

Numerical Investigation on Thermal Conductivity of Metal Nanoparticle Dispersed Composite Phase Change Materials

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Phase change materials (PCMs) possess excellent property to store thermal energy effectively at low cost. Thermal energy storage (TES) using PCMs are of current research hotspot as they contribute towards a) effective thermal management b) heat dissipation in electronic gadgets c) peak energy shift in building and d) to increase the renewable energy mix. In spite of numerous benefits, PCMs suffer due to low thermal conductivity which highly influences the energy storage rate. In this research investigation, using the existing numerical model a) Parallel Model, b) Series Model, c) Maxwell Model and d) Hamilton Model, the author determine and evaluate the thermal conductivity of composite PCMs. Both organic and inorganic PCM were opted for analysis with metal nanoparticles. Numerically determining the thermal conductivity of PCM would provide a vital significance to the research before carrying out any experimental evaluation, which would be time and cost saving. The research article will also provide future outlooks on nanoparticle dispersed PCM with a focus on scientific problems and practical difficulties when there is a non-uniform dispersion of nanoparticle with PCM.

Keywords: Phase change materials; thermal conductivity; thermal conductive nanoparticles; salt hydrates; thermal energy storage

Received: February 2024; Accepted: February 2024

Worldwide economic development and rapid growth of population causes sudden demand for fossil fuel which significantly affects the environment and paves for global issues like climate change, greenhouse gas emission and global warming [1]. With desire to limit the consumption of fossil fuels for day to day activities there arises the need for green, clean and sustainable energy, with better energy storage facilities. Most common energy storage forms include chemical energy, electromagnetic energy, mechanical energy and thermal energy. Among the aforementioned energy storage forms, thermal energy storage are preferable for civil fields and industries as they address major environmental problems and contribute to a cleaner atmosphere. As on current trend, thermal energy storage (TES) using phase change materials (PCM) s are of research hotspot as they hold good ability to store huge heat energy within a smaller volumetric space [2]. Thermal management of electronic gadgets, buildings [3], photovoltaics panels [4], photo-voltaic-thermal systems [5] and other heat generating units in an environmental friendly way are of utmost need as it cause's failure of electronic devices, disturbs

human livelihood conditions and reduces the performance of PV systems [6]. To ensure proper thermal regulation of the aforementioned system, PCM are much significant, however the thermal conductivity of PCM are of great concern. Figure 1 elaborates in detail the working of PCM with respect to change in temperature. At initial state of charging thermal energy the PCM exist in solid state; with increase in temperature of the working environment PCM melts and absorb energy during phase transition, subsequently with decrease in temperature of the working environment PCM freezes with release in heat energy and retracts to solid state [7].

Abundant research works are performed for improving the heat transport ability of conventional PCMs [3]. Predominant factor that influence the charging rate of PCM is their thermal conductivity, which hinders its applications. There exists a need for developing novel PCM with higher thermal conductivity without comprising the heat storage ability. As a result, multiple studies have been undertaken using dispersed metal foams, metal, and carbon

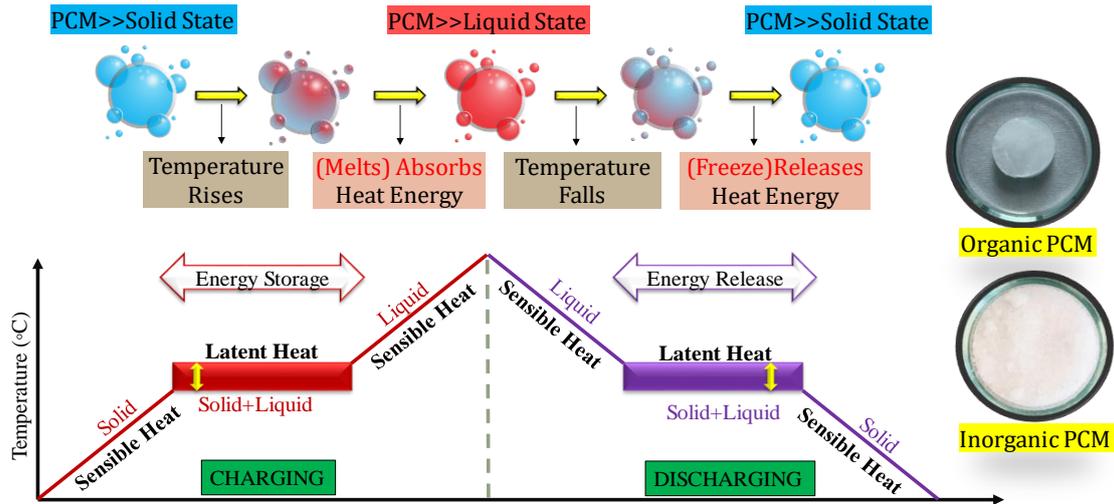


Figure 1. Energy storage and release in Phase Change Material with temperature change.

nanoparticles in various quantities. Carbon nanoparticles dispersed with the PCM are in the forms of carbon nano tubes, carbon fibers and matrix structures. Their do exist a lack of real time experimental proof to ensure uniform dispersion, and the results are not precise thereby main contributors come up with numerically enumerated correlation to determine the thermal conductivity of nanoparticle dispersed PCM.

Though numerous research are conducted with dispersion of nanoparticles and thermal conductive filler materials, they are time consuming and are very costlier in terms of economic as the research cannot have control over the reliability of the result. In the current numerical investigation the authors numerically evaluate the thermal conductivity of metal nanoparticle (Aluminium, Silver, Copper, Nickel & Titanium) dispersed organic (Paraffin & Stearic acid) and inorganic (Sodium Sulphate Decahydrate, Calcium Chloride Hexahydrate & Magnesium Chloride Hexa-

hydrate) PCM. Existing thermal conductivity models like, Parallel model, Series model, Maxwell Eucken model and Hamilton Crosser model are considered to determine the thermal conductivity of composite PCM at weight fraction of (0.1%, 0.3%, 0.5%, 0.7% & 1.0%). This numerical investigation will provide insights on the best opted numerical model, for dispersing metal nanoparticle with organic and inorganic PCM.

MATERIALS AND METHODS

Thermal Properties of Nanoparticles & PCMs

In this numerical investigation the authors have opted five metal (Silver; Copper; Aluminium; Nickel; Titanium) nanoparticles and five PCM (two organic PCM & three inorganic PCM) operating within the temperature of 28 °C to 68 °C. Table 1 provides the detailed information on the required thermal

Table 1. Thermal properties of metal nanoparticle and phase change materials (organic & I-inorganic).

Phase Change Materials					
Properties	Paraffin (Organic)	Stearic Acid (Organic)	Calcium Chloride Hexahydrate (Inorganic)	Sodium Sulphate Decahydrate (Inorganic)	Magnesium Chloride Hexahydrate (Inorganic)
Thermal Conductivity (W/(m·K))	0.2	0.29	0.540	0.519	0.704
Density (kg/m ³)	900	940	1802	1464	1570
Metal Nano Particles					
Properties	Silver (Ag)	Copper (Cu)	Aluminium (Al)	Nickel (Ni)	Titanium (Ti)
Thermal Conductivity (W/(m·K))	429	398	251	97.5	17
Density (kg/m ³)	10490	8960	2700	8900	4500

Table 2. Thermal conductivity models and correlations.

Thermal conductivity models	Correlations
Parallel Model [9]	$\alpha = (1 - V_f)\alpha_p + V_f\alpha_f$
Series Model [9]	$\frac{\alpha_p K_f}{\alpha_f(1 - V_f) + \alpha_p V_f}$
Maxwell Eucken Model [10]	$\alpha^{HS-} = \alpha_p \frac{2\alpha_p + \alpha_f - 2V_f(\alpha_p - \alpha_f)}{2\alpha_p + \alpha_f + 2V_f(\alpha_p - \alpha_f)}$
Hamilton Crosser Model [11]	$\alpha = \alpha_p \left[\frac{\alpha_f + (n - 1)\alpha_p + (n - 1)V_f(\alpha_f - \alpha_p)}{\alpha_f + (n - 1)\alpha_p - V_f(\alpha_f - \alpha_p)} \right]$

properties of the nanoparticles and PCMs required for determining the thermal conductivity of composite PCM.

Thermal Conductivity Models

In the current numerical investigation we consider, five thermal conductivity models namely; a) Parallel Model, b) Series Model, c) Maxwell Eucken Model and d) Hamilton Crosser Model [8]. Thermal conductivity (α) of the nanoparticle enhanced PCM matrix is related to the volume fraction of nanoparticle, density of nanoparticle, thermal conductivity of the base PCM matrix and the nanoparticle individually, shape and distribution of the nanoparticle. Correlation between thermal conductivity of PCM composite, and their influencing parameters with respect to each thermal conductive model are listed in Table 2.

Where α denotes thermal conductivity in W/(m.K), V represents volume fraction, likewise the subscript f and p indicates nanoparticle and PCM. $n=\psi/3$ (ψ is the sphericity of the nanoparticle).

RESULTS AND DISCUSSION

To ensure effective heat storage and release of PCMs, thermal conductivity of the base materials is a predominant factor. For any solid state material, free electrons and their atomic vibration are highly influence able for thermal conductivity. In organic PCMs, owing to the polymeric nature, phonons are responsible for thermal conductivity; likewise in inorganic PCM crystal lattice vibration are predominant as salt hydrate have very less number of free electrons [12]. Here in this numerical work, we have numerically determined the thermal conductivity of metal nanoparticle enhanced composite PCM. For a nanoparticle dispersed PCM, the significant parameters to consider are matrix of the base material, fraction of nanoparticle, nanoparticle size and structure, composition of nanoparticle, influence of agglomeration and clustering effect, methods of nanoparticle dispersion, operating temperature and the arrange of nanomaterial with PCM matrix [13]. The numerical models considered

in this numerical investigation are developed considering the aforementioned parameters with unique boundary conditions. Each thermal conductivity models has a unique feature based on the nanoparticle arrangement with the PCM matrix, and their size. Figure 2a and 2b represents the nanoparticle arrangement in PCM matrix with respect to parallel and series model. It can be observed that in parallel model, the nanoparticles are in close contact with each other to the direction of heat flux applied and contribute in improved heat transfer rate. On the contrary with series model, the nanoparticles are discrete and lack close network for better heat transfer rate. Nevertheless for a parallel-series effective model, the arrangement are comprised of close contact and discrete distribution. Herewith, in the upcoming session, we will discuss in details the numerically obtained thermal conductivity values, for the considered organic & inorganic PCM; metal nanoparticles with respect to the aforementioned numerical model at a nanoparticle fraction of 0.1%, 0.3%, 0.5%, 0.7% and 1.0%.

Paraffin with Carbon and Metal Nanoparticles

Commonly used organic PCM, amongst the researchers is Paraffin due to their non-corrosive property, wide range of phase transition temperature (40-100 °C), stable thermal cycles without degree of supercooling and heat storage potential [14]. However their low thermal conductivity is of utmost concern. Paraffin has the benefit to contribute in various solar thermal systems by providing facility to store thermal energy, hence it is important to understand their thermal conductivity improvement using numerical model.

In Figure 3, we represent the thermal conductivity values obtained used thermal conductivity model with paraffin as PCM. The results are arranged with respect to different metal nanoparticles (Figure 3a Paraffin + Silver; Figure 3b Paraffin + Copper; Figure 3c Paraffin + Aluminum; Figure 3d Paraffin + Nickel and Figure 3e Paraffin + Titanium) in ascending order of the thermal conductivity of metal nanoparticles

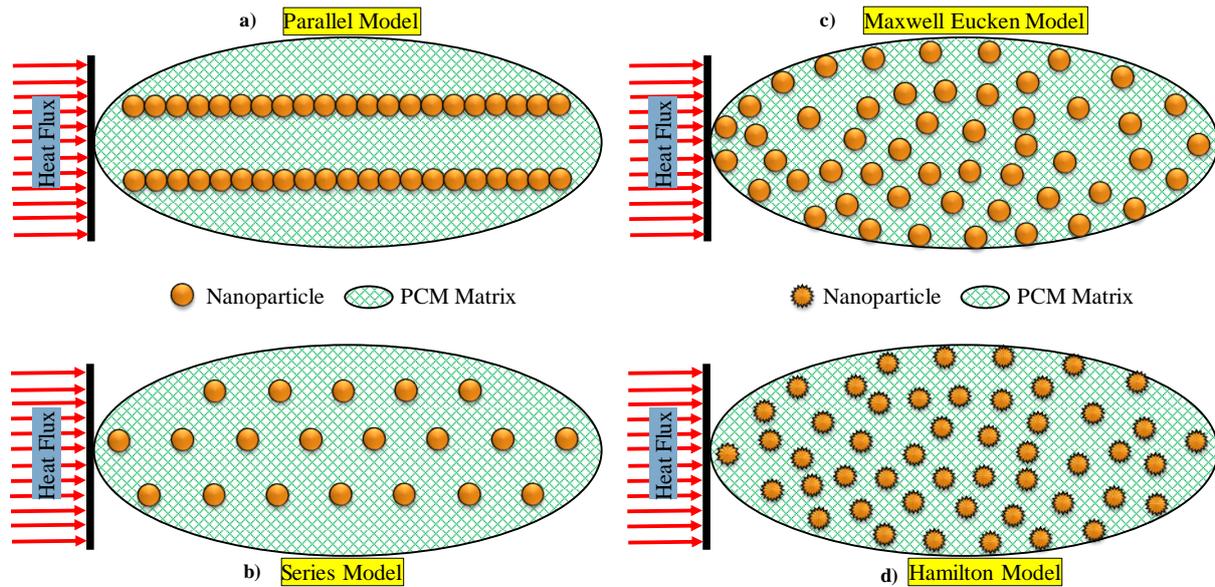


Figure 2. Representation of nanoparticle arrangement within PCM matrix in a) Parallel Model, b) Series Model, c) Maxwell Eucken Model and d) Hamilton Model.

as provided in Table 1. It can be witnessed from Figure 3a that the thermal conductivity value of paraffin with silver nano-particle of 1% shows a maximum increment of 185.65% from 0.2 W/(m·K) to 0.5713 W/(m·K) with parallel model. Whereas with parallel-series effective model, series model, Maxwell Eucken model and Hamilton modified model, the thermal conductivity of composite PCM (Paraffin + 1% Ag) increment was 92.85%, 0.1%, 123.85% and 130% respectively. Figure 3b shows the thermal conductivity value of paraffin with copper nanoparticle with weight fraction of 0.1%, 0.3%, 0.5%, 0.7% and 1.0%. With increase in nanoparticle the thermal conductivity value increase and it can be inferred that a maximum increment of 201.6% from 0.2 W/(m·K) to 0.6032 W/(m·K) with parallel model. Whereas with parallel-series effective model, series model, Maxwell Eucken model and Hamilton modified model, the thermal conductivity increase percent of composite PCM (Paraffin + 1% Cu) was 100.85%, 0.1%, 134.5% and 141.2% respectively.

In Figure 3c we depict the thermal conductivity of paraffin with aluminium nanoparticle for the numerical models considered. It can be deduced that composite PCM (Paraffin with 1% Al) to improve the thermal conductivity from 0.2 W/(m·K) for pure paraffin to 1.0416 W/(m·K), 0.6211 W/(m·K), 0.2007 W/(m·K), 0.7619 W/(m·K) and 0.7899 W/(m·K) with parallel model, parallel-series effective model, series model, Maxwell Eucken model and Hamilton modified model respectively which accounts for a increment of 420.8%, 210.55%, 0.35%, 280.95% and the maximum improvement (49.65%) was 0.2993 W/(m·K) from 0.2 W/(m·K) with 1% nickel with parallel model. Similarly Figure 3e shows

the titanium nanoparticle dispersion with paraffin PCM, where the maximum thermal conductivity increment was observed to be only 16.95%.

Insightful result to discuss is the thermal conductivity value of paraffin composite with aluminium nanoparticle dispersion in comparison to that of silver and copper nanoparticle. From Table 1 it is clear that the thermal conductivity of silver and copper nanoparticle are 70.91% and 58.56% higher than that of aluminium nanoparticle. However on dispersion of nanoparticle with paraffin at same proportion it can be observed that aluminium nanoparticle contribute to 420.88% whereas silver and copper nanoparticle contribute only 185.65% and 201.6% respectively. It can be inferred that irrespective of the thermal conductivity of the nanoparticle, the density of nanoparticle is very predominant, due to higher density of silver and copper nanoparticle, the settling is higher, thereby restricting uniform dispersion and increment in thermal conductivity of composite PCM.

Stearic Acid with Carbon and Metal Nanoparticles

Stearic acid PCM is the commonly used as a blend for organic-organic eutectic PCMs. Stearic acid holds higher latent heat value of 191J/g, corrosion resistance and low degree of supercooling. The major problem associated with stearic acid is their low thermal conductivity. For better economic benefits and time saving the thermal conductivity of nanoparticle dispersed stearic acid PCMs are numerically calculated and are represented in Figure 4. To begin within Figure 4a shows the numerically determined thermal conductivity of stearic acid PCM composite with silver nanoparticle is depicted. It can be observed that the thermal conductivity of stearic acid

has increased from 0.29 W/(m·K) to 0.6777 W/(m·K) contributing to 133.69% increment with parallel model for 1% silver nanoparticle. To add on Figure 4b displays the thermal conductance variation of stearic acid on dispersion of copper nanoparticle. It is noted that copper nanoparticle with 1% weight fraction onto stearic acid matrix contribute to thermal conductivity of 0.7110 W/(m·K), 0.5007 W/(m·K), 0.2903 W/(m·K), 0.5709 W/(m·K) and 0.5849 W/(m·K)

contributing to 145.17%, 72.66%, 0.103%, 96.86% and 101.69% with parallel, parallel-series effective, series, maxwell eucken and hamilton thermal conductivity models. As discussed in aforementioned section, thermal conductivity of aluminium nanoparticle enhanced composite PCMs exhibit higher thermal conductivity up to 1.1686 W/(m·K) thereby contributing to 302.96% increment. Low density of aluminium nanoparticle compared to Ag

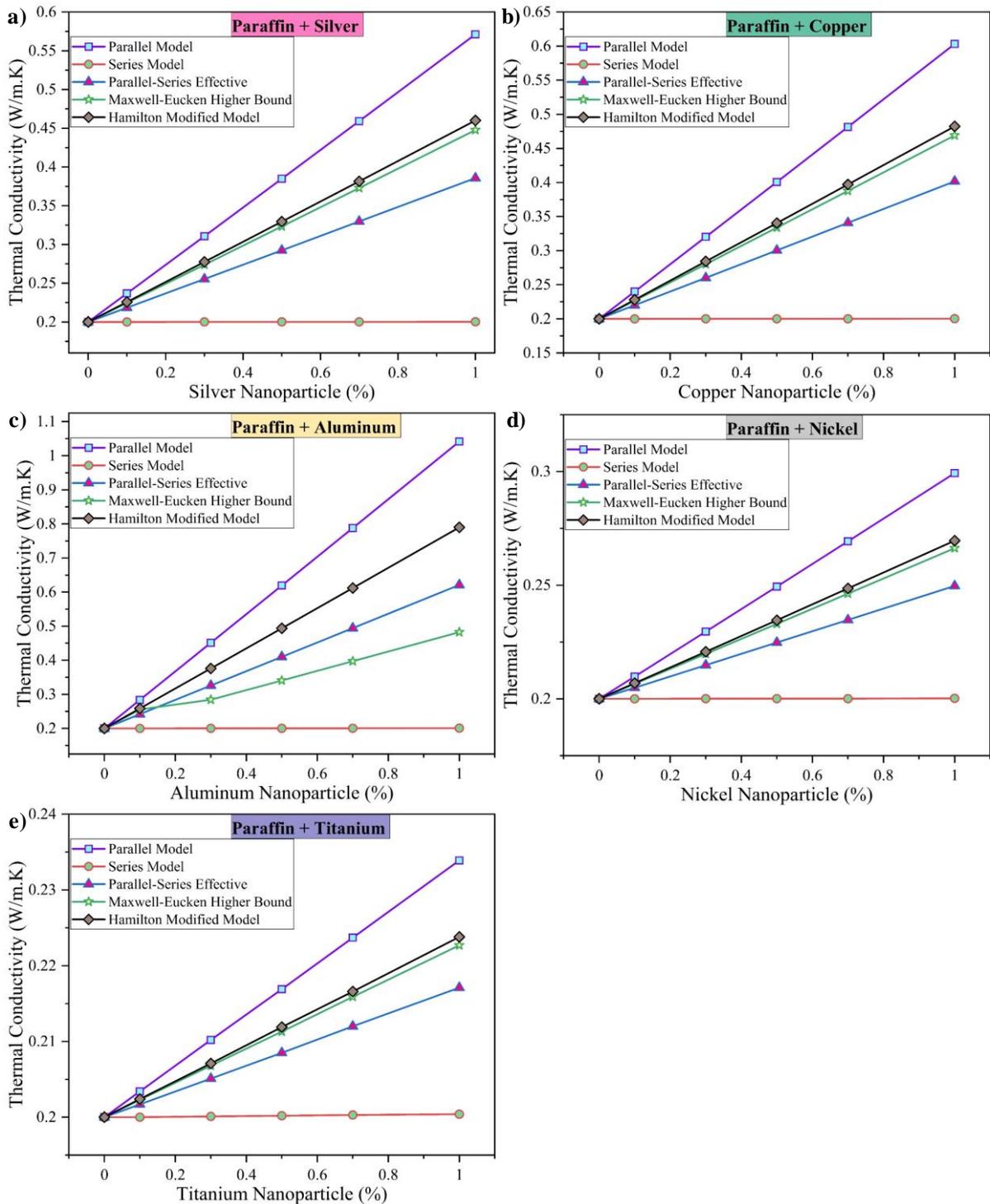


Figure 3. Thermal conductivity of organic PCM Paraffin at different weight concentration of a) Silver, b) Copper, c) Aluminum, d) Nickel and e) Titanium nanoparticle with respect to numerical models.

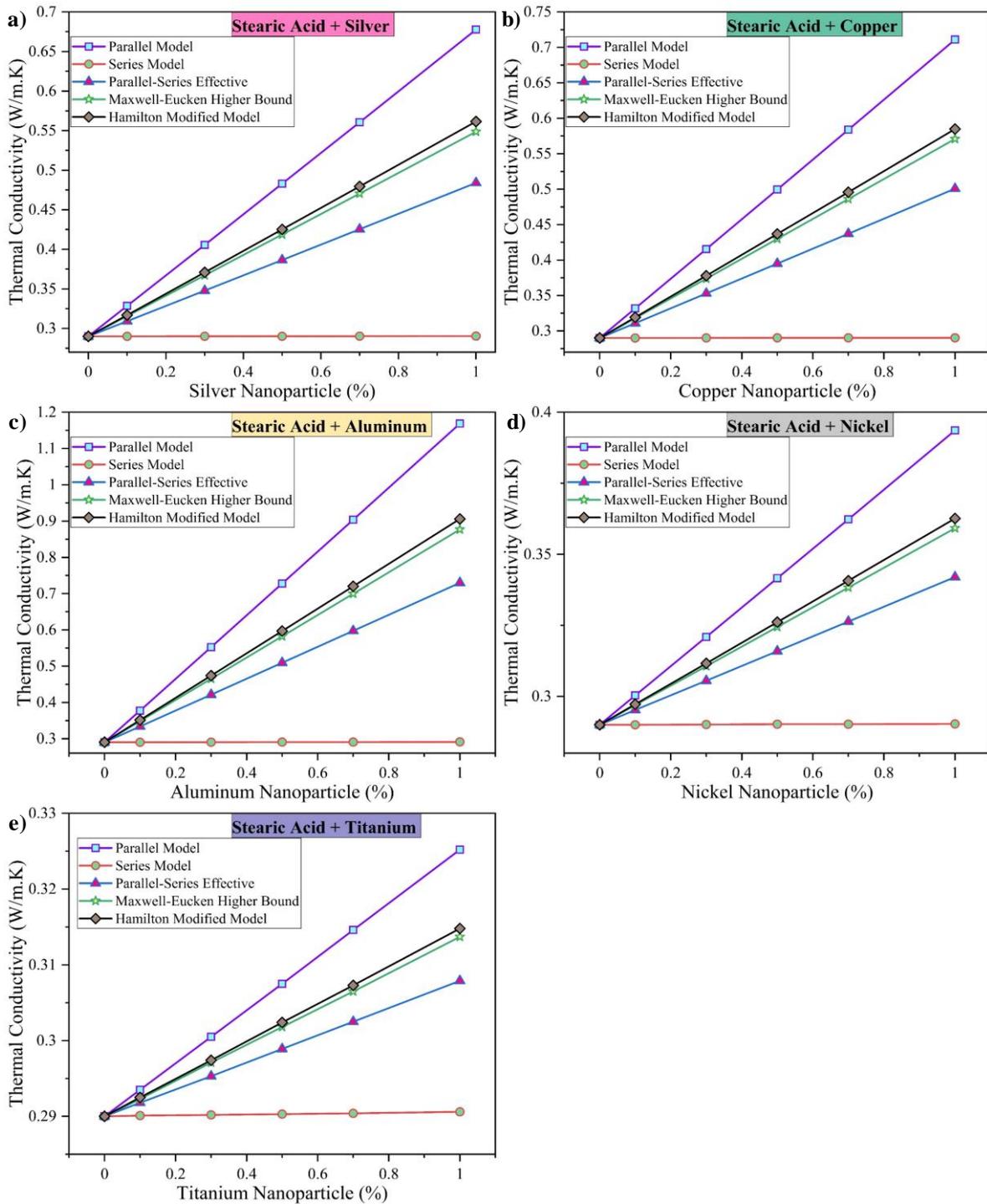


Figure 4. Thermal conductivity of organic PCM Stearic Acid at different weight concentration of a) Silver, b) Copper, c) Aluminum, d) Nickel and e) Titanium nanoparticle with respect to numerical models.

and Cu nanoparticle are very vital for higher thermal conductivity of Al dispersed composite PCM. Likewise Figure 4d shows the thermal conductivity of stearic acid with nickel nanoparticle, where the maximum improvement (35.72%) was 0.3936 W/(m.K) from 0.29 W/(m.K) with 1% nickel for parallel model. Similarly Figure 4e shows the titanium nanoparticle dispersion with stearic acid was observed to be only 12.13%.

In addition to the thermal properties of nanoparticle, which predominantly influence the heat transfer rate, it is vital to discuss the variation in thermal conductivity of the composite PCMs with respect to each numerical models. Figure 2 provides the nanoparticle arrangement pattern which ensures the better conductive path in parallel model, and the absence of developed conducting paths in series model tends to cause settling of nanoparticles and doesn't contribute

significantly towards thermal conductivity increment. However with parallel-series effective model, the calculated values lies between the thermal conductivity of composite PCM (Stearic Acid + Metal Nanoparticle) obtained using series and parallel models. In addition the special feature of Maxwell Eucken Higher bound model is that, it considers all nanoparticle to be of special shape with proper dispersion. The last one to discuss is the Hamilton model, which considers sphericity of the nanoparticle, as metals nanoparticles does not exactly exhibit a proper spherical structure, we assumed the sphericity 0.9 and the results depicts a reliable thermal conductivity incremental value.

Calcium Chloride Hexahydrate with Carbon and Metal Nanoparticles

Among the inorganic salt hydrate PCM, calcium chloride hexahydrate is very much attractive due to its economic viability, high heat storage potential and non-flammable nature. Nevertheless they do suffer due to degree of supercooling and corrosive nature. Calcium chloride hexahydrate offers heat storage at a temperature of 25-28 °C and are highly preferred for building cooling application.

Figure 5 depicts the thermal conductivity values obtained used thermal conductivity model with calcium chloride hexahydrate as PCM. It can be observed from Figure 5a that the thermal conductivity value of calcium chloride hexahydrate with silver nanoparticle of 1% shows a maximum increment of 137.45% from 0.54 W/(m·K) to 1.2822 W/(m·K) with parallel model. Whereas with parallel-series effective model, series model, Maxwell Eucken model and Hamilton modified model, the thermal conductance of composite PCM (Calcium chloride hexahydrate + 1% silver) was 0.9116 W/(m·K), 0.5409 W/(m·K), 1.0354 W/(m·K) and 1.0601 W/(m·K) respectively. Figure 5b shows the thermal conductivity value of calcium chloride hexahydrate with copper nanoparticle with weight fraction of ranging from 0.1% to 1.0%. With increase in nanoparticle weight fraction the thermal conductivity value increase and it can be inferred that a maximum increment of 149.22% from 0.54 W/(m·K) to 1.3458 W/(m·K) with parallel model. Whereas with parallel-series effective model, series model, Maxwell Eucken model and Hamilton modified model, the thermal conductivity increment of composite PCM (Paraffin + 1% Cu) was 74.70%, 0.203%, 99.62% and 104.58% respectively. In Figure 5c we depict the thermal conductivity of calcium chloride hexahydrate with aluminium nanoparticle for the numerical models considered. It can be deduced that composite PCM (calcium chloride hexahydrate with 1% Al) to improve the thermal conductivity from 0.54 W/(m·K) for pure

inorganic salt hydrate PCM calcium chloride hexahydrate to 2.2172 W/(m·K), 1.3804 W/(m·K), 0.5436 W/(m·K), 1.6618 W/(m·K) and 1.7175 W/(m·K) with parallel model, parallel-series effective model, series model, Maxwell Eucken model and Hamilton modified model respectively which accounts for a increment of 310.59%, 155.63%, 0.67%, 207.75% and 218.05%. Figure 3d shows the thermal conductivity of calcium chloride hexahydrate with nickel nanoparticle, where the maximum improvement (36.64%) was 0.7379 W/(m·K) from 0.54 W/(m·K) with 1% nickel with parallel model. With Maxwell Eucken and Hamilton model it was observed to increase by 24.51% (0.6724 W/(m·K)) and 25.72% (0.6789 W/(m·K)). Similarly Figure 3e shows the titanium nanoparticle dispersion with calcium chloride hexahydrate PCM, where the maximum thermal conductivity increment was observed to be only 12.28% at a concentration of 1% nanoparticle based on parallel model.

On close thought it is noticed that the thermal conductivity value obtained are very higher for parallel model. Though out primary task is to advance the thermal conductivity of the composite PCM, the increment must be within a permissible limit. Similar to charging rate of PCM, the discharging rate also depends on the thermal conductivity value. Higher the thermal conductivity higher is the charging as well as discharging of the stored thermal energy occurs. As well it can be observed that for all the cases, there is an increment in thermal conductivity values during numerical calculation, whereas this is controversial when we look into the experimental results.

Sodium Sulphate Decahydrate with Carbon and Metal Nanoparticles

For thermal regulation of ambient conditions at 32-35 °C, inorganic salt hydrate PCM sodium sulphate decahydrate are actively preferred. This PCM have considerably higher latent heat value compared to calcium chloride hexahydrate and are non-flammable in nature. Figure 6 displays the thermal conductivity of composite metal nanoparticle dispersed sodium sulphate decahydrate PCM. It can be observed that the thermal conductivity trends are similar to above observed results due to the same nanoparticle arrangement patterns. With silver nanoparticle a maximum increment of 116.23% is obtained, with copper nanoparticle the maximum thermal conductivity obtained is 235.07%, with aluminium it is 262.89%, with nickel it is 31%, and with titanium the thermal conductivity increment is 10.41%. All the aforementioned increment are observed in parallel model due to closed packed nanoparticles.

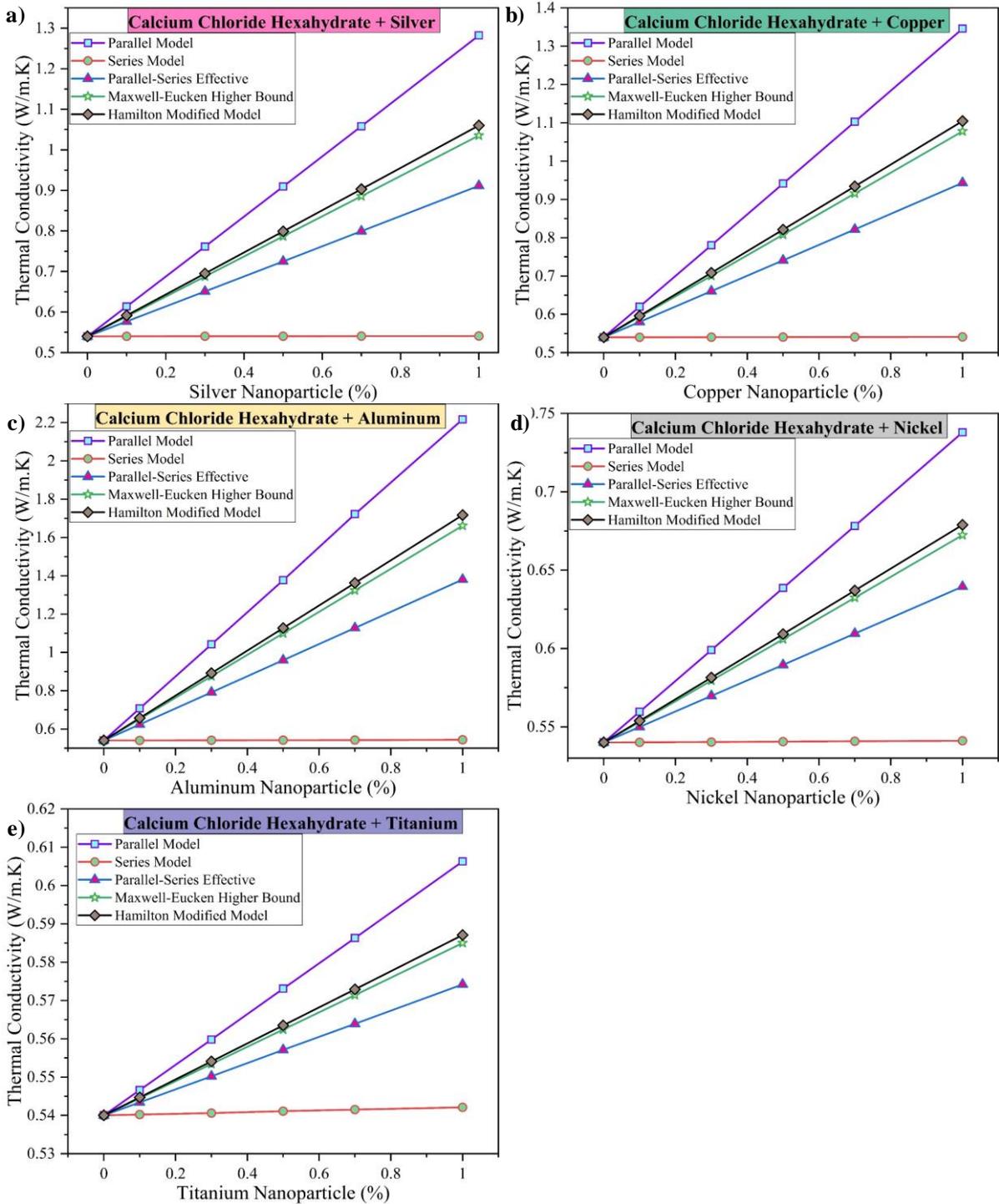


Figure 5. Thermal conductivity of inorganic salt hydrate PCM Calcium Chloride Hexahydrate at different weight concentration of a) Silver, b) Copper, c) Aluminum, d) Nickel and e) Titanium nanoparticle with respect to numerical models.

Magnesium Chloride Hexahydrate with Carbon and Metal Nanoparticles

Magnesium chloride hexahydrate with melting temperature of 50-52 °C are preferred for thermal management of PV panels. PV panels are integrated with a thermal system as PV/T system, which tends to make use of the excess heat generate and also

contribute in maintaining the optimal temperature of the system for better efficiency

To understand better on the thermal conductivity incremental pattern with different metal nanoparticle, considering their thermo-physical properties a numerical evaluation is carried out as they are time saving and economical beneficial Figure 7 shows the thermal

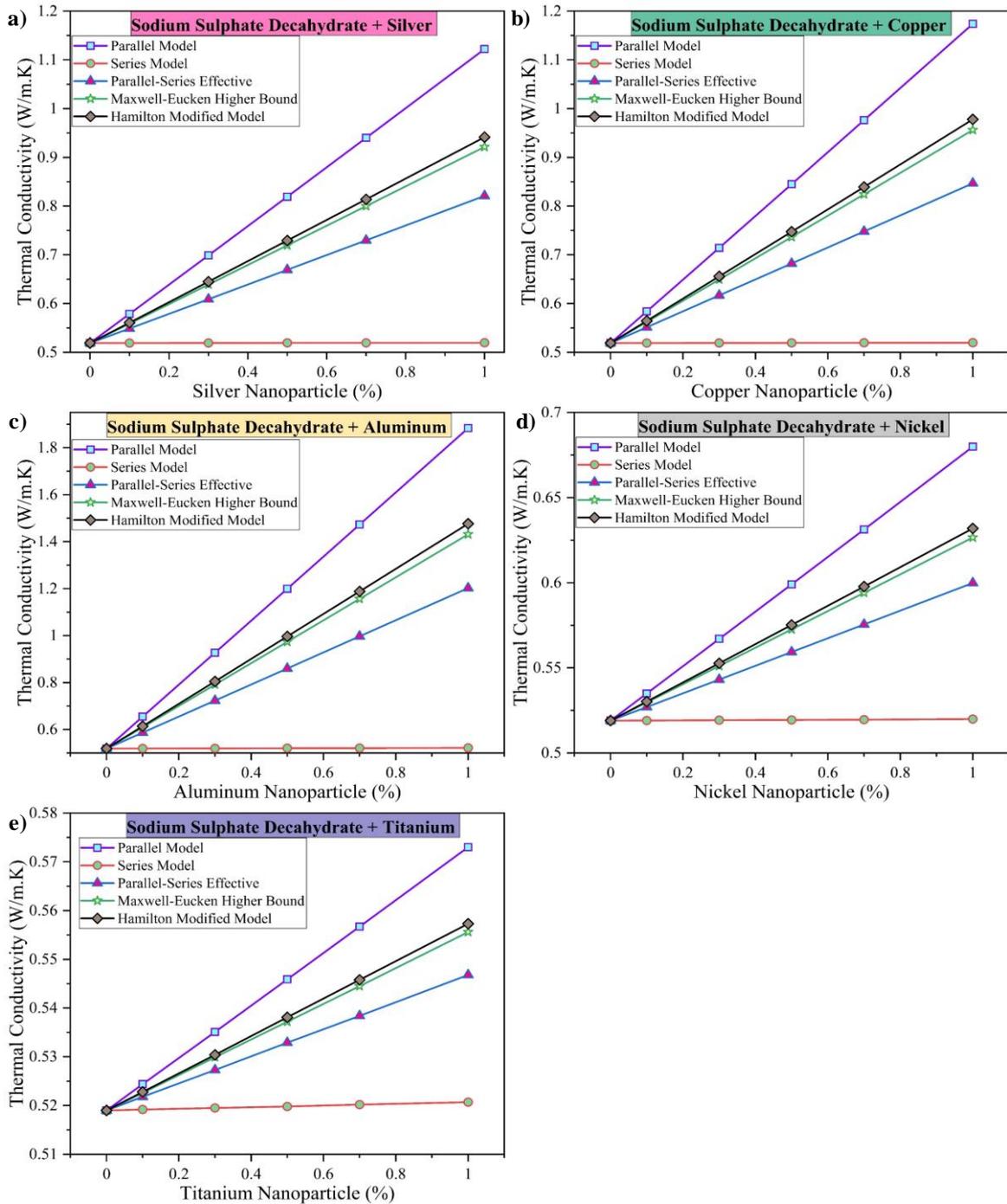


Figure 6. Thermal conductivity of inorganic salt hydrate PCM Sodium Sulphate Decahydrate at different weight concentration of a) Silver, b) Copper, c) Aluminum, d) Nickel and e) Titanium nanoparticle with respect to numerical models.

conductivity incremental trend obtained for various metal nanoparticle like Ag, Cu, Al, Ni and Ti based on numerical model at weight fraction of 0.1%, 0.3%, 0.5%, 0.7% and 1.0%. In Figure 7a we depict the numerically determined thermal conductivity of magnesium chloride hexahydrate inorganic PCM composite with silver nanoparticle. It can be observed that the thermal conductivity of stearic acid has increased from 0.704 W/(m.K) to 1.3505 W/(m.K) contributing to 91.84% increment with

parallel model for 1% silver nanoparticle. To add on Figure 7b displays the thermal conductivity of magnesium chloride hexahydrate inorganic PCM with copper nano-particle, where the increment is 99.70%. As discussed in afore-mentioned section, thermal conductivity of aluminium nanoparticle dispersed composite PCMs exhibit higher thermal conductivity up to 2.1655 W/(m.K) as in Figure 7c and contributes to 207.59% increment with parallel model. Low density of Al nanoparticle compared to Ag and Cu nano-

particle are crucial for uniform dispersion and floating of nanoparticle with the PCM matrix, whereas with higher density the nanoparticle tends to settle down and doesn't provide a well-developed thermal conductive networks. Similarly Figure 7d shows the thermal conductivity of magnesium chloride hexahydrate

inorganic PCM with nickel nanoparticle, where the maximum improvement (24.46%) was 0.8762 W/(m·K) from 0.704 W/(m·K) with 1% nickel for parallel model. Similarly Figure 7e shows the titanium nanoparticle dispersion with magnesium chloride hexahydrate was observed to be only 08.12%.

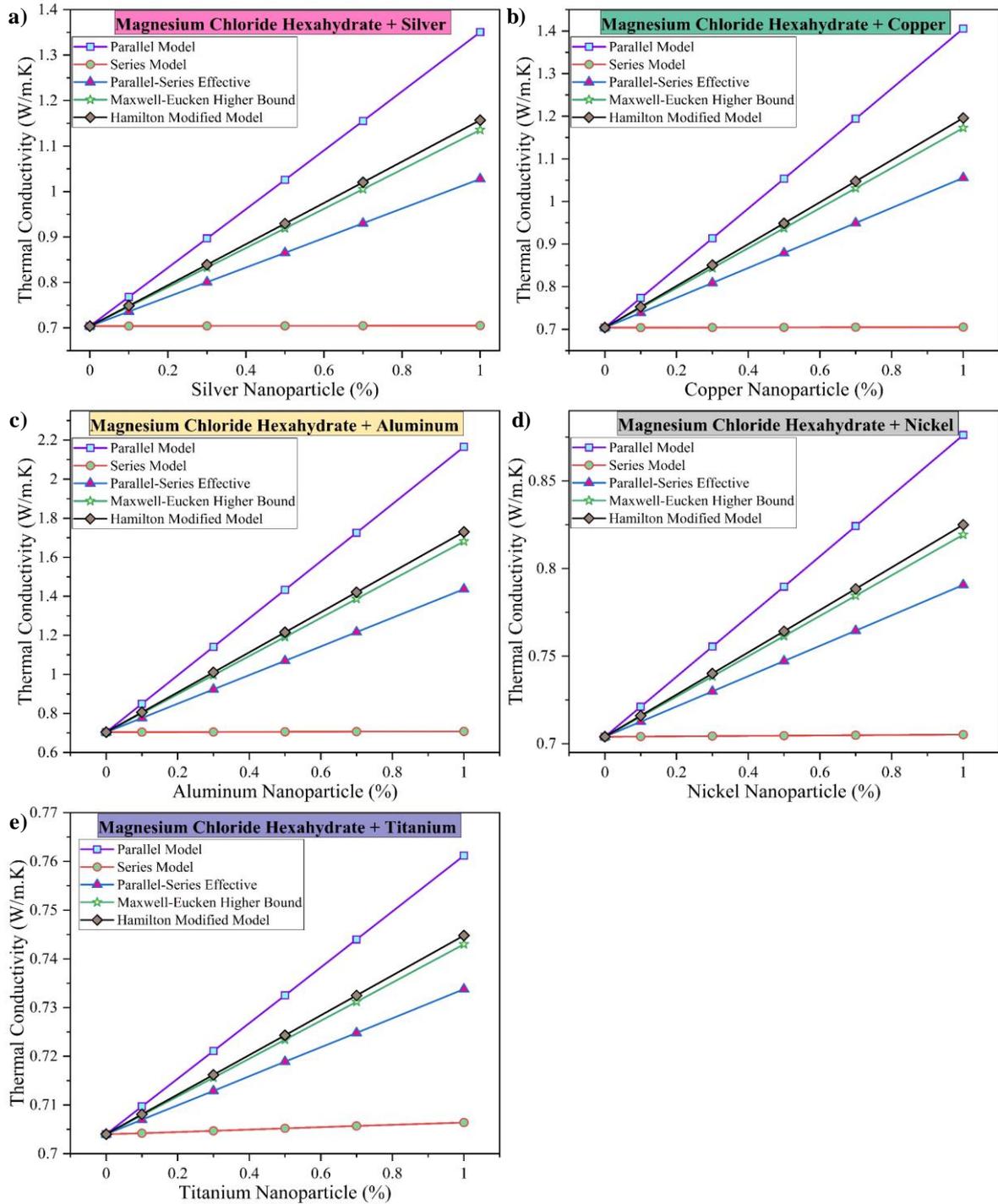


Figure 7. Thermal conductivity of inorganic salt hydrate PCM Magnesium Chloride Hexahydrate at different weight concentration of a) Silver, b) Copper, c) Aluminum, d) Nickel and e) Titanium nanoparticle with respect to numerical models.

CONCLUSION

This numerically work provides insights on the nano-material based composite PCM, based on developing thermal conductivity models, with focus on the volume fraction, thermal conductivity of filler nanomaterials and their shape. The numerically determined thermal conductivity are compared with the experimentally evaluated thermal conductivity of silver nanoparticle enhanced organic PCM to ensure the dependability and the most reliable model. From the numerical evaluations it can be inferred that parallel model and parallel-series effective model to be very reliable for metal nanoparticle dispersed composite PCM. The hindrance with the existing thermal conductivity model is that there is no parameter taking into consideration the agglomeration tendency of nanoparticle. Existing model reports surge in thermal conductance of the composite PCM with rise in volume fraction of nanoparticle, which is not similar to the experimental evaluation. Likewise no information on the critical size to achieve better stability and low agglomerate is not reported. We suggest the further research works on development of thermal conductivity models should have a significant focus on the aforementioned parameters, which will enhance the research progress of nanoparticle distributed PCM.

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