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THERMAL CONDUCTIVITY ENHANCEMENT BY USING NANO-MATERIAL IN PHASE CHANGE MATERIAL FOR LATENT HEAT THERMAL ENERGY STORAGE SYSTEMS

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Abstract: Paraffin wax used as a latent heat energy storage substance has a little heat transfer rates while melting/freezing processes due to its low thermal conductivity. In this paper, enhancing the thermal conductivity of paraffin wax by using two high conductivity materials was studied. Alumina (Al_2O_3) and TiO_2 nanoparticles added in a mass fraction of 1, 2, 3, 4 and 5% in Iraqi paraffin wax tested in the recent study. Iraqi commercially available paraffin wax used as a phase change material (PCM). The results indicate that the paraffin wax thermal conductivity increased with the risen in the nanoparticles mass fraction. The charging and discharging rates of thermal energy enhanced significantly by adding nanoparticles to paraffin wax compared to a net paraffin wax as PCM. The increase of the heat release rate of the nanoparticles enhanced phase change materials reveals its high potential for diverse thermal energy storage applications.

Keywords: Latent heat, thermal storage, Phase change material, Paraffin wax, Heat transfer fluid, Charging rate, nano-particles.

1. Introduction

The perennial growth in the greenhouse gas emissions level added to the climbing fuel prices caused driving forces to more utilization of renewable energy sources. Direct solar radiation can be considered the most prospective sources of energy in Middle East and North Africa countries (Kazem, 2012). The main obstacle that prevents the full use of this power is its fluctuation with time and the changes in the stored energy for night use. The enhancement of the energy storage system reduces the mismatch between supply and demand. Also, it improves the energy system performance and reliability and plays a significant role in conserving the energy (Sharma et al., 2009).

Phase change materials (PCMs) are used widely nowadays as storing thermal energy in solar energy applications. Phase change materials (PCM) are ‘‘Latent’’ heat storage materials where the thermal energy transfer occurs at the change of state, or ‘‘Phase” (when a material changes from solid to liquid, or liquid to solid). This process enables these materials to store about 5–14 times more thermal energy per unit volume compared to sensible storage materials like water, masonry, or rock. Paraffin wax as other organic PCMs is characterized by their low thermal conductivity. This property limited the rate of absorbing and releasing heat. Researchers used various high thermally conductive fillers to improve the effective thermal conductivity of phase change materials. In 1997, Velraj et al. used metallic fins, (Fukai et al., 2000) exploited ceramic powder fillers and graphitic carbon fibers, (Elgafy, 2005) applied carbon nano-fibers, (Pincemin et al., 2008) employed graphite particles and (Kim, 2009) used exfoliated graphite.

Nanoparticles present great physical and chemical properties differences compared to their bulk form (Abdel-Hameed, 2012). Various sorts of nanoparticles become easily produced due to the rapid advance in nanotechnology (Amna et al., 2012), mechanical and electronic engineering, and industrial processes (Cannio, 2012, Zhang et al., 2012 and Johnston et al., 2008). The high conductivity of the metal and/or metal oxide nanoparticles can be used to improve the heat transfer of generally low-conductivity

materials like PCM (Fan et al., 2012). The smaller the nano-particles size is, the higher thermal conductivity can be achieved. Improving thermal conductivity of PCMs causes an enhancement in its thermal properties (Wang et al., 2011 & Guo et al., 2010).

Wang successfully used dispersed nanoparticles into a paraffin wax matrix without any surfactant. The phase change temperature varies with adding TiO_2 nanoparticles into the paraffin wax. The thermal conductivity of the composites crucially augmented, and it thrived with increasing TiO_2 mass fraction at the tested temperatures (Wang et al., 2013). Fan investigated experimentally the effects of adding various carbon nano-fillers on the thermal conductivity and energy storage properties of paraffin-based nano-composite phase change materials (PCMs). The presence of the nano-fillers slightly decreased the phase change enthalpies and has negligible influence on the phase transition temperatures. The thermal conductivity of the nano-composite PCMs found to intensify with raising the stuffing. However, the relative enhancement in thermal conductivity depends on the size and shape of the nano-fillers (Fan et al., 2013).

(Shaikh et al., 2008) studied the effect of single walled and multi walled carbon nano tubes and on a paraffin wax with low melting point. The results showed that inclusion of nano-particles enhanced latent heat of mixtures. This enhancement referred to the intermolecular attraction between the molecules of nano-particles and wax. (Wu et al., 2010) developed a new sort of nano-fluid phase-change material by suspending a small amount of Cu, Al, and C/Cu nano-particles in melting paraffin to enhance the heat transfer rate of paraffin. The study concluded that Cu nano-particles have the best performance for heat transfer. (Ho, 2009) added Al_2O_3 nano-particles to paraffin (n-octadecane) emulsion using non-ionic surfactant and investigated experimentally its effect on thermo-physical properties. The results concluded that the relative increases of nearly 20% and more than 28% in the dynamic viscosity achieved for the paraffin containing 5 wt. % and 10 wt. % of alumina particles, respectively. (Yu et al., 2013) studied increasing thermal conductivity of liquid paraffin-based suspensions in the presence of carbon nano-additives of various sizes and shapes. The thermal conductivity of the suspended wax increased with enhances the loading of the carbon additives, and the extent of the relative increase depends strongly on their size and shape. (Molaba et al., 2014) studied adding silver powder as conductive filler paraffin wax for the improvement of thermal and electrical conductivities. The study showed that increasing the mixing temperature was found to decrease both the thermal and electrical conductivies of the nano-composites.

In the recent study, an experimental investigation is performed to investigate the performance enhancement due to the addition of variable nanoparticles in paraffin wax at various weight concentrations. The primary aim of the study is to evaluate the best rate of nanoparticles between several ones that can be added to Iraqi paraffin wax to enhance its thermal conductivity.

2. **Experimental Setup**

Iraqi paraffin wax with a nominal melting point around 45˚C was selected as the PCM in all experiments. The thermo-physical properties for the used wax are listed in Table 1. Two types of nano-fillers were used (Al_2O3 & TiO_2). These two nano-fillers used due to their low costs and availability in local markets. The suppliers and specifications of the carbon nano-fillers are listed in Table 2. The raw materials selected due to its availability and low cost; and used as received without further purification. The preparation of mixtures has been characterized by five phases:

1. Pre melting of pure PCMs (as they arrived by delivery), performed with the aim of homogenizing the pure material. The liquid paraffin has been poured into Vials to facilitate the handling in the following phases. The material has been cooled down at room temperature; the paraffin wax was pre-melted and degassed in a vacuum oven at 105ºC for 3 hours.

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Table 1: Thermo-physical properties for the paraffin wax:

Material properties		
Melting temperature	(°C)	44
Latent heat of fusion	(kJ/kg)	190
Solid density	(kg/m3)	930
Liquid density	(kg/m3)	830
Thermal conductivity	(W/m °C)	0.21
Solid specific heat	(kJ/kg °C)	2.1
Liquid specific heat	(kJ/kg °C)	2.1

2. Weighing of nano-filler and PCMs (solid) to prepare the correct samples. For each type of the nano-fillers, samples with elevated mass fractions from 1 wt. % up to 5 wt. % were prepared at an increment of 1 wt.%.
3. The nano-fillers were also pre-dried in the oven at the same condition as PCM.
4. The nano-composite PCM samples were prepared following a melt-mixing scheme. In the first dispersion step, the nano-fillers were added in the molten paraffin wax with desirable loadings, and the suspensions were then prepared by strong shear mixing with a magnetic stirrer for 15 min, followed by an intensive ultra-sonic shaking for 50 min. During this step, the temperature of the samples was maintained above the melting point of the paraffin wax at 65°C.
5. In the second solidification step, the suspensions were poured into a circular mold of the dimensions of 2 cm dia., and were then allowed to freely crystalline at room temperature (25°C) to form solid composite samples. Complete solidification of the samples took about 3 h.

Instruments

The adopted instruments were:

1. The mold used to form the required samples manufactured from copper foil to enhance heat dissipation to air when liquid wax was poured in it.
2. Supersonic shaker type (EXXX_1000) was used to mix nano-fillers with wax uniformly.
   Hot Disk Thermal Constants Analyzer was used to measure the thermal conductivity of the samples. The device use transiently heated plane sensor, referred to as the Hot Disk Thermal Constants Analyzer. The Hot Disk sensor consists of an electrically conducting pattern in the shape of a double spiral, which has been etched out of a thin metal (Nickel) foil. This spiral is sandwiched between two thin sheets of an insulating material (Kapton, Mica, etc.). When performing a thermal transport measurement, the plane Hot Disk sensor is fitted between two pieces of the sample – each one with a plane surface facing the sensor. By passing an electrical current, high enough to increase the temperature of the sensor between a fraction of a degree up to several degrees, and at the same time recording the resistance (temperature) increase as a function of time, the Hot Disk sensor is used both as a heat source and as a dynamic temperature sensor. The solution of the thermal conductivity equation is based on the assumption that the Hot Disk sensor is located in an infinite medium, which means that the transient recording must be interrupted as soon as any influence from the outside boundaries of the two sample pieces is recorded by the sensor. The Hot Disk Thermal Constants Analyzer has been used for studying a large number of different materials such as Metals, Alloys, Minerals, Ceramics, Glasses, Powders, Plastics, Building Materials, Biomaterials In Vivo or In Vitro, Liquids etc.

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Commercially available Hot Disk elements make measurements possible from cryogenic temperatures up to 1000 K. The highest temperatures reached so far with specially designed sensors are between 1700 K and 1800 K. The tests were performed according to ASTM E1530. The samples were prepared by cast molding, the average thickness of the sample is 5 mm, and it can be directly used for through-plane thermal conductivity measurement.

Table 2: the suppliers and the used nano-fillers specifications:

Item	Al_2O_3 specifications	TiO_2 specifications
Manufacturer	Yurui (Shanghai) Chemical Co., Ltd	Hongwu Nanometer
Appearance	White powder	White powder
Assay	99.99%	99.78%
PH value	7.5	7.3
Crystal and Type	a	a
Grain size nm	30-60nm	20-50 nm
bulk density	0.43	0.392
Loss on drying ≤	0.21	0.23
Sulphated assay ≤	0.42	0.201
Fe ≤ ppm	≤0.005%	≤0.009%
Si ≤ ppm	≤0.003%	≤0.003%
Mg ≤ ppm	≤0.001%	≤0.007%

It must be noted that all the data presented in this paper are the average values, where every test was repeated three times. The standard deviations were found to be less than 2% for the repeated measurements.

Test procedure

The tests started by preparing the wax samples. The second step was to prepare samples of nano-fillers and wax suspensions. After all the samples were prepared the thermal conductivity tests were started using Hot Disk Thermal Constants Analyzer. Both the melting and cooling behaviors (the charging and discharging periods) were tested by heating the samples in a container to 65°C and then leave it to cool by natural convection in air which its temperature was maintained at 25°C. The wax and wax-nano composites samples temperature was measured and recorded during each period. The results were analyzed and discussed.

3. Results

In view of the fact that the energy storage or release rate depends highly on the thermal conductivity of materials, then thermal conductivity of PCMs is an important property that must be defined. Thermal energy storage systems using PCMs exposed to environments with temperature variation. PCMs have both solid and liquid states in the range of working temperatures, and thermal conductivity varies with each state. Measuring the thermal conductivity of the composites at this working temperatures range shows the variations in thermal conductivity with temperature and phase state.

Fig. 1 shows the effect of temperature on thermal conductivity of paraffin wax and its nano-Al_2O_3 composites. Paraffin wax thermal conductivity reduced with increasing temperature. It reached its

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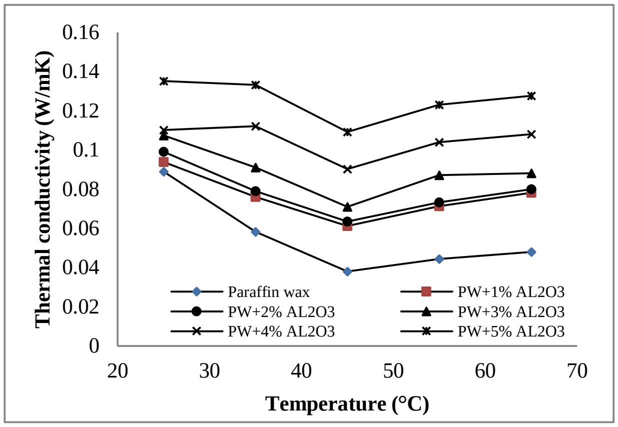
minimum value at melting point. After this point it relatively increased. Adding nano-Al_2O_3 affected the composite thermal conductivity even at low percentage as 1%. The figure curves are almost parallel to one another. These results indicate that there are independent influences referred to temperature and the nano-particles mass fraction.
The liquid part of PCM indicates the progress of the phase change process, the addition of nano-Al_2O_3 considerably enhances the heat transfer. The solid–liquid phase change (melting) period is responsible for the significant reduction in thermal conductivity at 45°C.

Fig. 2 represents the temperature effect on thermal conductivity when nano TiO_2 was added to PW in several mass fractions. The same effect of enhancing thermal conductivity can be seen in the figure, except the relative enhancement is lower than that with nano-Al_2O_3. The thermal conductivity of Al_2O_3 is higher and that's why its composite has higher thermal conductivity with each mass fraction addition.

(Luo, 2010) explained that heat transfer takes place by photons vibration at varying frequencies. These transporting photons from one platelet to another determine the rate of heat transferred. Since there is a difference in acoustic properties of PCM and the added nano-particle, then the photon spectrum will be different in these two materials. In addition, due to van der Waals interaction between paraffin and nano-particle, there are several frequency photon vibration modes which are available to carry heat energy. At melting point, the combined effect of photon mismatch and weak coupling with the matrix, the occurrence of high photon scattering results in high thermal interface resistance which reduces the capability of nano-composites in transferring heat.

Thermal conductivity of PW was enhanced with adding nano particles to it but this enhancement was different for each type, as fig 3 illustrates. Depending on (Gharagozloo et al., 2008) who introduced the relative thermal conductivity enhancement by the equation: Relative enhancement = $(k - k_0)/k_0$, to describe quantitatively the potential of an additive in thermal conductivity increase. Nano-Al_2O_3- PW overcome the TiO_2 nano particle in the improvement it achieved. Nano-TiO_2 addition to PW enhances paraffin wax thermal conductivity in a converging manner, but still its addition results in relatively high enhancement.

Thermal conductivity enhancement appears clear at charging period, as figures 4 & 5 represent. Increasing nano-Al_2O_3 enhanced thermal conductivity as well as reduced charging time from about 13 min to 5 min only with 5% mass fraction. Charging period is very important in some thermal storage applications. Thermal conductivity enhancement caused by adding nano particles results in lower charging time. Adding 5% of TiO_2 reduced charging time from 13 to 7 min.



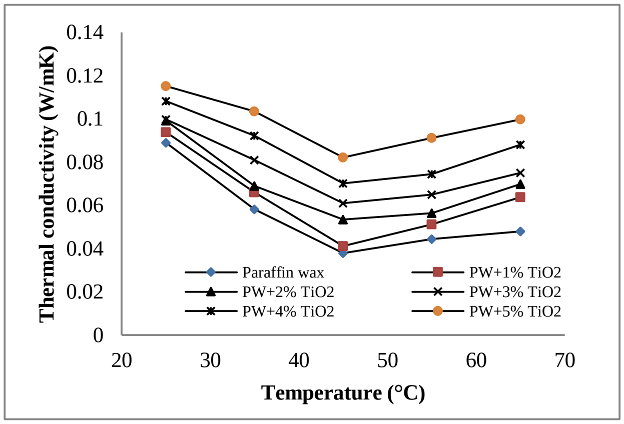


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Figure (1): Thermal conductivity vs. temperature for variable composites of PW and nano AL_2O_3

Figure (2): Thermal conductivity vs. temperature for variable composites of PW and nano TiO_2

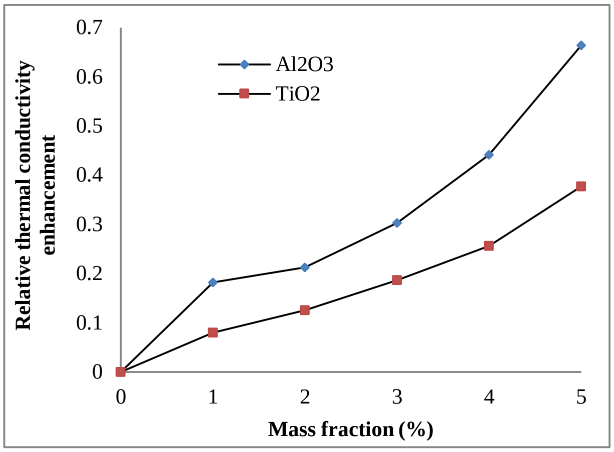

Figure (3): Relative enhancement in thermal conductivity vs. Mass fraction of the tested nano-composites

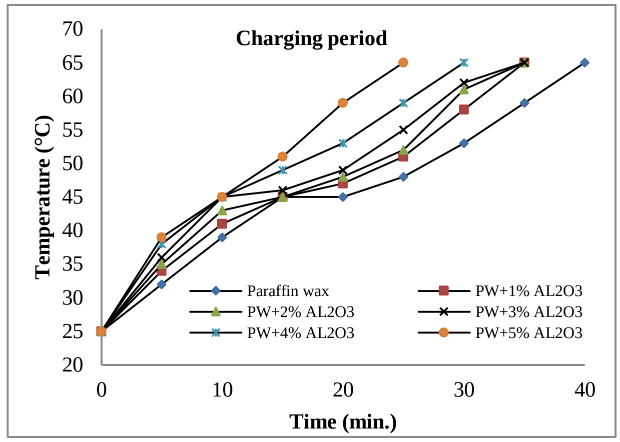

Figure (4): PW with nano- Al_2O_3 composites thermal behavior during charging period

Figures 6 and 7 show the effect of adding variable nano-particles to paraffin wax on discharging period when natural convection to air is used for cooling the samples. The effect of adding nano particles in this process is limited but still there is relative enhancement. For Al_2O_3 the discharging period was reduced from 22 min in pure paraffin wax case to 11 min with 5% nano Al2O3 addition. In TiO_2 case the reduction in discharging period was from 22 to 13 min with 5% mass fraction addition (fig. 7).

Comparison with other works

Comparison of the data among available new literature having studied adding nano-particles to PCM to posse better thermal conductivity is of great interest. It was unable to compare directly among various literatures due to different paraffin wax and nano-particle sizes and thicknesses used in these papers. Figures 8 & 9 show a comparison between the present results and the data reported in the available literature.

(Arusu, 2012) conducted a numerical analysis to study the enhancement of paraffin wax with nano-alumina (Al2O3) particles in comparison with simple paraffin wax in a concentric double pipe heat exchanger. (Wang et al., 2013 and Shi et al., 2013) added TiO_2 to paraffin wax to enhance its thermal conductivity. Their results give lower relative enhancement compared to recent study.

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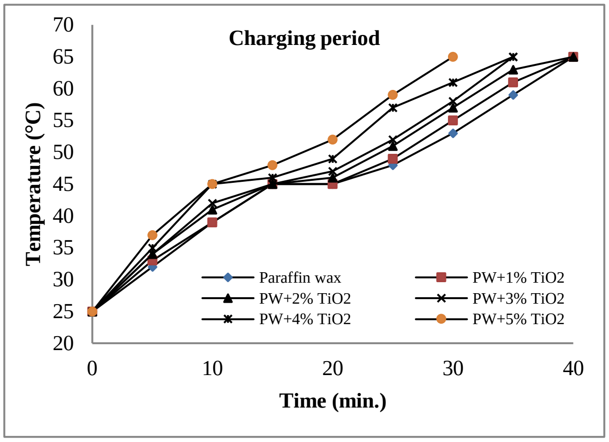

Figure (5): PW with nano- TiO_2 composites thermal behavior during charging period

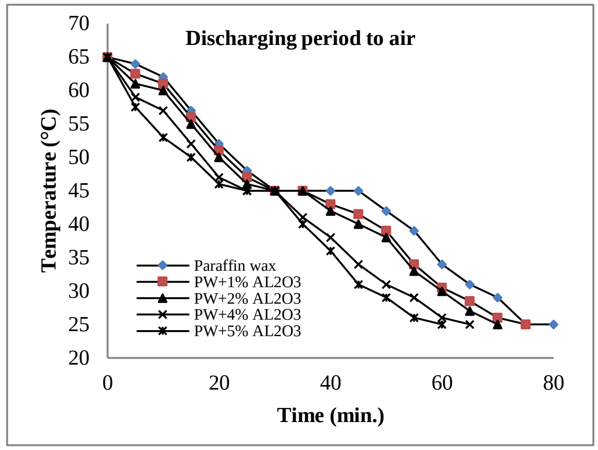

Figure (6) PW with nano- AL_2O_3 composites thermal behavior during discharging period

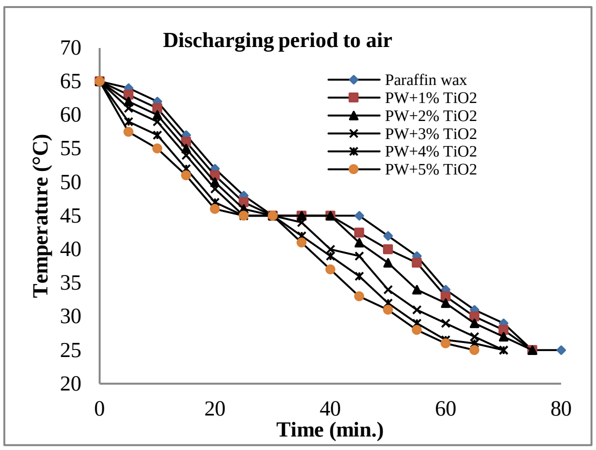

Figure (7): PW with nano- TiO_2 composites thermal behavior during charging period

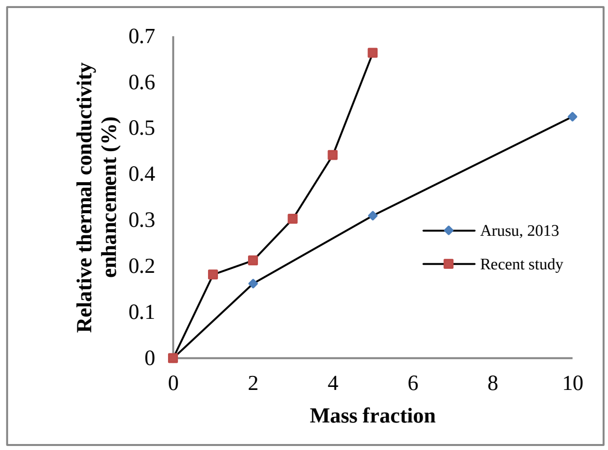

Figure (8) Comparison between studies added AL_2O_3 to paraffin wax

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4. Conclusions

Al_2O_3, TiO_2 and CNTs were successfully mixed with Iraqi paraffin wax to make a composite phase change materials (PCM) of high latent heat and high thermal conductivity. The resultant materials have many different properties than the original one. The distinctive enhancements in thermal conductivity were observed to increase with nano-particle mass fraction increase. The relative enhancement with mass fraction increase was 65, and 40 for 5% mass fraction addition of Al_2O_3 and TiO_2 respectively. Adding nano-particles to PCM reduced charging time at melting point highly but it effect on discharging time in air was limited. In summary, the added nano-particles have shown a promising method for preparing nano-composite PCMs with greatly enhanced thermal conductivity without decreasing energy storage capacity. The comparison with other published works gives some minor differences due to kind of the used PCM and size and shape of the used nano-particles. Future work is needed to reveal the dependence of enhancement on size- and shape of these nano-fillers.

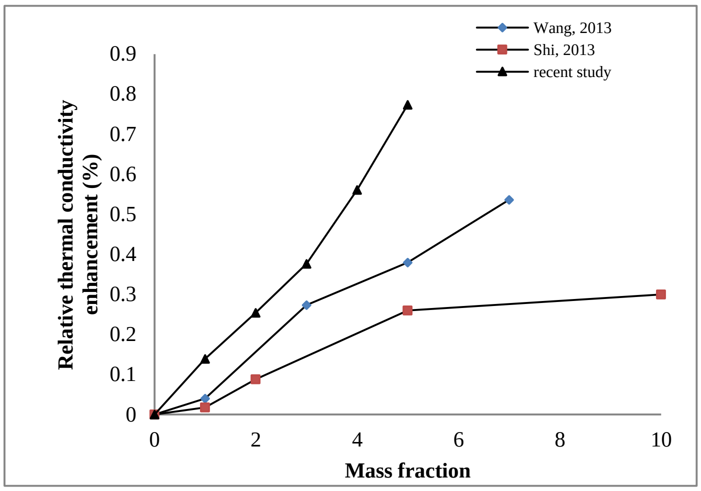

Figure (9): Comparison between studies added TiO2 to PW

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