* Phase-change materials for thermal management of electronic devices. Appl. Therm. Eng. 2022, 214, 118839, pp.15

[6] *Sharma A, Tyagi VV, Chen CR, Buddhi D.* Review on thermal energy storage with phase change materials and applications. Renew. Sust. Energ. Rev. 2009, 13, 318e345.

[7] *Bondareva NS, Sheremet MA.* Influence of PCM heat sink shape on cooling of heat-generating elements in electronics. Appl. Therm. Eng. 2022, 213, 118695, pp.12.

[8] *Yang G, Ji Yim Y, Lee JW, Heo YJ, Park SJ.* Carbon-filled organic phase-change materials for thermal energy storage. A Review, Molecules, 2019, 24, 2055, pp. 17.

[9] *Harish S, Orejon D, Takata Y, Kohno M.* Thermal conductivity enhancement of lauric acid phase change nanocomposite with graphene nanoplatelets. Appl. Therm. Eng. 2015, 80, 205-211.

[10] *Qureshi ZA, Ali HM*, Khushnood S. Recent advances on thermal conductivity enhancement of phase change materials for energy storage system. A review, International Journal of Heat and Mass Transfer. 2018, 127, pp. 838-856.

[11] *Cataldi P, Athanassiou A, Bayer I.* Graphene Nanoplatelets-Based Advanced Materials and Recent Progress in Sustainable Applications. Appl. Sci. 2018, 8, 1438.

[12] *Shoeibi S, Kargarsharifabad H, Mirjalily SAA, Sadi M, Arabkoohsar.* A comprehensive review of nano-enhanced phase change materials on solar energy applications. J. Energy Storage. 2022, 50, 104262, pp. 30.

[13] *Molaei MJ, Younas M, Rezakazemi M.* A Comprehensive review on recent advances in two-dimensional (2D) hexagonal boron nitride. ACS Appl. Electron. Mater. 2021, 3, 5165-5187.

[14] *Silakhori M, Fauzi H, Mahmoudian MR, Metselaar H.S.C, Mahlia TMI, Khanlou HM.* Preparation and thermal properties of form-stable phase change materials composed of palmitic acid/polypyrrole/graphene nanoplatelets. Energy Build. 2015, 99, 189–195.

[15] *Zhang X, An L, Bai C, Chen L, Yu Y.* Hexagonal boron nitride quantum dots: Properties, preparation and Applications. Mater. Today Chem. 2021, 20, 100425, pp. 17.

[16] *Singh P, Sharma RK, Ansu AK, Goyal R, Sarı A, Tyagi VV.* A comprehensive review on development of eutectic organic phase change materials and their composites for low and medium range thermal energy storage application. Sol. Energy Mater. Sol. Cells, 2021, 223, 110955, pp. 25.

[17] *K. Bala Subrahmanyam, A.Datta, P.Das.,* Parametric study of heat transfer performance including entropy generation of microchannel heat sink with fan cavity and different rib structure, J Process Mech Eng (2022), Vol. 236(2) 368–382.

[18] *Yavari F, Fard HR, Pashayi K, Rafiee MA, Zamiri A, Yu Z, Ozisik R, Borcatasciuc T, Koratkar N.* Enhanced Thermal Conductivity in a Nanostructured Phase Change Composite due to Low Concentration Graphene Additives. J. Phys. Chem. 2011, 115, 8753–8758.

[19] *Ke H.* Phase diagrams, eutectic mass ratios and thermal energy storage properties of multiple fatty acid eutectics as novel solid-liquid phase change materials for storage and retrieval of thermal energy. Appl. Therm. Eng. 2017, 113, 1319-1331.

[20] *Kahwaji S*, White MA. Prediction of the properties of eutectic fatty acid phase change materials. Thermochim. Acta. 2018, 660, pp. 94-100

[21] *Murugan P, Nagarajan RD, Shetty BH, Govindasamy M, Sundramoorthy AK.* Recent trends in the applications of thermally expanded graphite for energy storage and sensors. a review, Nanoscale Adv. 2021, 3, 6294-6309.

[22] *K. Bala Subrahmanyam, P.Das, A.Datta*., Numerical investigation on fluid flow and convective heat transfer in a microchannel heat sink with fan-shaped cavities and ribs, J Process Mech Eng (2021), vol. 235(4) 785-799.