

THERMOPHYSICAL CHARACTERISTICS OF MODIFIED PARAFFIN WAX WITH NANOMATERIAL

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> > KARABUK June 2021

I certify that in my opinion the thesis submitted by MAYTHAM TAREQ MAHDI MAHDI titled "THERMOPHYSICAL CHARACTERISTICS OF MODIFIED PARAFFIN WAX WITH NANOMATERIAL" is fully adequate in scope and in quality as a thesis for the degree of Master of Science.

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MAYTHAM TAREQ MAHDI MAHDI

ABSTRACT

M. Sc. Thesis

THERMOPHYSICAL CHARACTERISTICS OF MODIFIED PARAFFIN WAX WITH NANOMATERIAL

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Karabük University Institute of Graduate Programs The Department of Metallurgical and Materials Engineering

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In modern applications, energy storage and transmission is considered important, and in particular for photovoltaic thermal (PV/T) applications. phase change materials is considered one of the important developments used in these applications because they possess superior thermophysical properties and thus have a high storage of energy capacity within the shape of latent heat. However, Low thermal conductivity is one of the most important problems facing the widespread use of these materials. In this work, Nano titanium oxide (TiO₂) and Nano Iron (III) oxide (Fe₂O₃) are added to the paraffin wax to evaluate the thermophysical changes occur in the wax. Therefore, the most appropriate materials to be used in (PV/T) applications can be determined. Four samples were prepared for each type of nanoparticle used with percentage mass ratio (0.5, 1, 2, and 3) and one sample was prepared for pure paraffin. The results showed that adding any percentage of Nano Tio₂ and Nano Fe₂O₃ increases its viscosity and density. The density of the wax increases when adding TiO₂, Fe₂O₃ nanoparticles, since adding of 3% Nano- TiO₂, Fe₂O₃ the density of the wax increases by 5.5% and 5.9% respectively. The thermal conductivity is improved when add Nano- TiO₂ to 40%, 75.5%, 87%, and 96.35% for 0.5, 1, 2, 3 mass fractions added, respectively. And improved when Nano- Fe₂O₃ adds to 30 %, 60.5%, 77% and 86.3% for same mass fractions added. In addition, adding (Nano -TiO₂) and (Nano- Fe₂O₃) to paraffin wax reduces its thermal decomposition, which improves thermal stability.

Key Words : Transmission, photovoltaic thermal, Nano Tio₂, mass fraction, density

Science Code : 91505

ÖZET

NANOMATERYAL İLE MODİFİYE PARAFİN VAKSIN TERMOFİZİKSEL ÖZELLİKLERİ

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Modern uygulamalarda, enerji depolama ve iletimi, özellikle fotovoltaik termal (PV/T) uygulamaları için önemli kabul edilmektedir. Faz değiştiren malzemeler, üstün termofiziksel özelliklere sahip oldukları ve dolayısıyla gizli ısı şeklinde yüksek bir enerji depolama kapasitesine sahip oldukları için bu uygulamalarda kullanılan önemli gelişmelerden biri olarak kabul edilmektedir. Ancak düşük ısıl iletkenlik, bu malzemelerin yaygın olarak kullanılmasının karşı karşıya olduğu en önemli sorunlardan biridir. Bu çalışmada, vakşda meydana gelen termofiziksel değişiklikleri değerlendirmek için parafine Nano titanyum oksit (TiO2) ve Nano Demir (III) oksit (Fe2O3) eklenir. Böylece (PV/T) uygulamalarında kullanılacak en uygun malzemelerin belirlenmesi ön görülmektedir. Kullanılan her nanoparçacık türü için yüzde kütle oranı (0,5, 1, 2 ve 3) ile dört numune ve saf parafin için bir numune hazırlanmıştır. Sonuçlar, Nano Tio2 ve Nano Fe2O3'ün herhangi bir yüzdesinin eklenmesinin viskozitesini ve yoğunluğunu arttırdığını göstermiştir. TiO2, Fe2O3 nanoparçacıkları eklenirken vaksın yoğunluğu artmıştır, %3 Nano-TiO2, Fe2O3 eklendiğinden vaksın yoğunluğu sırasıyla %5,5 ve %5,9 artmıştır. Nano-TiO2 eklendiğinde sırasıyla 0,5, 1, 2, 3 kütle fraksiyonları için %40, %75.5, %87 ve

%96.35 eklendiğinde termal iletkenlik artmıştır. Aynı kütle fraksiyonları için Nano-Fe2O3 eklendiğinde %30, %60,5, %77 ve %86,3 eklendiğinde iyileşmiştir. Ek olarak, parafin mumuna (Nano - TiO2) ve (Nano- Fe2O3) eklenmesi, ısıl bozunmasını azaltarak ısıl kararlılığı arttırmıştır.

Anahtar Kelimeler :İletim, fotovoltaik termal, Nano Tio2, kütle oranı, yoğunluk.Bilim Kodu:91505

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SYMBOLS AND ABBREVITIONS INDEX

SYMBOLS

E : Energy
m : mass of matter whose phase changes
l : the latent heat associated with the phase change

ABBREVITIONS

РСМ	: phase change material
PVT	: photovoltaic
Nano PCM1	: 99.5 paraffin wax $+$ 0.5 nano-TiO ₂
Nano PCM2	: 99 paraffin wax+ 1 nano-TiO ₂
Nano PCM3	: 98 paraffin wax + 2 nano-TiO ₂
Nano PCM4	: 97 paraffin wax $+$ 0.5 nano-TiO ₂
Nano PCM5	: 99.5 paraffin wax+ 0.5 Nano - Fe ₂ O ₃
Nano PCM6	: 99 paraffin wax+ 1 Nano - Fe ₂ O ₃
Nano PCM7	: 98 paraffin wax+ 2 Nano - Fe ₂ O ₃
Nano PCM8	: 97 paraffin wax+ 3 Nano - Fe ₂ O ₃
SEM	: Scanning Electron Microscope
FTIR	: Fourier Transform Infrared Spectrometry

PART 1

INTRODUCTION

Sources of non-renewable energy are used widely to meet several requirements by transforming them into different forms of energy. These sources have been shaped by their exposure to different geological processes over long periods of time [1]. Nonetheless, examples of non-renewable energy sources are coal which is a type of sedimentary rock, composed mainly of carbon, hydrocarbon, is the most widely used fossil fuel throughout the world, used in several industries, such as paper production, concrete, and electricity generation, and coal use emits large amounts of carbon dioxide. Another example is natural gas, consisting mainly of methane gas, may form in swamps, landfills, is a commonly used source of less polluting coal, and natural gas must be first processed until it is suitable for use, as other compounds are removed from it, to obtain pure methane [2]. Additionally, uranium is a heavy, fissionable mineral that can be used to form electricity, by taking the benefits of the huge amount of heat that is caused by its division during a series of nuclear fissionable reactions, and it must be processed before the start of the fission process, although uranium does not produce any greenhouse gas during its use. But the potential for failure of nuclear fission can be an impediment to its widespread use [3]. Finally, petroleum is formed deep in the earth as a result of geological processes, known as crude oil. Oil is a toxic liquid composed of many hydrocarbons, and a large portion of these compounds are flammable. Petroleum is used for several purposes, in addition to diesel fuel, natural gas and liquefied petroleum gas (LPG), which are the most used fuels all-over the world. The list includes making plastics, medicines, asphalt, paraffin's and synthetic rubbers. Petroleum contains many hydrocarbons that require appropriate treatment for different uses [2-5]. However, there are several limitations facing the use of non-renewable resources such as pricing, economic and political issues. Despite the widespread use of non-renewable energy in various applications, these sources have caused an increase inglobal warming and climate

change, in addition to polluting the environment. Therefore, there is a global trend to gradually reduce dependence on these sources and replace them with renewable sources [6]. Examples of renewable sources is wind power which is used by electricity generation, by turbines, which can be formed in different places, such as farmland, and although wind is regarded as a clean source such as other sources of renewable energy, it can cause visual pollution and noise, which can disturb the population nearby. Another example Geothermal energy is Large heat within Earth which is a source of this energy, can be used to form electricity, that warm the building in winter, cool it in summer, and a clean source like other renewable energy sources, but it can emit few of the components that contribute to acid rain. In addition, the Hydropower is water potential of electricity generation, which can be utilized by operating of hydroelectric turbines that are built near water systems, for example rivers, and by storing water in dams, which affect the ecosystem, such as the movement of fish or a change in temperature [7].

1.1. SOLAR ENERGY STORAGE

The Solar energy is an crucial source for making the life possible on Earth, because they are they are used for different purposes, such as heating water for domestic purposes, heating air for comfortable purposes in homes at winter, as well as it can be used to generate electricity, either directly using photovoltaic modules, which convert the solar rays falling on them into electricity. Besides, solar radiation can be used in special stations to produce steam that is employed in power generators to generate electricity [8]. One of the most important reasons that must be considered and which gives preference to the use of solar energy as a source of renewable energy is that it is energy available around the world and is free, environmentally friendly and does not cause environmental pollution. What is wrong with solar energy is that it is available when the sun is present, so it is difficult to store it. There are several ways to store solar energy, including electrical and thermal storage [9]. Table (1) shows methods of electrical storage energy. The thermal energy storage usually is stored according to the use. The thermal energy that obtain from the solar cell energy can be stored firstly through thermophysical reaction such as, the changing in temperature or phase change material and secondly through chemical

reactions. Figure 1 shows the classifications of solar energy storage methods mentioned above. Table 1 shows the used method to store electrical energies [10].

	Classification According to Storage ²
electrical energy storage	direct electricity storage in devices such as capacitors or superconducting magnetic devices;
	those storage methods have the advantage of quickly discharging the energy stored
mechanical energy storage	storage of electrical energy in the form of kinetic energy such as flywheel or
	potential energy such as pumped hydroelectric storage (PHS) or compressed air energy storage (CAES)
chemical energy storage	storage in chemical energy form as in batteries, fuel cells, and flow batteries;
	chemical energy storage usually has small losses during storage
	Classification According to Usage ⁵
bulk energy storage	bulk energy storage has discharge power range of $10-1000$ MW, discharge times are $1-8$ h, and
	the stored energy range of 10–8000 MWh; the applications of such storage are in load leveling and spinning reserve
distributed generation	distributed generation storage has discharge power range of 100–2000 kW, discharge time range of 0.5–4 h, and
	the stored energy range is 50–8000 kWh; the application of such storage is in peak shaving and transmission
power quality	power quality storage has discharge time range of $0.1-2$ MW, the discharge time is $1-30$ s, and
	the stored energy range is 0.028–16.67 kWh. The applications are end-use power quality and reliability

Table 1.1. Methods of electrical storage [10].

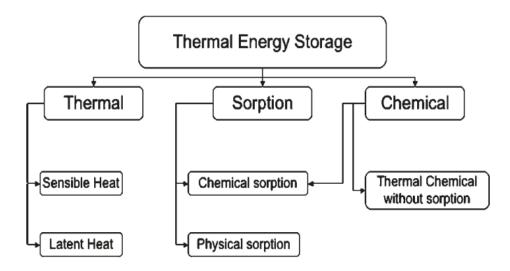


Figure 1.1. Thermal energies storage types [11].

1.1.1. Sorption Storage

It is kind of sorbate and sorbent, in sorbent means the gas or vapour fixed on the sorbent which is the substance of either solid or liquid. The method of sorption of gas on liquid is referred by absorption. However, absorption has two important approaches which are thermo physical reaction and thermochemical reaction [11]. The main aim of using sorption is to energy a storage purpose which is depending on physical chemical reaction. For instance, the sorbate/sorbent couple is A/B. When

applying heat on this system, AB is divided into two terms which are A and B which called phase charge or in other word regeneration:

AB +heat \leftrightarrow sorbate A + sorbent B. the storage A and B must be simultaneously. However, with ignoring of loss, the thermal energy storage of solar is regarded as the A and B chemical potential. The mixture of A and B to produce AB caused an emission of heat which is called discharge phase. Moreover, the sorption has the maximum density storage. However, there are many researches that have investigated the sorption as solar energy storage. But, till now and because of the costing issues, there are no commercial systems to be improved. Furthermore, there are several factors such as environmental, economic and technical aspects make the handful used in sorption reaction. For example, Li Br/H₂O, Na OH/ H₂O , Na OH /H₂O and Na₂S/H₂O . However, other materials have been improved in resent researches [12].

1.1.2. Sensible Heat Storage

The materials temperature, whether solid or non-liquid, is changed by using the solar energy formed at the peak hour. With the difference in the temperature of the material and the original temperature, the energy is stored. For example, solar water, air heaters, graphite and concrete storage are energy storage. The basis of the work of solar air and water heaters is to store the thermal energy in the air and water using solar radiation and because of its low cost and ease of manufacture, this method has become a common use. But one of the disadvantages of this method is the low density of thermal storage [13].

1.1.3. Solar Fuels

The Sun's scattered rays are concentrated by its visual energy and a chemical conversion can be made to produce a fuel that is stackable and portable by the heat generated by its solar concentric energy. Example (solar hydrogen, solar chemical heat pipes, solar metal). Figure 2 illustrates the above methods where concentrated solar energy is used to separate metal oxides as a heat source. The solar energy is

stored in the metal and can be used through the process of combustion. Tests have proven that zinc is suitable for this process [13-14].

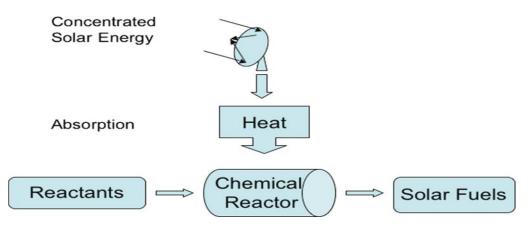


Figure 1.2. Solar fuels [11].

1.1.4. Phase Change Material Storage (PCMS)

In phase change materials (PCMs), the thermal energy storage is created through its phase change by exploiting the underlying material, which gave high energy densities. However, latent heat is the energy related to a change in the substance phase [15]. The phase of the substance changes caused heat absorption or emission. The latent heat material is considered better than the sensible heat because it stores 5 to 14 times more heat value for each unit volume [16]. The stored energy can be found when the phase changes, as in the following equation:

$$\mathbf{E} = \mathbf{m}\mathbf{L} \tag{1.1}$$

m: Represents the matter mass whose phase changes

L: The latent heat related to the phase change. Phase change materials (PCM) are divided into three sections inorganic (hydrates, molten salts, metal), eutectic (organic-organic, organic-inorganic, inorganic-inorganic compounds) and organic (paraffin, greasy acid) [15]. The organic `PCM has latent heat from 10 kJ/kg to 300 kJ/kg. As for the inorganic PCM has latent heat from 20 kJ/kg to 250 kJ/kg. Eutectic PCM consists of two or more components that are blended; it has a latent

temperature from 100-200 kJ/kg. Recently there have been developments in the storage of latent heat in solar and industrial applications. PCMs have become a promising way to store energy and reduce carbon dioxide emissions. A feature of using the latent heat storage is its high storage density, constant temperature, and can be used more than one time without fading reversible, so it is preferable to use it. However, phase change materials must be encapsulated so that liquid phase will not leak and avoid contamination especially when the (PCM) contains water in order to prevent evaporation or absorption of water [16].

The large volume of PCM is packed in a large container by means of microencapsulation technology, but because of PCM low thermal conductivity, the process may fail. Heat transfer cannot be done well when the PCM turns into two various phases with in one container. In small containers for example, cells, the PCM works better and the microcomputer is easily integrated and used in building materials. The problem of low thermal conductivity does not affect significantly on a small scale. More recently, and specifically after 2005, the concentrate has been on integrating the storage of latent heat in the solar energy, where a system is designed that contains a heat exchanger [17]. Figure 3 illustrates this as the saturated PCM is melted in the thermal storage block in order to collect energy from the sun to produce steam due to the heat emitted as a result of the phase change then generate electrical energy.

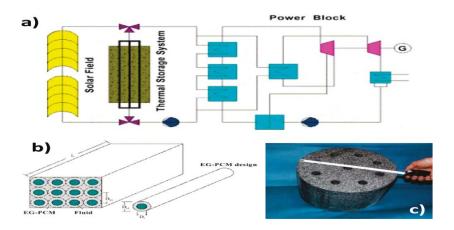


Figure 1.3. (a) concept of typical design of thermal energy storage built with in solar thermal parabolic trough power plants. (b) single storage block sketch. (c) segment storage with drillings for heat exchanger [11].

1.2. INTRODUCTION TO PARAFFIN WAX

Paraffin Wax is a pure mixture of saturated hydrogen charcoal and solid that form the chemical alkanes, which have a high molecular weight, expressed in the chemical formula ($CnH_{2}n + 2$). It is prepared from petroleum, and shale oil, and paraffin was known in the fifties of the nineteenth century when scientists were able to know how to separate waxy materials from petroleum. Paraffin wax can be dividing according to its hardness. Firstly, softer paraffin waxes: It is the wax that is distilled at low pressure, and its boiling point ranges between approximately 76-154 °C. So soft paraffin wax includes both (Slack Wax) [17-19].

It is the wax that is distilled at a temperature ranging between 27-38 degrees Celsius, and the percentage of oil present in it ranges between 10-35%.and (Sweat Wax) it is the wax that is in the solid state at a temperature of about 16 degrees Celsius, and this type of wax is used in the paper and textile industries.

Intermediate Paraffin Waxes: Its softness is moderate, and one of its types is Scale Wax, whose raw types range from white to yellow. White scaled wax contains less than 4% oil, while yellow scaly wax contains less than 2% [18].

Secondly, the Harder Paraffin Waxes: Contains a trace percentage of oils; as it is produced on this type by drawing the oils and liquid materials in the wax through the process of filtration. Paraffin wax has some properties: It is characterized by its white color or colorlessness. The melting point of paraffin wax ranges between 46-68°C. Paraffin waxes has a density of about 900 kg/m³. Paraffin wax dissolves in esters, ether, and benzene, and does not dissolve in water. Paraffin wax has a low burning rate. Paraffin wax is a thermoplastic plastic; where it remains in its solid state at room temperature, while it sticks to the surface when exposed to heat [19].

1.3. APPLICATION OF PARAFFIN WAX

It is used in many applications, the most important of which is: Candle making: Most candles are made using a 10% stayarine wax; to add transparent candle appearance and to slow the candle. Cosmetics industry: The importance of paraffin wax lies in its ability to soften the skin, maintain its smoothness, lighten its color, reduce wrinkles on the hands, and remove cracks and scars [20]. It is used in applications related to skin care such as paraffin wax baths, which help in increasing the smoothness of the skin, softening it, and giving it a beautiful and wonderful texture. Paraffin wax works to add luster to cosmetic products, in addition to being an important ingredient in many preparations for example Vaseline; its purpose is in keeping the skin smoothness, in moisturizing creams and lotions, in the manufacture of lipstick, products of hair care for example shampoo and conditioner, and in products of hair removal [19-21].

Food industries: Paraffin wax is used in the manufacture of preservatives in some food stuffs, and it is also used as a stiffening agent in order to give the material an appropriate degree of hardness, in addition to its use in order to add gloss to food, and as a coating to protect food products from moisture and mold, and to keep them for the longest possible period such as cheese and fruits Paraffin wax is an essential ingredient in making chewing gum, and it is also added to chocolate during its manufacture to give it a shiny appearance when it dries [19].

Medical uses: Paraffin is used in the treatment of many diseases such as: back and spine pain, muscle strains and cramps, tendinitis, fibrous infections, joint infections, joint stiffness, subcutaneous muscular syndrome, elbow inflammation, rheumatoid disease, stadium injuries, and skin diseases. Like psoriasis and eczema, paraffin wax is also used as an aid in treating movement disabilities and paraplegia, in addition to its contribution to stimulating blood circulation and increasing blood flow in areas of muscle injury [22].

Agriculture: Paraffin wax is used in the manufacture of fertilizers as an anti-caking substance, so that it contributes to facilitating the process of processing, transporting

and distributing fertilizers. Various industries: Paraffin wax is used in many different industries such as: packaging, shoe making, furniture manufacturing, cigarette packaging, and sticks matches, textiles, rubber, explosives, cork, and many other electrical and electronic applications. Additionally, Paraffin wax used for solar energy storage applications, like, "water heaters", "air heaters", "solar water distillers", and "photovoltaic thermal (PV/T) systems" [17 and 18].

The objective of this study is to enhance the conductivity and viscosity of the material for photovoltaic thermal PV/T applications. Additionally, the objective of this project is to analyze the thermal and physical characteristics of modified paraffin wax with two types of nanoparticles (Fe_2O_3 , and TiO_2) with different percentage weight. The results of this work will come up with important data that can assist the designers in choosing the best mixture for photovoltaic application which use the phase change materials. However, this will help to increase the stability of the thermal conductivity which considered as a limitation for using PCMs method in various applications [21].

PART 2

LITERATURE REVIEW

As we mentioned earlier, there are non-renewable sources of energy that are processed to be usable to meet life's needs. This energy was formed as a result of its exposure to multiple geological processes and for long periods of time. An example of these sources is fossil fuels that were discovered in the form of layers in the earth millions of years ago when sediments and large quantities of plants and the remains of dead animals were buried and isolated from air, heat and pressure for millions of years and chemical reactions occurred. Between these materials until the formation of fossil fuels, which has several types, the most important of which is coal, which is sedimentary rocks and consists mainly of carbon in addition to varying proportions of other elements led by hydrogen, sulfur, oxygen, nitrogen and was used as fuel mainly before the industrial revolution and is currently used in the paper industry And the generation of electricity and several other uses. Second, natural gas where is lighter than air and has no colour or odor. It is often composed of methane. Methane is a chemical compound consisting of carbon and hydrogen atoms, and its chemical composition, which means the union of a carbon atom with four, "CH₄ 4," (hydrogen atoms as in the form number 24) and natural gas is often found near petroleum below the surface of the earth, and it is transported in tubes Even in storage areas, except that it is mixed with a chemical substance that gives it a pungent odor that resembles the smell of rotten eggs in order to identify it in the event of a leak, which prevents the occurrence of fires [12-16].

Natural gas is the best type of fuel that can replace petroleum products, which by burning produces carbon dioxide gases. It causes many environmental problems. Petroleum oil, or petroleum for short, is a type of fossil fuel that dates back 300 million years. Scientists believe that micro-organic materials are the main source of petroleum. Organic materials are very small marine creatures the size of a pinhead

whose function is to convert sunlight into stored energy, which, once it dies, falls to the sea floor, to be buried under sedimentary rocks and other rocks, and by the effect of the pressure of these rocks on the organic materials, they retain the stored energy. Usually oil and gas are found above layers of rocky sediments that were formed when the area was submerged in water, and the remains of plants and animals that lived in the seas were buried under the sediments, to be transformed by pressure and heat for millions of years into petroleum oil and natural gas that collected in the form of pockets - wells. It is the most widely used as it is used in the manufacture of paraffin, plastic, pharmaceuticals and synthetic rubber, in addition to diesel fuel. Since fossil resources are formed in millions of years, we will not be able to quickly replace the quantities used, especially if the formation period is compared to the consumption period, so these resources are not renewable [15-18].

Uranium is a heavy fissionable metal that is used in the production of nuclear energy for military purposes and in the manufacture of missiles and tanks. It can be used in the production of electrical energy as it is used from the great heat that is produced when it is split during nuclear fission reactions and there is an obstacle to its widespread use due to the possibility of nuclear fission failure. There are several problems and disadvantages of using non-renewable energy, the most important of which is Non-renewable energies lead to high levels of pollution as the fossil fuels we consume represent about 28% of global greenhouse gas emissions released each year. Eliminating this problem by itself could reduce the number of premature pollution-related deaths by nearly 50%, and the cost savings that families, health care providers, and governments would achieve with this result could be around \$ 500 billion annually. Non-renewable products can become the basis of political conflict as most countries fight wars repeatedly due to access to required resources, and our economy's dependence on non-renewable energy creates the basis for future conflicts. Plants and animals also face the same problems that humans do with nonrenewable energy sources: Although some plants thrive in environments that contain large levels of carbon dioxide, most plants and animals require the same health processes that humans do to support good health, When we expose these creatures to fossil fuels in unnatural ways, their health is immediately at risk [18-20].

Refining non-renewable energy destroys the environment, as when we make improvements to our support network for non-renewable energy we also increase the negative risks that the environment faces every day, as the construction of manufacturing hubs, refining systems and transportation methods, for example, requires investments from fossil fuels at a much higher level than the structures used for components. Like solar and wind energy, all of these activities enhance the impact of emissions on our atmosphere [22]. Finally, although estimates of the availability of fossil fuels have changed continuously over the past 30 years, there is always the possibility that some non-renewable resources will become unavailable in the future. Because of the above reasons, there is a global trend to use renewable energy and reduce the use of non-renewable energies. Where renewable energy can be defined as the energy produced from natural sources that can be renewed without being exhausted or disappearing, available permanently, and does not harm the environment and does not generate greenhouse gases, and renewable energy includes Wind energy, as it is the oldest type of renewable energies in use, as people used it in windmills to grind grain, and it is used today to generate electrical energy, as wind power plants are built in a way similar to farms and are called wind farms and can also be placed in water to benefit from the winds over the seas, There are obstacles to the use of wind energy, which is the visual effect of turbine rotation and the noise emitted by it may disturb people living near wind fields, and to reduce these effects, it is preferable to establish wind fields in areas far from residential areas and Although it is a renewable energy, it is seasonal and sometimes the wind speed does not match the electric power, Geothermal energyIt is a very high thermal energy present in the ground of the earth, and the temperature rises as we go deeper into the ground. This energy is used mainly in generating electricity and heating buildings, and this energy can be sufficient to cover the world's need of energy for thousands of years, but converting it into electrical energy is a very expensive process [23].

Due to drilling operations and the need for pipes in large quantities, Hydropower, which is produced using the water of rivers and dams, as this energy is obtained by taking advantage of the flow of water from rivers and dams, which works to move the turbine blades to produce mechanical energy, and then a generator converts this energy into electrical energy, as it is known as electrical energy The result of this process in the name of hydroelectricity, and it is worth noting that hydropower represents about 17% of total electricity production, and the countries that use the most hydropower include China, Brazil, Canada, the United States and Russia. Despite the many advantages of using hydropower, there are also a set of drawbacks that can be faced when using this energy, including the use of hydropower can cause great damage to habitats on the banks of rivers [24]. as a result of reducing levels of dissolved oxygen in the water and affecting fish populations, and that is By preventing her from emigrating. Solar energy is the energy produced and generated by the sun that reaches the earth in the form of solar radiation Solar energy can be used in two ways, The first is solar thermal energy, which is a conversion process Solar energy into thermal energy by solar thermal energy concentrators, And the second way it Solar electric energy in which the solar radiation is converted into electrical energy directly by solar panels or cells, Solar energy is available and free energy and does not cause damage to the environment, so it is preferable to use it, but there is a problem facing the use of solar energy, which is storage, because one of the disadvantages of solar energy is that it is available only when the sun is present[25-27]. Therefore, there is a need to find ways to store alternative energy, in particular the areas where solar energy is used. There are several methods of storing the energy obtained from the sun, which are in two forms, thermal energy from concentrated solar energy(CSP) and electrical energy from photovoltaic (PV). These methods are classified according to use and storage, as in the following table.

Chemical Energy	As in fuel cells and batteries, losses are usually small for
Storage	storing chemical energy
Mechanical	Electrical energy is stored in the form of potential energy,
Energy Storage	such as pumping hydroelectric energy storage, or in the form
	of kinetic energy such as a flywheel.
Electrical Energy	These are characterized by the speed of discharging stored
Storage	energy. For example of this type of storage are capacitors and
	magnetic devices that have very high conductivity.

Table 2.1. Classification by storage.

Table 2.2. Classification by use.

Power Quality	The stored energy ranges between 0.028 - 16.67 kWh. Discharging power range from 0.1 to 2MW, discharging power needs 1 to 30 seconds. Applications are the ultimate power quality and reliability
Distributed Generation	The stored power is from 50 to 8000 kWh, the discharge time is from 0.5 to 4 hours, the discharge capacity is from 100 to 2000 kW. It is used in transmission and peak shaving applications.
Bulk Energy Storage	The stored energy is from 10 to 8000 MWh, the discharge time is from 1 to 8 hours, the discharge capacity is from 10 to 1000 MW. It is used in applications spinning reserve and load levelling.

2.1. METHODS OF THERMAL ENERGY STORAGE

Sensible Heat Storage: The solar energy that is generated in the peak hour is used to change the temperature of the material, whether liquid or solid. And by the difference of the original temperature with the temperature of the material, the energy is stored. An example is the storage of concrete, graphite and solar air and water heaters. The idea of air and solar water heaters is a simple idea, which is to store thermal energy in water and air using solar radiation. Due to its somewhat lower cost and ease of manufacture, this method has become popular. But the density is lowered for thermal storage [28].

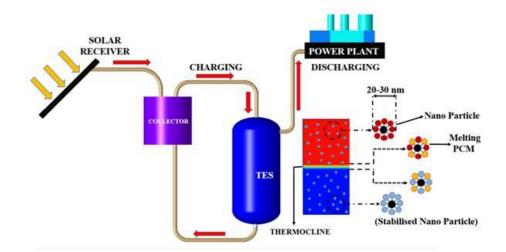


Figure 2.1. System of sensible heat thermal storage [29].

Sorption Storage: It is the process of fixing or capturing the vapor of Gas (Sorbent) by means of a solid liquid substance (Sorbent). Absorption means absorption of a gas by means of a liquid, Adsorption means absorption of gas by solid matter. Adsorption consists of two methods and it is a reaction by means of van der Waals forces called the thermophysical reaction (physisorption) and by valence forces a reaction called a thermochemical reaction takes place (chemisorption). Chemisorption has a capacity to store heat more than physisorption, but it may not be recoverable. Several couples of materials have been studied; each couple has disadvantage that not allowed its practical use. For LiCl/H2O, LiBr/H2O, and NaOH/H₂O, Absorption process may occur. The LiCl/H₂O combines has High storage density of up to 253 kW / m^3 , and because LiCl salt is very expensive, it is therefore not suitable for seasonal use [39]. LiBr / H₂O has a storage density of 180310 kWh / m³ [40]. The NaOH / H₂O couples must be handled meticulously when using it because it is highly corrosive. MgSO₄ / H₂O and Na₂S / H₂O are two systems that can be utilized for chemisorption. The Na₂S / H₂O pair has a high thermal power density and a high energy storage density as well, reaching 1300 kWh / cubic meter for refrigeration, 1980 kWh / cubic meter for heating [30]. However, this material must be operated in a vacuum environment because it is highly corrosive.

Solar Fuels: by optical devices, can be concentrated the scattered sunlight and the heat generated by concentrating solar energy can be used to conduct a Heat absorbent chemical shift to obtain a fuel that can be stored and transported . Examples include solar chemical heat tubes, solar metal, and solar hydrogen. There are several methods of generating hydrogen from solar energy: photochemical, electrochemical, and thermochemical. In addition, solar energy can be stored directly as solar fuel. But it isn't productive to change over power into thermal energy and after that creates hydrogen. Fossil fuels and water can be used as sources of hydrogen by route of thermochemical. Where solar energy can be stored in minerals and can be released during the combustion process, considering the concentrated solar energy as a source of heat to separate the oxides. Experiments have proven that the suitable mineral for this process is zinc [30].

Phase Change Material Storage (PCMS): When a substantial experience a phase change, heat is released or absorbed. Latent heat refers to the energy that occurs as a result of the phase change. The latent heat materials have the ability to store 5 to 14 times more than the sensible heat materials Phase .change materials can be divided into three classes: Organic as (fatty acid, paraffin), Inorganic such as (molten salts, hydrates, and metals), Eutectic as (inorganic inorganic compounds, organic inorganic, organic). Organic PCM has a latent heat ranging from 10 kJ / kg to 300 kJ / kg. The latent temperature of inorganic PCM ranges from 20kJ / kg to 250kJ / kg. A eutectic may be a blend of two or more components, to play down the melting temperature of the blend. The eutectic material has a latent heat range of 100 -200 kJ/kg. Reliance on solar heat is considered one of the promising ways to save energy and reduce CO₂ emissions. Therefore, there has recently been an improvement in storing latent heat. The preferences of utilizing latent heat storage s the heat storage have larger density and steady temperature. Therefore, the storage of thermal energy must be developed to a temperature relevant to solar thermal power plants. The design of a PCM storage system includes a heat exchanger implanted inside the storage material. By melting the saturated PCM into the thermal storage square, the energy from the sun is collected. The heat released by changing the phase of a substance is used to generate electrical energy and produce steam [31].

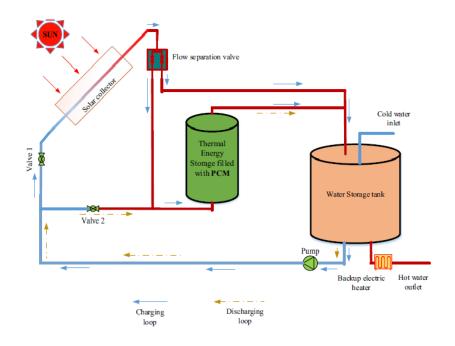


Figure 2.2. Thermal energy storage with PCM [30].

2.2. PROPERTIES OF PHASE CHANGE MATERIAL

The use of PCM in thermal storage because it has several thermal, physical and chemical characteristics, the most important of which are, it has a high latent temperature, has an additional heat storage capacity, possesses a suitable phase balance; high density for litter container volume, the steam pressure is reduced to reduce the containment problem, Non-explosive, non-toxic, environment-friendly, non-chemically degraded, and after a number of freezing cycles, melt does not deteriorate, Recycling is easy, available and inexpensive.

Disadvantages of PCM is that the main problem in PCM is its low thermal conductivity and thermal stability, as it ranges from 0.4 and 0.7 watts / ml Kelvin for salt hydrates and for organic materials it is 0.15 and 0.3 watts / ml Kelvin. As for thermal stability, the PCM may decompose with several storage cycles, which affects its thermal and physical properties over time, making it undesirable. The PCM is said to be reliable whenever it is thermally and chemically stable with several thermal operation cycles. Paraffin wax is one of the most common types of PCM, because of its characteristics, which we will talk about [30-32].

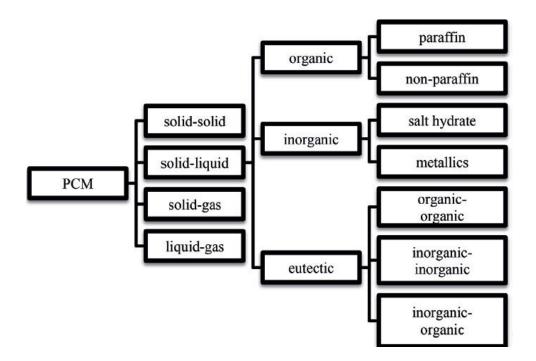


Figure 2.3. Pcm classifications [31].





Figure 2.4. Some types of PCM [31].



a) Paraffin wax b) stearic acid

c) sodium hydroxide

2.3. PARAFFIN WAX

Paraffin comprise of a series of n- alkanes CH_{3-} (CH_{2}) – CH_{3} . Immaculate paraffin waxes are exceptionally costly. Commercial paraffin wax is inexpensive and has a moderate thermal storage density (150 MJ / m³) and a melting point ranging from 10 ° C to 67 ° C. It is chemically inert and stable without phase separation. It is also environment-friendly, non-corrosive, available, comforts to it, non-toxic and long-term. Commercial paraffin is produced by distillation of crude oil; most paraffin's consist of a mix of saturated hydrocarbons with diverse numbers of carbon atoms in the molecules. It has many uses such as the cosmetic industry, the food industry as it is used in the manufacture of preservatives for some foodstuffs, paraffin is used in the treatment of many diseases such as: (back and spine pain, muscle fatigue and cramps, tendinitis), It is also used in solar energy storage applications, such as "water heaters", "air heaters", "solar water distillation" and "photovoltaic thermal systems (PV / T) [32-33].

In modern applications, speed and heat storage have become important topics, especially in photovoltaic thermal (PV/T) applications. The latest development in this field is the use of phase-change materials because they have the capacity to store their thermal energy in the form of its latent heat. There are many researches published in this field. Firstly Add nano-Al₂O₃, nano-ZnO₂ and nano-SiC to paraffin wax. Where changes in the physical and thermal properties were studied to choose the best suitable material to be used in (PV/T) applications in the future. The results showed an increase in the density and viscosity when adding any nanoparticles from

the studied materials. The research has found that adding 5 present of each of nano- Al_2O_3 , nano- ZnO_2 and nano-SiC has an impact of increasing the density of wax by 6.5, 6.84 and 5.8present respectively, hence increasing viscosity of paraffin by 10.2, 9 and 4.5 present, respectively.

Furthermore the research has been enhanced the thermal conductivity by 3.3%, 1.8% and 4.2% by adding 1 present for each nano-Al₂O₃, nano-ZnO₂ and nano-SiC. However, the results showed a slight or limited increase in heat capacity, which depends on the thermal conductivity of the additive. The highest conductivity of the wax was due to the addition of nano-SiC, which increased to 0.12% when adding 0.1% of nano-SiC. Therefore, nano-SiC is considered the most suitable nanomaterial of the materials used, as it showed improvement in thermal properties with a slight increase in the density and viscosity of the wax. As for , nano-ZnO₂, it showed the worst results[1]. In another research, micron / nano Aluminum nitride was mixed with a compound phase change material from Sodium acetate trihydrate –Acetamide with Melting point 47.3 °C In the application of solar heat pump. 10 wt% of Acetamide were used to reduce the melting point of Sodium acetate trihydrate It was added micron / nano Aluminum nitride to improve thermal conductivity And reduce supercooling. The mixture was tested DSC,SEM, XRD,FTIR For the purpose of testing the thermal properties of the compound and the appropriate proportions, the results showed that mixing 3 µm and 30 nm mixed Aluminum nitride It is more effective as a kernel and thermal conductivity agent and 5wt% Aluminum nitride Reduce the degree of supercooling to 0.27 °C and improve thermal conductivity to 0.6484W/m·K. And the latent heat became 226.8 kJ/kg. After 100 cycles of gain and loss of heat. Light microscopy showed that Aluminum nitride promotes crystal growth and gives a stable, uniform granular shape. The SEM showed that 30 nm tend to clump due to their small size, while 3 µm prevents clumping, which leads to an effective heat transfer due to the formation of a network of small molecules between which there are large particles [34]. Also In another study, paraffin was used after combining it with nano-Zno and nano- Cuo in order to study the photothermal properties as a result of adding nanoparticles to paraffin as well as analyzing the thermophysical and optical properties of paraffin enhanced with nanoparticles. The results showed that the permeability of paraffin decreases, but when the temperature

rises, there is a slight increase in the permeability of paraffin. The results also showed that the nanoparticles used show weakening or attenuation of the light And an increase in thermal conductivity, as it increases by 5.87% when adding nano-Zno and 13.12% When adding Nano- Cuo at fraction of volume of 5×10^{-4} . The maximum desperation ratio is 6.3% as it effect cannot be avoided. The thermal performance, depending on the different temperatures, showed that paraffin enhanced with Nano Cuo could absorb more energy. From 5×10^{-4} to 1.5×10^{-3} volume fraction we get the best thermal performance [35].

Further A variable phase change material (Paraffin RT21) was used, and its thermal properties (thermal conduction) and rheological properties (density, viscosity, and shear stress) were studied. The researchers dispersed multi-walled carbon nanotubes with paraffin in several concentrations and the results showed that paraffin reinforced with carbon nanotube has higher efficiency. From non-reinforced paraffin and the thermal conductivity increased to 70% at a concentration of 1.32%, this research opened the way for the design of a thermal energy storage system used in the free cooling of buildings [36].

In addition, one research has used an OM35 chemical mixture as the phase change material and the study was done with both pure PCM and Nano enhanced PCM so that that a comparison was done.. This study used the electrical heater to reduce the temperature effect of concentrated photovoltaic. The heater was attaching with heat sink, so the PCM absorbs the heat from heater that the heat sink stored. Moreover, the results achievements were minimizing the temperature of the concentrated photovoltaic with using the new enhanced PCM hence the efficiency and output power were improved significantly. The temperature reduction was about 12 O C and 15 O C. The improvement was 7% and 6% for output power and efficiency respectively. The study used 0.5 % as nano PCM concentration [37].

Another research used a nano carbon to enhance the performance of the PCM paraffin storage. The concentration of the nanocarbon used in this study was 0.02, 0.06, 0.1 wt%. in this study both of infrared camera and thermocouples used to monitor the performance of nano carbon melting point to compare it with pure one.

The results showed that the enhanced PCM melting point was accelerated without dispersant at 0.02 wt% of concentration of carbon; hence maximized the thermal conductivity of enhanced NePCMs. The study demonstrated that the decelerated in melting process was due to natural convection suppression and nano carbon agglomeration. This decelerated occurred when the concentration increased, as the study stated. However, the study added that increasing in the concentration of nano carbon yield accelerated in melting process. The results of this study illustrated the enhancement of the adding nano carbon by 21% than bare paraffin. However, the study showed some of limitations in the accuracy of the recorded information of the melting process from thermocouples due to agglomeration by dispersant. heat transfer was improved further with oleic acid and secondly, The sensible heat storage and fastest latent storage was noticed with concentration of 0.06 wt% NG and concentration of 2.0 wt% oleic acid [38].

Additionally, other study stated that a combination of 1% of nano-CeO₂ with nano embedded phase change material NEPCM gives a best performance of the enhanced paraffin in terms of energy storage. This study was done in real time solar performance for five different cases: without paraffin as PCM, without PCM and with three different concentration of nano-CeO₂ as 0.5%, 1%, and 2% wt. However, each experiment case last for 12 hours. The main results of this study were firstly, the thermal conductivity of NEPCM was enhanced by increasing the percentage of nano-CeO₂. Secondly, the nano-CeO₂ had no effect on the chemical stability of paraffin throughout the whole interaction between both. As results, the study found that the energy efficiency increased significantly by adding 1% of nano-CeO₂ and reached 79.2%. Adding more than 1% of nano-CeO₂ concentration had no impact on the energy efficiency [39].

Another n-heptadecane type PCM and well prepared sio₂ nanoparticles were used as the support and the saturation method was used for the purpose of obtaining a balanced mixture from n-heptadecane - sio₂ nanoparticles with different proportions of the PCM. X-Ray diffraction ,SEM, FTR spectrometer devices were used The degrees of freezing and melting of the Nano composite have become 120.9 and 123.8 J /g, respectively. The DSC device was used to measure the mass tolerance ratio of the Nano composite, which was approximately 54.6 wt.%. The results showed an improvement in the thermal conductivity of the nanocomposite better than the pure PCM. The nanocomposite appeared to control the temperature in an acceptable manner when placed on a gypsum composite board compared to the regular gypsum board. So this compound can be used in buildings to regulate temperature and store energy [40].

Another research group has been reported a thermal behavior of a system of latent heat thermal energy storage of porous occupied with nano-PCM. Firstly, the group has been design this system and a scale analysis was done in order to integrate the process of phase change which is an important factor in such design system. Therefore different parameters has been simplified for instance, Fourier number, Rayleigh number, Stefan number, porosity of the porous medium, Nusselt number and nano particle volume fraction. Secondly, a numerical method has been applied on the process of melting natural convection of nano-PCM within the medium of the porous. The Darcy model was applied within the medium of the porous. The result of study illustrates that the nano-PCM melting process passes through four sequence regimes, and each one of the regime step has its own scaling rules of melting front location and it has a certain Nu. Furthermore, the results are showed in terms of heat flux vectors, isothermal lines, location of melting front, the Nu as functions of Ra and Ste Fo and streamlines. Both techniques demonstrate that convection and conduction heat transfer in are faded due to the existence of the nano-particles in the cavity system. However, the position of melting front illustrates that the PCM melting process has been prolonged during the addition of nano-particles [41].

Moreover, another study showed that the nano fluid of Al₂O₃\liquid paraffin synthesis has significant impact on the thermal conductivity performance. This experiment used a Oleic acid of nano fluid sample preparation in order to increase the stability of the work. The nano fluid prepeartion was done in two steps, firstly, the impact of magnetic stirring duration and time of sonication on the properties of nano fluid thermal conductivity at several temperatures and concentration of nanoadditive values. The results of experiment shows that the best time period of sonication was 3 hours to 15 minutes, however above this values it will causes thermal conductivity reduction due to the bond between the surfactant and nanoadditives the will be broken in case of the increasing the time. Additionally, the results showed that the optimal time duration of the magnetic stirring was 20 and 40 minutes for the first and second stage respectively. This duration was improved the thermal conductivity by 3.14% and 2.3% for the first and second stage. However, another finding in this work was about the increasing or decreasing of both concentration and temperature in the first stage of the process which have no effect on the stirring time [42].

Another researcher from Firat University has study a new design of heat transfer fins. This design has approved in enhancing the storage of melting process in thermal energy. The study compared the results with the melting process without these new design fins. The base nano PCMs and Nano-PCM of mixed paraffin wax with CuO melting process were examined at several heat transfer fins. The most significant findings of the study was that the new design fins had an impact on improving the process of melting in storage of thermal energy in terms of minimizing the weight and cost of TES. In addition, adding fin 1 has influence on the process of melting and maximizes the melting process Of PCM and fin 2 has impact on reducing the time of melting point at 120 minutes while with using fin 1 the base PCM reached the melting point at 44 minutes so that the paraffin wax melted as well in 51% of its weight. It can be conclude from the study that using the fin 1 has a significant impact on the enhancing the thermal energy storage performance and the melting time of both the PCM and Nano-PCM [43].

Nevertheless, a study of a research group from Canada have been numerically and experimentally investigated of a bio-based Nano-PCM considering all of heat transfer, melting process and properties of energy storage in a C-TES system. With different weight of nanoparticles and Rayleigh number, the nanoparticles of copper oxide have been dissolved within coconut oil inside the C-TES system. The most powerful finding in this study were, firstly, during the melting process, the force of buoyancy exceeded the forces of viscous which have an impact of the continuous

increasing in the melting of natural convection. Another finding related to copper Nano oxide addition to coconut oil had no influence on the melting rate at the beginning of the melting process. However, as long as the time of the process increase, the nanoparticles dissolved within the oil yield an enhancement in the melting rate. Furthermore, at early steps of the melting process, the Nusselt number value was relatively high, because of a high effect of both heat flux and temperature. As the time of the melting process advanced and due to the Rayleigh number, the Nusselt number was significantly minimized which refer to the creation of the layer of the thermal boundary and convection initiation. Adding more weight of the nanoparticles had an impact on minimizing of the total energy storage within the mentioned system. Finally, the result shows a very stable and enhanced value of thermal energy and the performance of the system [44].

Further research has been done on combination of heat storage and phase change material, since it can be consider as a crucial method. The aim of this research was to eliminate the time of discharging of the PCM through the process of solidification, and this was done in this research by solving nanoparticles into paraffin with modifying the surface by making it a wavy surface for the inner duct. However, the results showed that the wavy surface or sinusoidal surface and nanoparticles addition was an effective technique to improve the thermal energy storage of the paraffin wax. Again this study had been approved that the heat flux reduces as the time advances. Additionally, the wavy surface significantly contributes in increasing the discharge rate [45].

The same research group from Canada has been investigated a geometry of TES filled enclosure of nano PCM by using all of the experiment, scale and numerical analysis. The shape of the system that filled with PCM was square with one vertical absorbance wall and the other insulated walls. The absorbance material was the nanoparticles of CuO dissolved in coconut oil with weight present from 4% to 5%. These values of the weight of nanoparticles were examined the heat transfer rate, the flow and liquid fraction through the process of melting of modifies PCM. Additionally, depending on the size of the enclosure, the Rayleigh range value (10⁴-

 10^8). However, the experimental and numerical results illustrate an enhancement of the process of melting with the addition of nanoparticles to PCM [46].

Furthermore, one recent research has been used a compound improvement method. Its involved cooling approached by using water combined with different concentration of nanoparticles of Al₂O₃/PCM mixture through the channel of Al under the PV system. It is found that the new approach of compound has been achieved a better performance of the PV system rather than the previous study of cooling system. However, this technique has a drawback in terms of the output power which was not highest but at the same time it is regarded as a better cooling approach rather than water. From the important findings of this study was about increasing the nanoparticles has a positive effect on the reducing the temperature of the PV panel [47].

PART 3

MATERIAL AND DEVICES

3.1. MATERIALS

In this work, White paraffin wax was used as shown in the figure (3.1).



Figure 3.1. White paraffin wax.

The Nano (TiO₂ and Fe₂O₃) used in the study was purchased from local markets and is produced by Sky spring Nanomaterial, Inc. As shown in the figure (3.2) and (3.3)



Figure 3.2. Nano – TiO₂.

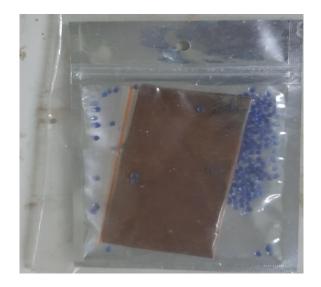


Figure 3.3. Nano – Fe₂O₃.

3.2. MEASURING DEVICES

Many instruments were used in this study as an example.

3.2.1. Scanning Electron Microscope (SEM)

Model / VEGA SEM, Made in the Czech Republic. It is used to study the outer surface of samples. A small amount of electronic radiation scans the sample and the electrons emitted from the sample combine to form the image. The main distinguishing feature of the (SEM) device is that it uses a narrow electron beam to scan the biological model, and this beam moves back and forth as it passes through the examined body, which will emit secondary electrons that are used to form the image, meaning that the sample causes the secondary electrons to reflect and can be used to produce the image. Figure (3.4) explain the device.



Figure 3.4. VEGA SEM.

3.2.2. Vacuum Drying Oven German Origin

It is used to dry and protect samples that change with temperature during drying. The temperature range is between 70 $^{\circ}$ C to 200 $^{\circ}$ C. Figure (3.5) shows the device.



Figure 3.5. Vacuum drying oven.

3.2.3. KQ3200E Ultrasonic Bath

It is used for mixing samples. It has a storage capacity of 12 liters and a frequency of 30 kHz and an electric heater of 800 watts. Made in china. Figure (3.6) show the device



Figure 3.6. KQ3200E ultrasonic.

3.2.4. Fourier Transform Infrared (FT-IR) Spectrometry

Model 8400S Japanese company Shimadzu. This device is characterized by being fast and very sensitive. The power source in the FT-IR spectrometer is the LASER Monochromatic source. The FT-IR does not contain a monochromatic, so the incident beam contains all of the medium-range infrared wavelengths 5000-400 cm-1. FT-IR spectrometer analyzes smaller samples faster and more accurately than a regular device. And It can analyze air pollutants such as carbon monoxide, ethylene oxide, and others. Figure (3.7) show the device.

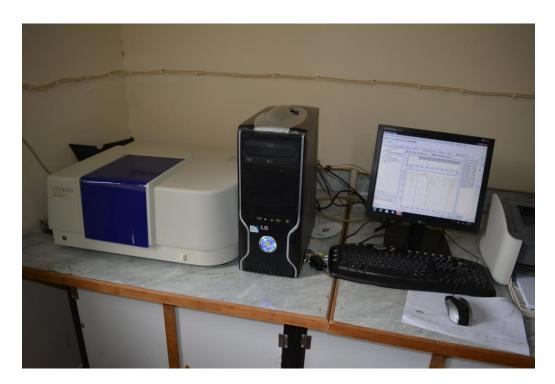


Figure 3.7. Fourier Transform Infrared (FT-IR) Spectrometry.

3.2.5. Brookfield DV-II+ Pro Viscometer Made in USA

It is used to measure the viscosity of compound materials. It is characterized by the ease of preparation and installation as well as the ease of reading the values through a digital screen and it can measure viscosity even with a small amount of the sample (15 ml). Figure (3.8) show the device.



Figure 3.8. Brookfield DV-II+ Pro viscometer.

3.2.6. HOT DESK TPS 500 Thermal Conductivity Meter Made in Sweden

It is used to measure thermal conductivity, specific heat and thermal diffusivity. Figure (3.9) explain the device.



Figure 3.9. HOT DESK Tps 500 thermal conductivity meter.

3.2.7. Sensitive Balance (Type EJ6I0-E) POLAND (EU).

The purpose of the device is to weigh the materials in four orders after the sorter to the extent of 220 grams. Figure (3.10) explain the device.



Figure 3.10. Sensitive balance.

3.2.8. Thermal Convector Equipped with Magnetic Drive

The purpose of the device is to heat and stir the liquid forms. Figure (3.11) show the device.



Figure 3.11. Thermal convector equipped with magnetic drive.

3.2.9. Thermocouple Sensor Type pt100 and Thermometer

It is a sensor to measure the temperature. Figure (3.12) show the device.



Figure 3.12. Thermocouple sensor and Thermometer.

PART 4

METHODOLOGY

The following paragraphs describe a method for preparing and testing paraffin- Nano $(TiO_2 \text{ and } Fe_2O_3)$ composites. In this work, White paraffin wax was used and is available in the market, and tests were performed on it to know the thermophysical properties as shown in a table(4.1) are suitable for use in PVT applications and its cost is cheap (US \$ 1.3 per kilogram). This paraffin is characterized by the fact that the temperature at which its phase changes from solid to fluid (melting point) is suitable for PVT applications in hot climates of Iraq. The Nano (TiO₂ and Fe₂O₃) used in the study was purchased from local markets and is produced by Sky spring nanomaterial, Inc. This material was selected because it has high thermal conductivity and low cost. Table (4.2) lists the properties of the Nano (TiO₂ and Fe₂O₃) used.

Paraffin properties	White paraffin		
Melting point	41°C		
density of Liquid state	830 kg/m ³		
density of Solid state	940 kg/m ³		
Latent heat of fusion	191 kJ/kg		
Thermal conductivity	0.2 W/m °C		
specific heat of Liquid	2.1 kJ/kg		
state			
specific heat of Solid state	2.2 kJ/kg		

Table 4.1. Paraffin was thermophysical properties.

Characteristic	Nano TiO ₂	Nano Fe ₂ O ₃
Manufacturer	Sky spring nanomaterial	Sky spring nanomaterial
	,INC.	,INC.
Appearance	White powder	Red brown
Purity	99.5%,	99.5%
PH value	6.2	6
Grain size (nm)	25-30nm	30-50 nm
Bulk density (g/cm3)	4.23	5.242 g/cm ³
Lose of drying %≤	0.076	0.056
Molar mass (g/mole)	79.87	159.69
Melting point (°C)	1843	1565
Thermal conductivity	11.6	4.66
(W/m K)		

Table 4.2. Characteristic of Nano (TiO₂and Fe₂O₃).

We prepared nanoparticles by dividing them into different weights at rates of 0.5%, 1%, 2%, 3% for each Nano type by means of Sensitive balance that measures with high accuracy up to three levels after sorting to the extent of 120 grams, where we put a container on the scale and then zero The device and then we add the materials as in Figure (4.1).



Figure 4.1. Prepare sample weights.

Then we put the nanomaterial's in an oven at 200 $^{\circ}$ C for a period of 15 minutes to get rid of the moisture. Then we melted the paraffin wax with a heat heater and then poured it into a silicon mold as in the figure (4.2) and Leave it until it hardens.



Figure 4.2. Paraffin wax molding.

Then the nanoparticles were added to the paraffin wax, where ten samples were prepared as shown in the table (4.3)

Sample	Sample components in gram
Paraffin	100 paraffin wax
Nano- PCM 1	99.5 paraffin wax+ 0.5 nano-TiO ₂
Nano- PCM 2	99 paraffin wax+ 1 nano-TiO ₂
Nano- PCM 3	· ·
Nano- PCM 4	98 paraffin wax+ 2 nano-TiO ₂
	97 paraffin wax+ 3 nano-TiO ₂
Nano- PCM 5	99.5 paraffin wax+ 0.5 Nano - Fe ₂ O ₃
Nano- PCM 6	99 paraffin wax+ 1 Nano - Fe ₂ O ₃
Nano- PCM 7	98 paraffin wax+ 2 Nano - Fe ₂ O ₃
Nano- PCM 8	97 paraffin wax+ 3 Nano - Fe ₂ O ₃

Table 4.3. The ratio of Nano-TiO2 and Fe2O3 with paraffin wax for the studied samples.

The VEGA SEM instrument was used to test the properties of the used nanoparticles. The first step is to turn on the device and the computer connected to it and press the device icon (VEGA) on the desktop, then we enter the sample after preparing it, as the sample must be dry and not wet, during the examination the chamber should not be opened for a long time to avoid contamination, and then we enter gas Nitrogen to the chamber to expel the oxygen. and completely empty the air and make sure that there is nothing that exists on the device table to prevent the occurrence of vibrations, after which we conduct the scanning process of the sample. Then we mixed the samples using an ultrasound device that contains a 12-liter container in which distilled water is placed. The temperature was set at 65 °C to keep the wax melting and we let the samples mix for three hours and a half to ensure the consistency of the wax with the Nano and prevent clumping of the nuclei particles to get more products Stable. Figure (4.3) shows the mixing process. The approval of this mixing period was made according to the REF (47), after which the samples were poured into the mold to conduct tests of the thermophysical properties of the studied samples (viscosity, density, stability and thermal conductivity).



Figure 4.3. The mixing process in ultra-sonic.

To ensure molecular bonding and to verify chemical interaction between nanoparticles and paraffin Fourier Transform Infrared (FT-IR) Spectrometry was used. The samples were put in the device, measured and stored the results in the computer. The device cover should not be lifted during the examination, nor should the device table be moved to obtain an accurate measurement. The thermal conductivity of the tested samples was measured using HOT DESK Tps 500 thermal conductivity meter (KIJTALEY, Sweden) that have an uncertainty of 0.31%. The

examination process is carried out by placing the sensor in the device between two identical samples (the same material and the same size) so that it touches the surface of the sensor. The device's program was used through the computer, then the data was entered and the examination was started. The test was conducted at a temperature of 25°C to avoid the temperature factor that increases the thermal conductivity. The viscosity of the samples was tested by Brookfield DV-II+ Pro viscometer, which was calibrated and its uncertainty was 0.89%. The tests were conducted by placing the sample in the container after melting and then the device is turned on and the speed of the spindle is determined. This process was performed under different temperatures from (25°C-65°C). The Sensitive balance (type EJ6I0-E) was used in samples preparation and measuring studied composite materials densities. This balance has an uncertainty of 0.24%. In the density measurements a simple procedure was used, which is measuring the weight of a specific volume and dividing the weight on volume to specify density.

The paraffin-nanoparticles mixtures stability was studied and checked by using the thermal conductivity degradation method of the samples according to Ref. [48]. The nanoparticles-paraffin samples were melted and left to solidify at room temperature several times, and then the thermal conductivity of the mixtures was measured. The melting-solidification process caused movements of nanoparticles, which may result in its accumulation and then they deposits. If the nanoparticles deposit, the thermal conductivity of the mixture will be reduced and deteriorated. As long as the nanoparticles are suspended in the mixture and dispersed, their thermal conductivity of the mixture will remain high. However, when it is agglomerated or precipitated, the mixture's thermal conductivity will be greatly reduced. The stability of the thermal conductivity after several melt-solidification processes means good diffusion of the nanoparticles in the mixture as a result of the successful mixing process. The melting - solidification process was repeated for 50 days while the thermal conductivity measurements were continued to measure the stability of the samples. Thermocouple sensor type PT100 and Thermometer and Thermal convector equipped with magnetic drive to evaluate the melting and solidification points. The samples were heated slowly (to monitor changes in the temperature of the paraffinnanoparticle mixture). Thermocouple type K was used in this measuring process to evaluate the phase shift point (at melting point, the sample remains at constant temperature for a period until all the paraffin is melted). After all paraffin is melted, the mixture temperature rose. The degree at which the temperature is fixed is called the melting point (the phase change point). After the samples reached 60°C, they were left to cool down to the room temperature (25°C). During the cooling of the samples, temperatures and time are measured to determine the solidification point and the time spent for this process. Figure (4.4) explains the melting-solidification processes measurements.



Figure 4.4. Melting and solidification process.

PART 5

RESULTS AND DISCUSSIONS

5.1. OPTICAL PROPERTIES

Figure (5.1) shows mixing Nano -Fe₂O₃ with paraffin at different mass fractions. The Iraqi paraffin used has a moderate melting point (40°C), and its colour is white. Adding Fe₂O₃ nanoparticles caused changing the mixture colour as it transformed to black. References [1 and 48] considered that complete paraffin discoloration is evidence of successful mixing. Figure (5.2) shows the mixing of Nano-TiO₂ particles with paraffin. All products were coloured white because titanium oxide is also white in colour.

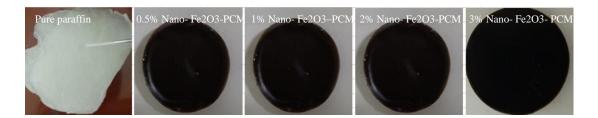


Figure 5.1. Images of four variable mass fractions of added Nano- Fe₂O₃ to paraffin.

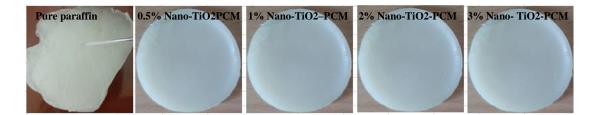
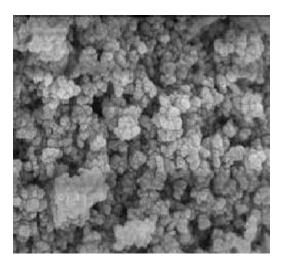


Figure 5.2. Images of four variable mass fractions of added nano-TiO₂ to paraffin.

It is possible to take advantage of the scattering and absorption of light by any material to ensure the quality of the resulting mixing. The paraffin chains composed of hydrogen and carbon have a uniform crystalline configuration, which will be affected by the entry of the nanoparticles into it. This means that the molecular structures of the mixture will be changed. Figure (5.3) and Figure (5.4) show SEM images of the used nano-TiO₂ and Nano–Fe₂O₃. It is noted from the images that the used particles are spherical in shape and have a size from 25 to 30 nm for Nano TiO₂ and nano-Fe₂O₃ have size from 30 to 50 nm. This has a great influence on the thermophysical properties of the mixture, as indicated by the REF [49].



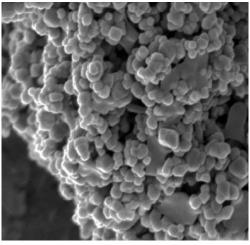


Figure 5.3. SEM test for Nano Fe₂O₃

Figure 5.4. SEM test for nano-TiO₂

Figures (5.5) and (5.6) represent the results of the FTIR test for 1% and 3% for Nano-paraffin mixture for each type of nanoparticle used. In figure (5.5) strong vibration appears at sharp peaks 3005, 3069, as well as peaks at 736 and 1518, indicating that the structure is shaking. At 3100 a slight peak appeared, and this indicates asymmetric vibration. After discussing all the peaks with the other sample, it is surprising No other peaks appeared in the other sample, and this indicates that no chemical reaction occurred between the nanoparticles of the TiO₂ and paraffin wax. Likewise, for samples mixed with Nano Fe₂O₃ in figure (5.6), the two samples exhibit the same peaks and vibrations, where sharp peak appear at 3954, and peaks also appear, but in a smaller form at 3,657, 3158 and 2227. This indicates that there is no chemical reaction between the Nano and paraffin molecules.

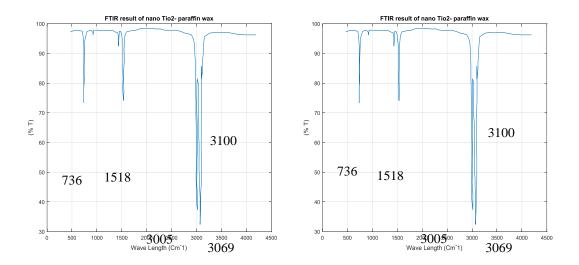


Figure 5.5. FTIR result of nano TiO₂ with paraffin wax.

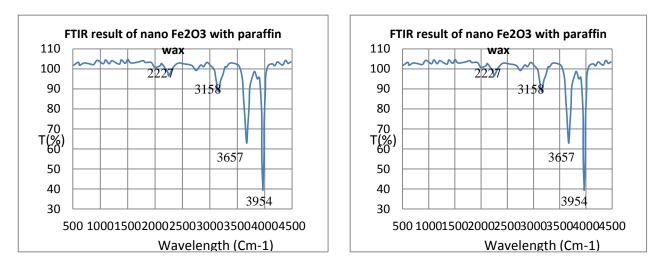


Figure 5.6. FTIR result of nano Fe₂O₃ with paraffin wax.

5.2. THERMOPHYSICAL PROPERTIES

5.2.1. Density

Figure (5.7) shows the density variation with nano-TiO₂ and Fe₂O₃ added. The results show the density increased for the composite material while added nanoparticles is increased. Higher density was achieved when adding nano-Fe₂O₃. When 3% Nano-TiO₂ and Fe₂O₃ was added, the density of the composite material was increased by 5.5% and 5.9% respectively. Usually, an increase in density is

harmful if there is fluid movement, but in PVT applications there is no movement of the composite material. So, this increase does not harm this aspect. However, the abutments bearing the composite material tank must be strengthened due to the increased weight.

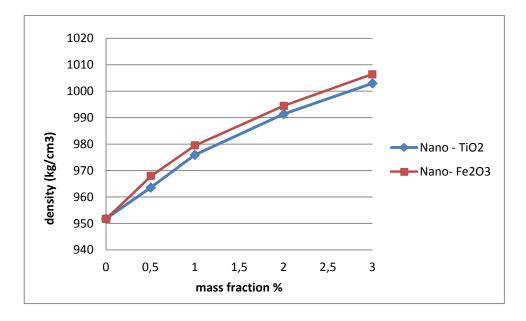


Figure 5.7. The effect of adding Nano (TiO₂ and Fe₂O₃) on the composite material density.

5.2.2. Viscosity

Viscosity is defined as the resistance of a fluid to flow due to the pressure difference on its sides. In the case of PVT applications the fluid of the composite material is not deprived of its place, so the effect of its viscosity is limited. On the other hand, the heat energy is stored into potential energy when the paraffin phase changes from solid to liquid. In this case, Viscosity has an important role in stabilizing composite materials by maintaining the dispersion of nanoparticles. The temperature was increased from 25 ° C to 65 ° C expressing the PVT temperature range. The results show that the viscosity changes to a limited extent for all tested samples. With an increase in a higher rate for samples mixed with Nano FE₂O₃. Tables (5.1) and (5.2) Illustrates the Viscosity (m Pa·s) of the studied samples variations with the change of temperature.

Temp (°C)	Paraffin	Nano- PCM 1	Nano- PCM 2	Nano- PCM 3	Nano- PCM 4
25	0.09	0.092	0.093	0.094	0.095
35	0.061	0.064	0.065	0.066	0.067
45	0.051	0.053	0.054	0.055	0.057
55	0.048	0.051	0.053	0.054	0.055
65	0.04	0.043	0.044	0.046	0.048

Table 5.1. Viscosity (m Pa·s) of the studied samples variations with the change of temperature for PCM-nano-TiO₂.

Table 5.2. Viscosity (m Pa \cdot s) of the studied samples variations with the change of temperature for PCM-Nano Fe₂O₃.

Temp (°C)	paraffin	Nano-PCM 5	Nano-PCM 6	Nano-PCM 7	Nano-PCM 8
25	0.093	0.095	0.096	0.097	0.098
35	0.062	0.065	0.066	0.068	0.069
45	0.053	0.055	0.056	0.057	0.058
55	0.49	0.053	0.055	0.058	0.059
65	0.042	0.044	0.046	0.047	0.049

5.2.3. Thermal Conductivity

An important factor that has a role in increasing the heat transfer of heat storage materials is the thermal conductivity. It is clear that diffusion of nanoparticles improves thermal conductivity. With the help of a hot disk thermal constants analyzer, the thermal conductivity of the samples was evaluated and measured. The results obtained are shown in Figure (5.8). The results show that the improvement in the thermal conductivity of samples mixed with nano-TiO₂ is better than samples mixed with nano-Fe₂O₃ and the higher the proportion of nanoparticles, the higher the thermal conductivity. The improvement was not linear, and after adding 1% to a mass fraction there was no significant increase, Where when adding 1% of nano-TiO₂ to paraffin, we see the rate of improvement in conductivity up to 75.5. Also when adding 1% nano-Fe₂O₃ to paraffin, we see the improvement rate up to 60.5% as we can see from the figure that the slope decreased after this percentage.

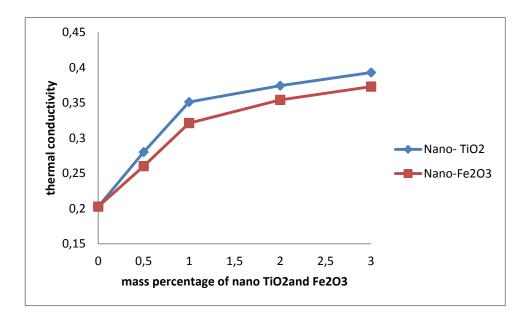


Figure 5.8. Thermal conductivity after adding Nano Tio₂ and Nano Fe₂O₃.

5.2.4. Composite Material Stability

The stability of paraffin-Nano means that the nanoparticles are not clumped together and then keeps at the lower of the container, which reduces a thermal conductivity of a product. Therefore, checking the stability of any mixture is very important. The stability was studied using the method that originated the Ref. [47], which is by borrowing samples to several charging and discharging operations and then measuring their thermal conductivity. In this work, a thermal conductivity of the samples was tested after every ten melt-hardening cycles. The study considered that the deterioration of the thermal conductivity means the accumulation of nanoparticles and their deposition during the fluid phase of the mixture and the decrease in product quality. Fifty tests for thermal conductivity were performed at a rate of 1 test per day (for 50 days). Figure (5.9) and (5.10) illustrate the deterioration in a thermal conductivity of the studied samples. With 50 melting-solidification cycles, a deterioration in a thermal conductivity relatively appears low, and this decrease reaches an average of 1.81%, 2.06% for the case of adding 1% mass fraction of the nanoparticles from TiO₂, Fe₂O₃, respectively and increases with the increase in the percentage of added particles by weight to reach 2.32 %, 2.4% for the case of adding 3% TiO₂, Fe₂O₃ nanoparticles. By increasing the tests numbers, the composite materials thermal conductivity decorated. These results confirm that the mixing process was efficient. Also, it is suggested to re-mix the composite material after five hundred melting – solidification processes.

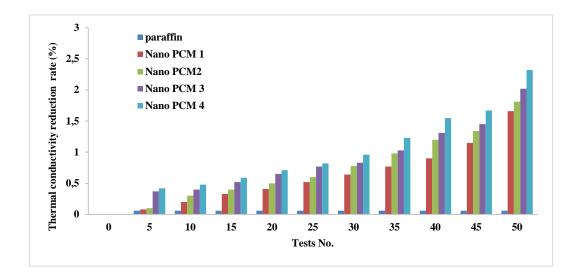


Figure 5.9. The impact of melting-solidification cycles on the thermal conductivity reduction rate.

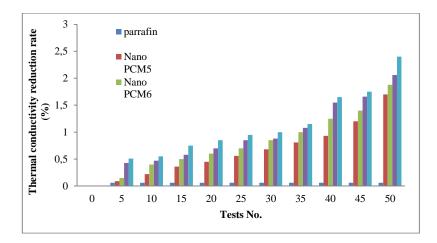


Figure 5.10. The impact of melting-solidification cycles on the thermal conductivity reduction rate.

5.2.5. Melting Point

In PVT applications, charging and discharging processes are important considerations because they determine the time required to draw heat and transfer it to the coolant from the photovoltaic. System efficiency increases when these two processes are rapid. Figure (5.11) illustrate the time required to charge the examined materials. The charging time decreases with the increase in thermal conductivity, as this period is directly affected by the thermal conductivity of the studied samples. Paraffin has a higher melting point than the rest of the samples and the phase change period from solid to liquid takes longer. The fastest melting samples with a shorter phase change period are paraffin containing nano-TiO₂. The temperature of paraffin and composites increases after their phase change, which is an increase due to the sensible heat, while the latent heat is stored in these composite materials during the phase change period. During the phase change period, the samples temperature is fixed until all the composite material is melted. The measurements show that there is a tiny reduction in the melting point due to nano-TiO₂ addition.

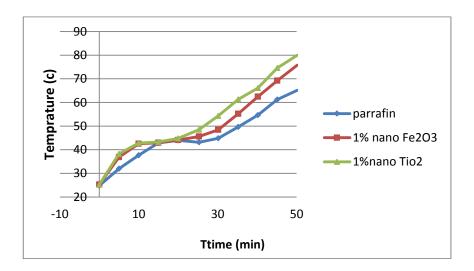


Figure 5.11. Charging period effect on the studied materials.

5.2.6. Solidification Point

The discharging process is just as important as charging process. In PVT applications, the heat gained must be disposed of so that the paraffin absorbs more of the additional heat. When using pure paraffin, this situation is difficult to achieve because paraffin has a low thermal conductivity, which leads to a delay in the disposal of the heat gained. Figure (5.12) illustrate that paraffin containing Nano-TiO₂ has the shortest discharge time compared to pure paraffin which has the longest discharge time. Also, a solidification point is relatively affected by the nano-TiO₂,

 Fe_2O_3 addition as this point has tiny reduction. Besides, the composite materials cool down to temperature less than pure paraffin.

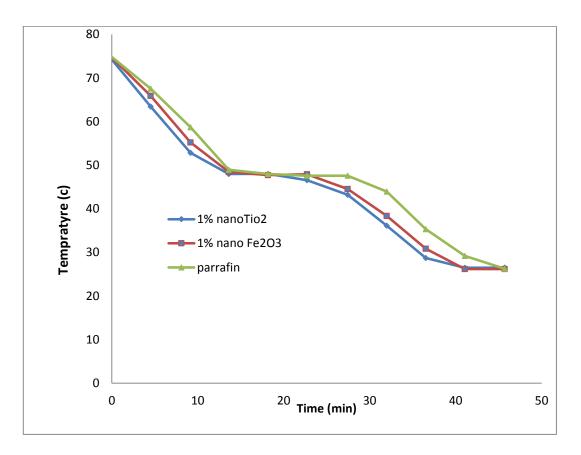


Figure 5.12. Discharging period effects on the studied materials.

The phase change temperature of the paraffin used is suitable for PVT applications in hot climates and can cool such systems efficiently. The results above indicate the possibility of using paraffin and nano-TiO₂ in mass fractions such as 1% or 2% to improve the efficiency of heat transfer and storage. These composite materials can be proposed for PVT applications in Iraq and considered as a suitable solution to reduce photovoltaic temperatures.

5.3. CONCLUSIONS AND RECOMMENDATIONS

Recently, the world has moved to rely more on clean energy and renewables to get rid of environmental pollution caused by fossil fuels due to emissions of gases, as it is not sustainable and suffers from price fluctuations, which causes economic and

political problems among countries, such as (solar energy, wind energy, fuel energy etc.). Renewable energy is characterized by being abundant and free of charge. One of the most reliable renewable energies is solar energy. But there are obstacles in using solar energy, the most important of which is storing energy, because solar energy is that it is available only with the presence of the sun, so we need to store it. Therefore, researchers have tended to find the best materials for use in storage, and one of the latest methods is to use phase-change materials, especially in PV/Tapplications, due to their high energy storage capacity in the form of latent heat. But one of the drawbacks of this material is its low thermal conductivity. Therefore, recent research indicated the addition of nanoparticles with high thermal conductivity to improve their thermophysical properties. In this work, Nano-TiO₂ and Fe₂O₃ was added to paraffin wax. Four samples of each Nano-type were prepared with proportions (0, 0.5, 1, 2, and 3). The viscosity of the wax increases when adding TiO₂, Fe₂O₃ nanoparticles, adding of 3% Nano- TiO₂, Fe₂O₃ the viscosity of the wax increases. This results are quite coincidence with recent research of Jawad AQ et al [1] [50]. The density of the wax increases when adding TiO₂, Fe₂O₃ nanoparticles, adding of 3% Nano- TiO_2 , Fe_2O_3 the density of the wax increases by 5.5% and 5.9% respectively similarly with research study of [26] [29] [50]. The thermal conductivity is improved when add Nano- TiO₂ to 40%, 75.5%, 87%, and 96.35% for 0.5, 1, 2, 3 mass fractions added, respectively. And improved when adds Nano- Fe₂O₃ to 30 %, 60.5%, 77% and 86.3% for same mass fractions added the mentioned above and this is quite similar behavior to similar mixture of the nanoparticles additions of [1] [21, 22] [26] [29].

The melting point relatively reduced by increasing the nano-TiO₂, Fe₂O₃ mass fraction in the composite material as well as the phase change period is reduced. In the solidification process, the solidification point reduced by increasing nano-TiO₂, Fe₂O₃ mass fraction as well as the discharge period is reduced. After the phase change period is finished the composite material temperature increase more that the case of pure paraffin in the melting process. The opposite is happened at solidification process, as the cooling temperature reduced by this addition. PCM-TiO₂ shows the highest melting point and lowest solidification point. The stability tests manifest high stability period. The compound of pcm - TiO₂ showed higher

stability. where With 50 melting-solidification cycles, a deterioration in a thermal conductivity relatively appears low, and this decrease reaches an average of 1.81%, 2.06% for the case of adding 1% mass fraction of the nanoparticles from TiO₂, Fe₂O₃, respectively and increases with the increase in the percentage of added particles by weight to reach 2.32 %, 2.4% for the case of adding 3% TiO₂, Fe₂O₃ nanoparticles. The experimental examination for these composite materials insures that these materials can be used in PVT application in hot weathers countries such as Iraq.

This study proved that the use of Nano–TiO₂ and Nano –Fe₂O₃ with Iraqi-made paraffin for a melting point and solidification of 40 $^{\circ}$ C is suitable for working in the Iraqi airspace in applications of thermal storage in PV/T systems. However, the study recommends the following:

- 1- Using other nanomaterial's to be added to the paraffin wax that has a higher thermal conductivity than the one used for the two materials used in this study, such as carbon nanotube CNT, gold and silver.
- 2- Using other types of phase-shifting materials that have a high thermal storage capacity and a melting point in the range from 40° C to 45 ° C.
- 3- Study the possibility of reducing the mixing time and the conditions necessary to reach this goal.
- 4- Finding types of nanoparticles that can reduce the melting point and solidification to be added to the paraffin wax types with a melting point in a range higher than 45 C°.
- 5- Study the effect of the tank type and the internal fins on the efficiency of heating and cooling on the efficiency of the used Nano.

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RESUME

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