

Thermophysical Property Modeling of LA/MF Encapsulated Phase Change Material Slurry as a Heat Transfer Fluid

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Abstract

This study aimed to obtain a heat transfer fluid (HTF) using water as the carrier fluid by encapsulating a phase change material (PCM) and to perform hydrothermal characterization of the aqueous solution containing encapsulated PCM (ePCM) in different volume ratios (ePCM-S) as a heat transfer fluid (HTF). Lauric acid (LA) was used as the core PCM in this study due to its melting temperature falling within the nominal operating cell temperature range. LA, encapsulated with a melamine formaldehyde (MF) shell via the in-situ polymerization method, was incorporated into the carrier fluid (water) at volume concentrations of 1%, 1.5%, and 2%. With 1% MF/LA ePCM-S, the specific heat capacity of the HTF in the melting range at 318 K could be improved by 7.58% at the expense of a marginal 2.9% increase in viscosity. It has been demonstrated that ePCMs improve the thermal properties of CF and that ePCM-S can be used as an enhanced HTF when the inlet and outlet temperature range matches or falls within the melting range of the PCM.

1. Introduction

Today, due to the rapid depletion of fossil fuels [1–4] and the rapidly increasing energy demand [5,6], the existing potential will not be able to meet the rapidly increasing energy needs for a long time [7]. The negative environmental impacts of fossil fuels [8,9] also pose a major challenge. Consequently, research into developing new technologies for using renewable energy sources and achieving higher efficiency in existing technological applications has become increasingly important [10,11]. This need has increased further following recent developments such as the COVID-19 pandemic and its ongoing effects on the global energy system [12] and the reduction of greenhouse gas emissions, as well as growing international calls for the promotion of renewable energy sources [13]. Indeed, [14] reported that the share of renewable energy in global energy production, which was only 13.5% at the beginning of 2009, rose to 19% by the end of 2011 with a rapid increase. Extensive research has been conducted on all renewable energy sources, and significant progress has been made [15]. Undoubtedly, solar energy is the most promising in terms of both total potential and accessibility [16,17] and in terms of the diversity of applications beyond energy production, such as drying, dehumidification, desalination, distillation, etc. [18] it is the most prominent [19].

Among solar energy applications, liquid-cooled PVT systems are finding increasingly wider application. While it has been shown that PVT-water systems provide approximately a 15% increase in electrical efficiency compared to traditional PV [20], the quest to develop new and high-performance HTFs is gaining momentum [21]. The main idea has always been to recover waste heat and prevent efficiency losses with as little pumping power as possible, while also minimizing expenditure on HTF and related system components. In this context, the new HTF should have a high specific heat capacity, be inexpensive and readily available, and not require significant pumping power. Numerous studies conducted to date have shown that water-based special-purpose fluids are quite good alternatives.

Thermal energy storage, as shown in Figure 1, involves active or passive cooling in PVT systems[24] or their effective [25].

Depending on system characteristics such as capacity, installation location, and desired thermal efficiency, various HTF's ranging from tap water to water-based solutions of different chemicals have been used for energy storage and transfer. Due to their higher thermal conductivity compared to CF, the use of nanofluids as HTF has become widespread and proliferated. Currently, nanofluids are widely used in different applications. Their use in heat exchangers and PVT systems is also increasing. However, nanofluids exhibit different characteristics in terms of performance and applicability. There is a lot of research on determining the best nanofluid that can be used in PVT systems [26,27]. Among these are new types of hybrid nanofluids containing multiple dispersed nano-materials within CF [28].

Single-phase fluid systems require circulation at high flow rates due to their lower energy density. This consequently increases the required pumping power and renders the efficiency gains achieved through system cooling meaningless. It has been suggested that increasing the thermal capacity of HTF by providing latent fusion heat in addition to sensible heat content could solve this problem [29]. However, during flow, the solid-liquid or liquid-gas phase change of the HTF is sometimes impractical or causes significant problems, making it unfeasible. For this reason, it has been considered to add phase change materials (PCMs) to the base fluids used as carriers so that the phase change occurs only in a portion of the fluid and the problems caused by the phase change can be eliminated. This approach is also effective in overcoming technological limitations and handicaps associated with solar collectors [30]. PVT systems using ePCM-S as the working fluid are still a relatively new topic, considered to be in the early stages of research. However, as in the case of PV, ePCM-S was only available on a laboratory scale about twenty years ago, but over the years, technology has made it possible to develop these special fluids as an applicable and efficient option for heat transfer processes [31–33].

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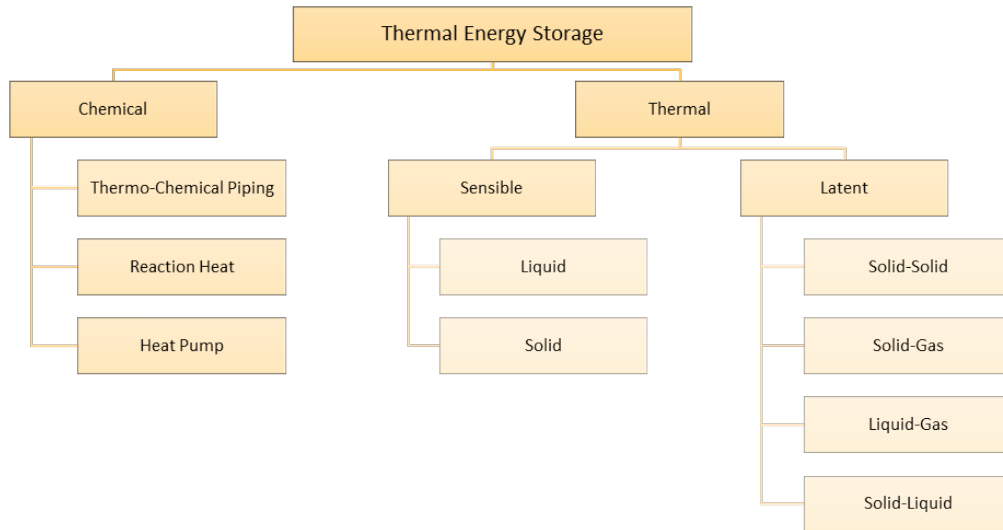


Figure 1. Thermal energy storage systems [22,23]

Thus, it will be possible to extract more heat within the same temperature range by utilizing latent heat. As can be seen, the amount of heat stored per unit mass/volume of an environment, i.e., the storage density, is significantly higher in latent heat storage (☞, provided that a phase change occurs within the temperature difference range) compared to sensible heat storage. This increase in the amount of energy stored per unit volume can be as high as 5 to 14 times greater [22,34]. Furthermore, certain properties such as thermal conductivity and storage capacity can be further enhanced by adding nanoparticles to PCM [35].

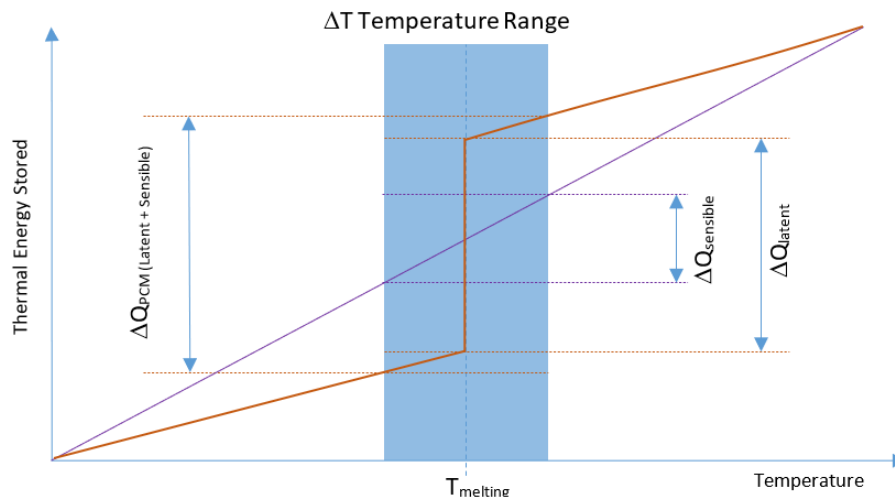
Particularly in recent years, advances in technology, especially in nanotechnology, have led to the incorporation of PCMs into HTF, emerging as an alternative that will serve to meet the need for HTFs with better properties [36]. With the inclusion of PCM, latent heat storage becomes possible in addition to sensible heat storage, which increases the thermal storage capacity of the HTF. Thus, circulation at lower flow rates is sufficient for the same heat transfer rate [37,38].

The heat transfer mechanism in a phase-change medium is non-linear and quite complex, making it difficult to fully evaluate the performance of a phase-change thermal system [39] and requiring further research and investigation. The total storage capacity of a phase change system is equal to the sum of the sensible and latent heat storage capacities and is expressed as follows [22]:

$$Q_{total} = Q_{sensible} + Q_{latent} \quad (1)$$

$$Q_{total} = \int_{T_i}^{T_e} mC_p dT + \psi m \Delta h \int_{T_e}^{T_o} mC_p dT$$

Here, ψ is the percentage fraction of PCM in the liquid. The duration and temperature range of the phase change process vary depending on the mass, latent heat capacity, and thermal conductivity of the PCM, as well as other factors that improve heat transfer [40].

Figure 2. Comparison of the amount of heat stored as latent and sensible heat in heat storage systems at a given temperature difference of ΔT [24,41]

In a heat transfer process shown in Figure 2, if a phase change occurs at a melting temperature (T_e) between the initial temperature (T_i) and the final temperature (T_f), the total amount of heat transferred is equal to the latent heat of phase change plus the heat of fusion, the total amount of heat transferred is greater than that in a process without phase change by the latent heat of phase change and is obtained using Equation 2 [42].

$$\int_{T_e}^{T_i} mC_p dT + mH_e + \int_{T_s}^{T_e} mC_p dT = m [H_e + C_k(T_e - T_i) + C_s(T_s - T_e)] \quad (2)$$

However, the full implementation of phase change materials in heat transfer fluids is far from ideal due to various operational problems such as pipe clogging and low thermal conductivity. These problems have significantly limited or delayed the usability of phase change materials. As a result of technological advances and new approaches to these problems, micro-/nano-encapsulation technology has been developed. This technology enables PCMs to be incorporated into carrier fluids by encapsulating them, thereby offering the possibility of largely resolving these operational problems.

Special fluids prepared with ePCMs and their incorporation into HTF, called ePCM Slurry (ePCM-S), have rapidly become widespread and gained momentum. Encapsulation of PCMs eliminates [43] and eliminates other issues caused by volume changes and low thermal conductivity [44], thereby improving performance. Furthermore, encapsulation ensures that the phases remain separate during the heat transfer process [38], thus, an ePCM-S offers all the advantages of two-phase flow at the micro level, while the flow itself remains single-phase at the macro level [45].

In recent years, as a result of increasing research in this field, encapsulation technologies have been continuously developing, the scope of application has been expanding, and the materials used have been diversifying. Today, commercially produced encapsulated phase change materials (ePCM) are available on the market [38] and are readily available for use in many applications. As a result, encapsulated phase change material solutions (ePCM-S) are used as HTF in a wide range of applications, including the cooling of PVT systems, and the number of scientific studies in this field is rapidly increasing. Currently, ePCM-S have been developed to increase transfer rates and have found applications in various fields such as heating, cooling, air conditioning, heat exchangers, and ventilation ([46,47]. [48,49]. However, their use in PVT systems is relatively new, and very little research has been conducted to date on their use in cooling PV cells [50] and in solar collectors [30][51].

The thermodynamic properties of fluids used to extract heat from PV systems are generally important. The specific heat capacity and viscosity of the fluid used are primary determinants of the pumping power required to circulate the fluid in the system. For fluids such as air and water, the flow rates corresponding to the total heat value that must be extracted from the system increase in proportion to their specific heat capacities. Increased flow rate requires more power (fan power or pump power) to circulate the fluid. Research on the applications of PCMs and ePCMs has also included PVT systems. While there are studies on systems that directly use PCMs, generally referred to as PVT/PCM in the literature, PVT systems that use ePCM-S as the working fluid are the most prominent systems in terms of benefiting from the advantages offered by PCMs while eliminating their disadvantages. The pumping power required to extract the same amount of heat with ePCM-S and pure water is much higher for pure water.

ePCM-S helps increase the amount of energy stored per unit volume by 5 to 14 times because it stores part of the energy it gains during heat transfer as latent heat [22]. Therefore, the same amount of heat can be extracted with less fluid or at a lower flow rate, i.e., with up to 5 times less pumping power. For example, to extract 1000 Watts of heat, nearly five times the pumping power is required with pure water. Furthermore, while the relationship between pumping power and heat extracted is parabolic for pure water, it is nearly linear for ePCM-S.

Another parameter is viscosity and fluid velocity; the higher the viscosity of the fluid, the more power is required to circulate it in the system, so it is desirable to use a fluid with low viscosity.

52[52] investigated the thermal conductivity of ePCM-S containing ePCM at different concentrations by weight and reported that each addition of ePCM resulted in greater thermal conductivity. A 0.5% ePCM content caused an increase of nearly 15% in the thermal conductivity of the fluid. However, since it also increases the viscosity of the fluid, and thus the pumping power required to circulate the fluid in the system, the optimal ePCM content may vary depending on the shell material and particle size, but a weight percentage of approximately 2 to 5% has been reported as optimal.

53[53] reported that using ePCM-S as the working fluid in PVT systems at approximately the same pumping power resulted in an improvement in both the thermal and electrical efficiency of the systems.

Specifically for this study, when considering the core material of a capsule to be used in a PVT system, from a thermodynamic perspective, it is desirable that the latent heat of fusion required for the melting of a unit volume be as high as possible, as this will maximize the amount of heat that can be stored per unit volume. Furthermore, since the solid-liquid phase change occurs at a constant temperature, this temperature value should be equal to the optimum operating temperature of the system to be used. Thirdly, since it will be located within a closed system, it is desirable that the volumetric change between phases be very small and that the vapor pressure be low. High thermal conductivity and density, as well as stable and uniform phase changes over time, are preferred. From a kinetic perspective, nucleation rate and crystal growth rate should be high. [54–58] should be non-toxic, have a long economic life, be harmless to health, be readily available, and have a lower cost relative to the benefits it provides.

The aim of this study is to synthesize ePCM and characterize the thermophysical behavior of ePCM-S comprising %1, %1.5, and %2 MF/LA ePCM.

2. Material and Method

Phase-changing materials increase thermal capacity by up to four times when added to secondary heat transfer fluids because they extract latent heat required for phase change in addition to sensible heat during heat exchange. However, they cannot be widely used due to problems such as clogging or narrowing the system because of limited heat transfer rate and adhesion to pipe and channel surfaces in the solid phase. For example, salt hydrates flow in humid areas, and changes in humidity can cause changes in the number of hydrates. When hydrocarbons melt, their viscosity may decrease, allowing them to flow through the walls of the building. They can also increase the volatile organic compound content of the air above the limit values through evaporation. To overcome these problems, encapsulation of phase change materials is a viable option [31,59].

Encapsulation also offers solutions for some fundamental problems associated with PCMs, such as low thermal conductivity, volumetric change, and unstable melting. The capsule consists of a polymeric shell and a phase-change material (core) enclosed by this shell. Shell materials should be selected from an inert material relative to the core material. Gelatin, gum arabic, alginate, agar, starch, and other natural polymers, as well as synthetic polymers such as polyamide, polyester, polyethylene glycol, polystyrene, stearic acid, and styrene maleic anhydride, are among the materials used as shell materials [59].

Capsules can be customized according to specific needs in terms of particle size and structure, core material, shell material, shell thickness and properties, additives, and permeability. This versatility enables their application across a wide range of fields, from engineering to medicine, pharmacy to cosmetics, textiles to food, electronics to construction materials, and even agriculture. [38].

As a result of the literature review, the melting temperature of 42–44°C, the latent heat of fusion of 178 kJ/kg, the thermal conductivity of 0.1921 at 72.5°C and 0.1852 at 90°C, and the density of 862 kg/m³ at 60°C and 1007 kg/m³ at 24°C are suitable for use as a core PCM. Melamine (99% pure) and formaldehyde (37% aqueous solution by weight) were used as the shell material. Surface-active agents (surfactants) such as Sodium Dodecyl Sulfate (SDS), Twin 80, and CTAB were used as emulsifiers. Resorcinol (1,3-benzenediol, 99% pure) was used as a binder for the melamine formaldehyde shell, and pure ammonium chloride was used as a core-forming agent.

The properties of the core and shell materials of ePCM are given in Table 1 and Table 2.

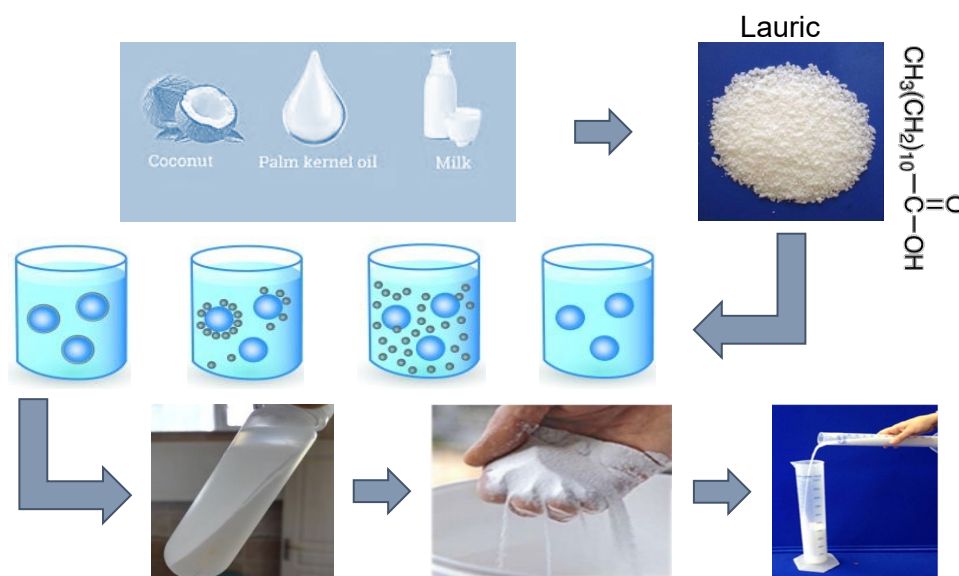


Figure 3. Production of ePCM-S

Table 1. Properties of Melamine Formaldehyde [60]

Parameter	Value
Thermal Diffusion	0.28 mm ² /s
Density	1.49 g/cm ³
Decomposition Temperature	350 °C
Specific Heat Capacity	1200 J/kgK
Thermal Expansion	6E-06 1/K
Thermal Conductivity	0.5 W/mK
Elastic Modulus	7.0 GPa
Tensile Strength	30 MPa

Table 2. Properties of Lauric Acid [60]

Parameter	Property
Solidification Temperature (K)	316
Melting Point (K)	318
Phase Change Enthalpy (J/kg)	183200
Specific Heat Capacity (J/kgK)	2180 (solid) / 2390 (liquid)
Thermal Conductivity (W/mK)	0.1921
Density (kg/m ³)	940 (solid) / 883 (liquid)
Thermal Diffusivity	6.5E-05 mm ² /s
Thermal Expansion	9.6E-04 1/K

2.1. Encapsulation method

Although microencapsulation technology has been known for decades, the process was considered too expensive for practical application. However, thanks to the development of new synthesis methods and the improvement of existing methods with new techniques and technological capabilities, costs have fallen, and microencapsulated PCMs have found various fields of application. New fields of application are being added every day. To date, approximately 25 chemical, physical, and physicochemical capsule synthesis methods have been reported in the literature. However, among these methods, the most widely used group is chemical methods, and among chemical methods, in-situ polymerization is the most developed and commercialized [61] and the most widely used [62] method.

The in-situ polymerization method enables the production of the highest quality microcapsules in terms of diffusion tightness of their walls and encapsulation of particles ranging in size from 5 to 100 µm. For this reason, in situ polymerization methods are widely used in the manufacture of microencapsulated phase change materials [63].

In-situ polymerization is a method that combines two immiscible liquids, such as water and an organic solvent, which contain complementary, directly effective organic intermediates that react with each other to form a pre-condensate. All polymerization occurs in a continuous phase rather than in two phases, as in interfacial polymerization. The distinguishing feature of in-situ polymerization, a method very similar to interfacial polymerization, is that there are no reactants in the core material [63]. In-situ polymerization, a chemical method in which the monomer and catalyst dissolved in the continuous phase are separate from the core material and the prepolymer gradually forms on the surface of the core material as the polymerization reaction progresses [52], has been used in numerous encapsulation studies [64].

Within the scope of the thesis study, considering the existing laboratory facilities and the applicability of the production method, it was determined that the in-situ polymerization method is suitable for the production of micro/nano capsules to be used in my thesis study. Capsule synthesis was also performed using the in-situ polymerization method. The synthesis procedure for in-situ polymerization and the production process followed in the thesis study are given below.

2.2. Synthesis procedure for the in-situ polymerization method

Although the procedures vary slightly depending on the starting materials and formulations, the basic steps of the in-situ polymerization method for encapsulating a water-immiscible oil have been outlined by 61[61] as follows:

- Distributing the oil phase (O/W, oil-in-water) in water containing the reactants (i.e., melamine-formaldehyde or urea-formaldehyde resin prepolymer) to form a stable emulsion with the desired oil droplet size
- Polymerization from the aqueous phase and precipitation of the monomer/oligomer onto the oil phase
- Shell formation and curing ([61])

In the first stage, oil-in-water or water-in-oil emulsions are prepared depending on the structure of the core material. After adding the shell material to this mixture, the pH value of the environment is lowered to achieve condensation and phase separation. After the shell material begins to bond to the core surface, melamine is added to the environment and the temperature is increased to harden the shell material. In this way, the core material is encapsulated.

During the shell formation stage, the droplet rate and the mixing speed of the emulsion have a decisive effect on the capsule size, sphericity, and physical structure of the capsules. As the mixing speed increases, the capsule size decreases [62]. However, the temperature of the reaction environment is also among the important parameter factors.

Within the scope of the study, microcapsule synthesis was performed using in situ polymerization, with lauric acid as the core material and melamine formaldehyde as the shell material. The general steps of the method were as follows. 100 g of lauric acid and 15 g of surfactant (SDS, CTAB, and Tween 80) were dissolved in 100 mL of pure water. The mixture was then stirred in 1000 mL of pure water at 8°C using a magnetic stirrer.

Table 3. Components and Quantities Used in Pre-polymer Formation

Component	Quantity
Melamine (g)	30
Deionized Distilled Water (mL)	100
Surfactant (CTAB) (g)	15
Formaldehyde 37% (mL)	60

After dissolving 30 g of melamine and 37% formaldehyde in 100 mL of pure water in a separate flask, the pH was adjusted to 8.5-9 with ethanolamine and stirred for 1 hour to prepare the pre-polymer. The materials and quantities used in the preparation of the pre-polymer are listed in Table 3.

The melamine-formaldehyde mixture placed on the drip funnel was slowly added (400 drops/minute) onto the oil emission. The pH of the medium was adjusted to 5.5 with a 10% ammonium chloride solution and refluxed at 65°C for 2 hours. After stirring for 30 minutes, the mixture was washed with ethyl alcohol and water, and the resulting capsules were dried in an oven at 40° C for 24 hours and stored. These steps were repeated until a sufficient amount of capsules was obtained.

3. Property Characterization and Modeling

3.1. Encapsulation ratio

The encapsulation ratio (ER) indicates the ratio of the core and shell materials that form the capsule. More accurately, it indicates the amount of core material inside the microcapsule [65]. It is the percentage ratio of the latent heat of encapsulated PCM determined by DSC analysis ($\Delta H_{\text{micro-PCM}}$) to the latent heat obtained for the pure core material (ΔH_{PCM}). It indicates the measure of an PCM's effective performance within the capsule and is calculated as shown in Equation 3 [37,38,66,67].

$$ER = \frac{\Delta H_{\text{erime,kFDM}}}{\Delta H_{\text{erime,FDM}}} \quad (3)$$

The percentage value calculated using the equation 3 expresses how much of the capsule's weight consists of PCM. Thus, it can be said that the remaining part of the capsule structure consists of shell material. It is observed that as the surface areas and/or shell thicknesses of encapsulated PCM materials increase, the encapsulation ratio decreases.

3.2. Encapsulation efficiency

For a fully reversible PCM, the latent heats of melting and crystallization (freezing) must be the same. A difference between these two values indicates that the PCM has an excessive cooling problem or mismatched melting and solidification processes.

$$EE = \frac{\Delta H_{erime,kFDM} + \Delta H_{donma,kFDM}}{\Delta H_{erime,FDM} + \Delta H_{donma,FDM}} \times 100 \quad (4)$$

Encapsulation efficiency (EE) is defined as the ratio of the sum of the latent heat of fusion and solidification of ePCM to the sum of the latent heat of fusion and solidification of PCM, [65,67] expressed as a percentage as given in Equation 4. High encapsulation efficiency means high mechanical strength and leak-tightness. The phase change enthalpy of ePCM is a strong function of the encapsulation ratio and encapsulation efficiency [68], and encapsulation efficiency is a critical parameter in determining the amount of PCM to be encapsulated [37].

Table 4. PCM and ePCM Information

Property	PCM	ePCM
Solidification Temperature (K)	317	316
Melting Temperature (K)	323	319
Phase Change Enthalpy (J/kg)	183200	125,290
Specific Heat Capacity (J/kgK)	2180	2018.79
Thermal Conductivity (W/mK)	0.1921	0.1784
Density (kg/m ³)	883 (solid) – 940 (liquid)	1094.4
Viscosity (Pa·s)	0.008 (liquid)	-
Encapsulation Ratio	-	68.39

Further information can be found in [60].

3.3. Solution Characterization and Determination of Hydrodynamic Properties

Solution characterization can also be calculated using certain correlations based primarily on CF and ePCM properties and the concentration of ePCM in CF [69] or measured experimentally. When the thermophysical properties of CF and ePCM are clearly known, all properties of ePCM-S can be obtained with high accuracy using correlations.

3.3.1. Density

The density of ePCM-S depends on the density of CF, as well as the density of the core PCM and the shell material. In this context, the density of ePCM-S is primarily determined by the density of ePCM, calculated based on the DSC results obtained separately for PCM and ePCM or determined experimentally, and depends on the percentage fraction of ePCM in CF and the density of CF.

Since density is also a function of temperature, the densities of the core and shell materials will differ at different temperatures. Thus, the density at a specific temperature is obtained as follows:

$$\rho(T) = \rho_0 - \left((\beta * \rho_0 * (T - T_{kati})) + 1 \right) \quad (5)$$

Here, β represents the thermal expansion coefficient, T_s represents the solidification temperature, ρ_0 represents the density at temperature T_s .

In this context, the density of ePCM-S must also be expressed as a function of temperature as follows:

$$\rho_{ePCM-S}(T) = \rho_{su}(T) * (1 - \phi) + \rho_{kFDM}(T) * \phi \quad (6)$$

Since the synthesis process was carried out at a temperature where PCM was in the liquid phase and the phase change within the shell occurred in the capsule shell, where the volume change was independent of the PCM phase, it is acceptable to take the density of PCM as the liquid density. In this regard, the change in ePCM-S density with temperature depends only on the change in CF density with temperature and the thermal expansion coefficient of the shell material MF.

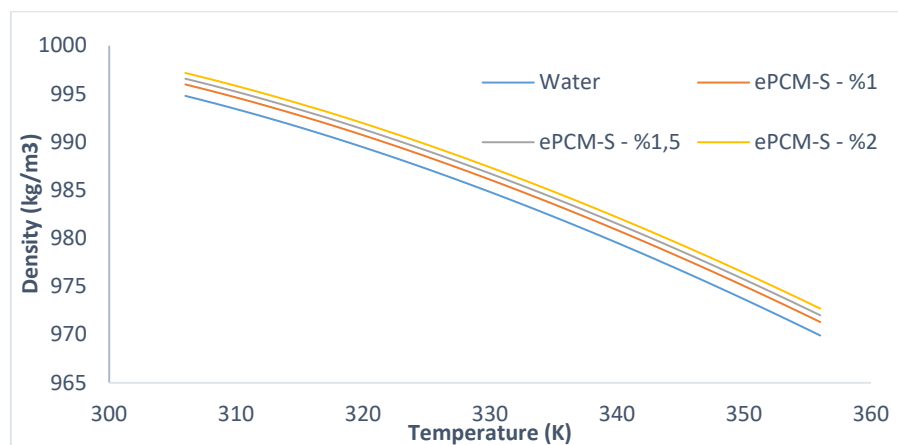


Figure 4. Change in the bulk density of the slurry at different temperatures versus capsule concentration.

Considering the density change of CF and the thermal expansion coefficient of MF, the change in the bulk density of the slurry at temperatures corresponding to a range of 306K and 356K, which corresponds to a solid temperature below 10K and a liquid temperature above 25K, is shown in Figure 5 for different capsule concentrations.

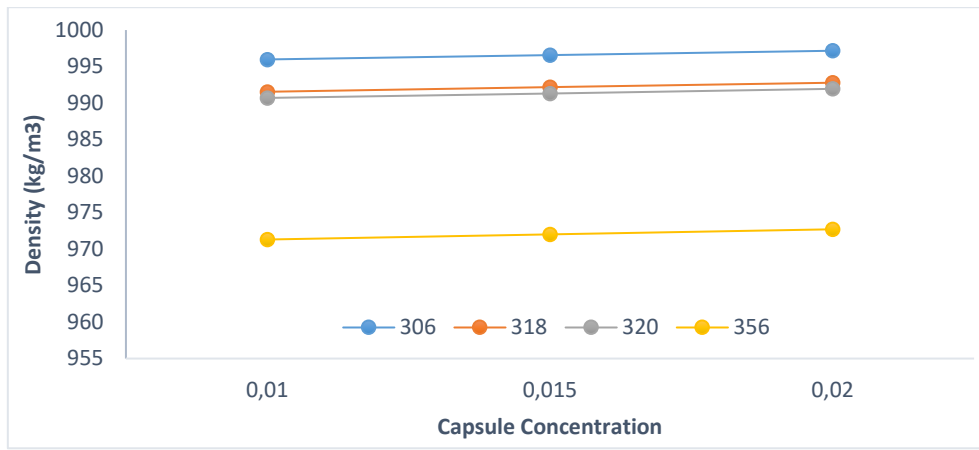


Figure 5. Change in bulk density of the slurry against temperature for different capsule concentrations

As seen in the figure, despite being a very small amount, the relative density of the ePCM slurry is higher than that of CF due to MF's 1.5 times higher density.

3.3.2. Specific heat capacity

The heat capacity of the prepared ePCM-S ($C_{p,solution}$), can be calculated using a composite approach based on the previously calculated heat capacity of ePCM and the mass fraction of ePCM in CF, using the following equation [70,71].

$$C_{p,ePCM-S} = W_{kapsül} C_{p,kapsül} + W_{su} C_{p,su} \quad (7)$$

The same calculation can also be performed using volumetric fractions by including temperature-dependent density values in the equation:

$$C_{p,ePCM-S} = \frac{(1 - \phi) * (\rho_{su} * C_{p,su}) + (\phi * (\rho_{ePCM} * C_{p,kFDM}))}{\rho_{ePCM-S}} \quad (8)$$

Here, ϕ represents the volumetric concentration of ePCM within the CF.

As the fraction of ePCM in the CF increases, higher heat capacity is obtained [31]. The use of ePCM in thermal circuits greatly increases the effective specific heat of the HTF and reduces the temperature rise [72]. In contrast, the increase in viscosity is relatively negligible. The pumping power required to extract the same amount of heat was reported to be much lower in ePCM-S than in pure water [73].

To determine the effective specific heat of an ePCM-S, the specific heat capacity of the capsule must first be determined. The properties of mixtures are obtained in direct proportion to the fractions of the liquids forming the mixture, depending on the properties of the components. The specific heats of the ePCMs synthesized and characterized within the scope of the thesis work have been determined and are presented above.

Normally, the specific heat capacities of PCM and ePCM are smaller than that of water, but the effective specific heat capacity shows a sudden increase in the phase change temperature range due to the distribution of latent heat absorbed at constant temperature during phase change over C_p . Accordingly, the change in specific heat of ePCM-S with previously determined volume concentrations of 1%, 1.5%, and 2% with respect to temperature is shown in Figure 6.

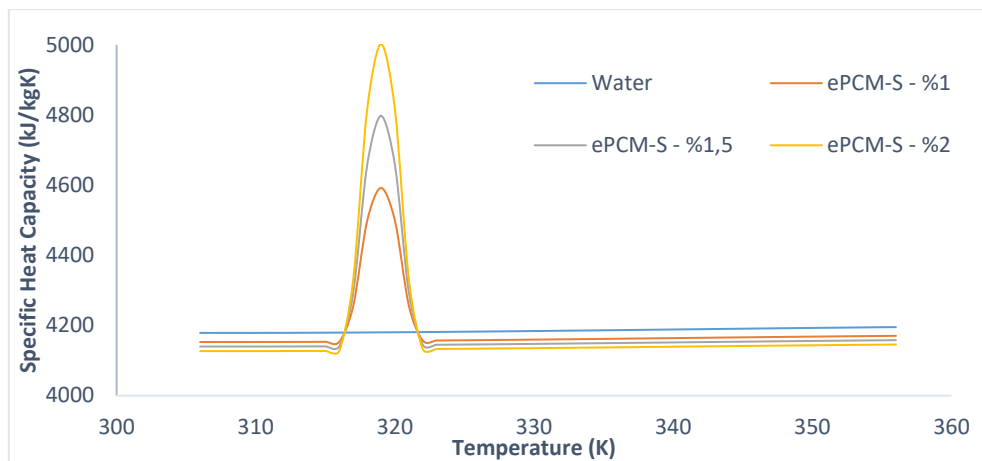


Figure 6. Temperature-dependent specific heat of water and ePCM-S with 1%, 1.5%, and 2% concentrations

As seen, the effect of the latent heat of phase change on the specific heat capacity of ePCM-S is significantly large. This behavior is consistent with the specific heats of ePCM-S with different weight or volume fractions reported in previous numerical and experimental studies [70,74,75].

When this effect is linearized, the effective specific heat capacity of ePCM-S at different volume concentrations varies depending on whether it is inside or outside the phase change region, as shown in Figure 7.

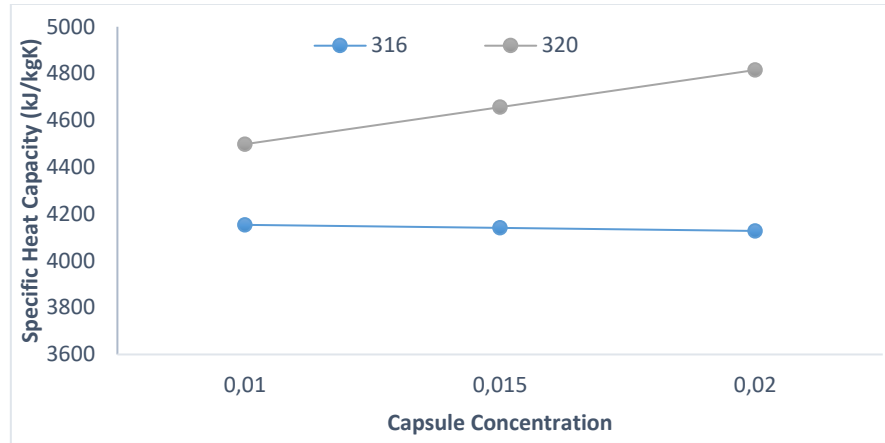


Figure 7. Change in linearized effective specific heat capacity with ePCM concentration, in and out of phase change range

3.3.3. Thermal conductivity

Thermal conductivity is an important parameter affecting the overall thermal performance of a PVT system. Therefore, it is desirable for thermal conductivity to be as high as possible. However, it is known that the thermal conductivity of almost all PCMs is lower than that of water. However, this is true in the static state; due to the particulate structure of ePCMs, the effective thermal conductivity they create within the CF is higher.

The thermal conductivity of ePCM-S in a static state can be calculated using the following equation obtained using Maxwell's equations [63,76].

$$k_{ePCM-S} = \frac{2k_{cf} + k_{ePCM} + 2W_{ePCM}(k_{ePCM} - k_{cf})}{2k_{cf} + k_{ePCM} - W_{ePCM}(k_{ePCM} - k_{cf})} \quad (5)$$

A similar formulation is given below [16,77]:

$$\frac{k_{ePCM-S}}{k_{cf}} = \frac{2 + \frac{k_{ePCM}}{k_{cf}} + 2\phi \left(\frac{k_{ePCM}}{k_{cf}} - 1 \right)}{2 + \frac{k_{ePCM}}{k_{cf}} - \phi \left(\frac{k_{ePCM}}{k_{cf}} - 1 \right)} \quad (6)$$

When the equation is rearranged [70]:

$$k_{ePCM-S} = k_{cf} \left[\frac{2 + \frac{k_{ePCM}}{k_{cf}} + 2\phi \left(\frac{k_{ePCM}}{k_{cf}} - 1 \right)}{2 + \frac{k_{ePCM}}{k_{cf}} - \phi \left(\frac{k_{ePCM}}{k_{cf}} - 1 \right)} \right] \quad (7)$$

However, the thermal conductivities of ePCM-S materials depend on many other factors, such as particle size, thermal expansion coefficient, and Brownian effects, and these relationships do not account for the effects of these factors. These parameters are generally time-dependent, requiring the effective thermal conductivity of ePCM-S to be a time-dependent function [78].

Consequently, the effective thermal conductivity should be expressed as the sum of the steady-state thermal conductivity and the enhancement factors [79]:

$$k_{eff} = k_{static} + k_{brownian} \quad (8)$$

Here, steady-state thermal conductivity is [80]:

$$k_{static} = k_{cf} * \left[1 + 4.4 \text{Re}^{0.4} * \text{Pr}^{0.66} \left(\frac{T}{T_{freeze}} \right)^{10} \left(\frac{k_{ePCM}}{k_{cf}} \right)^{0.03} \phi^{0.66} \right] \quad (9)$$

while the Brownian motion effects are:

$$k_{brownian} = (5 \times 10^4) \beta \phi \rho_{cf} C_{p,cf} \sqrt{\left(\frac{K_{boltz} * T}{\rho_{ePCM} * d_{ePCM}} \right)} * f(T, \phi) \quad (10)$$

is expressed as follows. Here, β is a constant, where:

$$\beta = (5 \times 10^4) (Z_1 * (100 * \phi)^{Z_2}) \quad (11)$$

$f(T, \Phi)$, which appears in the equation 10, is the temperature function is defined as follows:

$$f(T, \Phi) = ((c_1 * \Phi + c_2) * T) + (c_3 * \Phi + c_4) \quad (12)$$

Effective thermal conductivity is also expressed as the static thermal conductivity multiplied by a coefficient that accounts for all the effects mentioned above [8]:

$$k_{eff} = f * k_{ePCM-S} \quad (13)$$

In this approach, f [8,81,82]:

$$f = 1 + B + \phi Pe_{ePCM}^m \quad (14)$$

$$\begin{cases} B = 0, m = 1.5 & Pe < 0.67 \\ B = 1.8, m = 0.18 & 0.67 \leq Pe \leq 250 \\ B = 3.0, m = \frac{1}{11} & Pe > 250 \end{cases}$$

$ePCM-S$ can be calculated based on the $ePCM$ concentration within $ePCM-S$ and the Peclet number, which represents the ratio of the diffusion transport rate to the advection transport rate. The Peclet number is:

$$Pe_{ePCM} = \frac{\gamma d_{ePCM}^2}{\alpha_{cf}} \quad (15)$$

is expressed as follows. Here, α is the thermal diffusion coefficient, γ is the shear velocity, and d is the $ePCM$ diameter.

Thermal conductivity was calculated separately for steady-state and flow conditions, taking into account the effects of Brownian motion, and are given in Figure 8 and Figure 9.

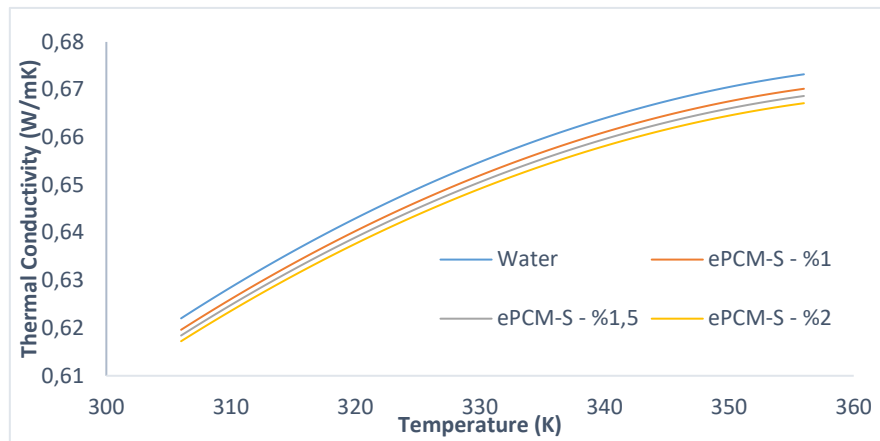


Figure 8. Temperature-dependent thermal conductivity of water and $ePCM-S$.

In a stationary state, $ePCM$ has a lower thermal conductivity than water due to its low thermal conductivity. However, in a flow state, the effective thermal conductivity of $ePCM-S$ is higher than that of water due to the particle effect.

Brownian effects, which vary proportionally to the number of particles moving in the fluid, can provide a greater improvement than the thermal conductivity of CF. However, considering the increases in viscosity and the required pumping power, it is generally operated with a particle content below 5%. This provides an improvement of between 10% and 30%.

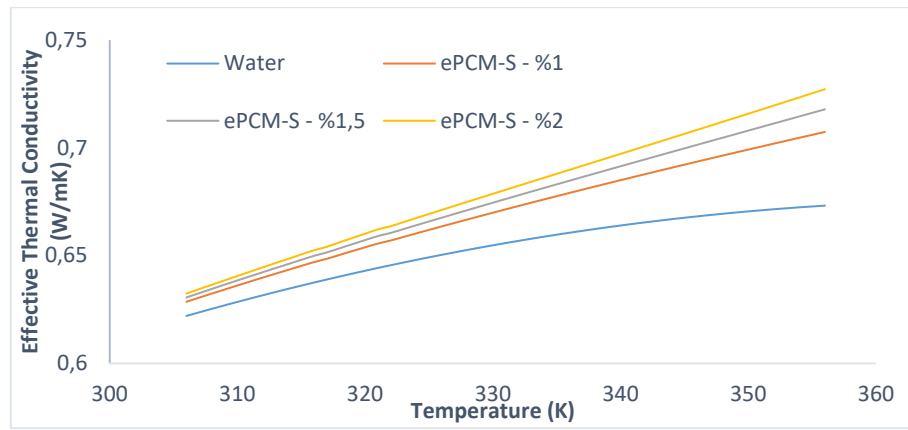


Figure 9. Change in effective thermal conductivity of water and ePCM-S with temperature under Brownian effects.

The effective thermal conductivity of the MF/LA ePCM-S synthesized in this study was calculated as shown in Figure 9. At a temperature of 318K, the thermal conductivity value of water is 0.640322W/mK, while the effective thermal conductivity of ePCM-S containing 2% ePCM at the same temperature, including Brownian effects, was calculated as 0.753273. Accordingly, the thermal conductivity improvement provided by ePCM is 17.6%.

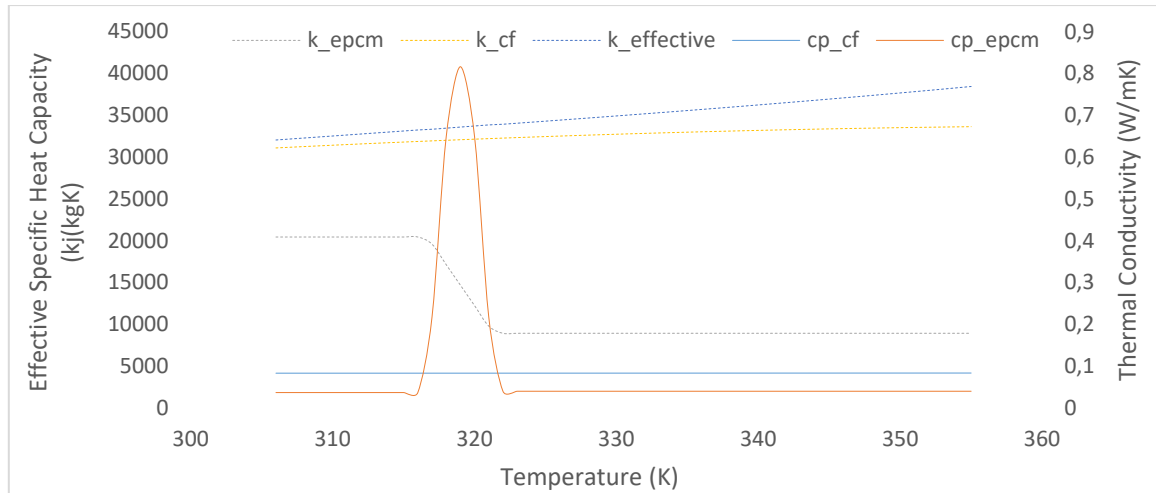


Figure 10. Specific heat capacity of MF/LA ePCM compared to water and thermal conductivity of 5% MF/LA ePCM-S

3.3.4. Viscosity and concentration determination

The idea behind cooling PVs is to maintain the optimum operating temperature, thus keeping electrical efficiency at the highest level. Cooling also positively affects the service life of PV modules and prevents thermal fatigue, but the amount of energy recovered through cooling is considered a threshold in terms of efficiency and applicability in the payback of cooling system operating and investment costs. Therefore, the share of the pumping power requirement in the recovered energy must be low. Consequently, the viscosity of the cooling fluids is of great importance, because increasing viscosity values lead to higher pumping power, and a larger portion of the recovered energy is spent compensating for the increased power demand, which causes cooling to become inefficient and ineffective.

The incorporation of hard particles such as ePCM into the CF will cause an increase in viscosity.

It is observed that the relative viscosity is quite small for values below 5%, and is very close to 1, especially for values such as 1% and 2%. Therefore, it was decided to prepare the solution at mixing ratios of 1%, 1.5%, and 2% so that the increase in the viscosity of the HTF would not be significant.

$$\frac{\mu_{\text{ePCM-S}}}{\mu_{\text{su}}} = (1 - \phi - A_{\phi}\phi^2)^{-2.5} \quad (16)$$

Here, ϕ is the volumetric concentration of ePCM in the solution. A_{ϕ} , which depends on the particle size, shape, and type, is an experimentally determined proportional constant (denoted by q in the Vand formulation).

The correlation given by 83 [83] has been used to calculate solution viscosities in the following general form by 84[84], 85[85] and [63] and has been reported to be valid. 63[63], in their studies on the properties of ePCM-S and their use in solar systems, stated that the A_{ϕ} proportion constant for commercial microcapsules is 3.7 [63].

$$\frac{\mu_{\text{ePCM-S}}}{\mu_{\text{su}}} = (1 - \phi - 3,7\phi^2)^{-2,5} \quad (17)$$

There is a high degree of agreement between the relative viscosity values obtained from the formula and the measurement results, especially at values below 25% by volume. 86[86] states that this ratio is 97.5%, but that the agreement decreases progressively with increasing concentration, for example, to 60% at 40% concentration and to 8.7% at 60% concentration, and therefore it is not reliable for high concentrations. 86[86] also created a variant of Equation 17 that provides better fit, expressed as:

$$\mu_{\text{eff}} = \mu_{\text{su}} + 2.5\phi + 10.05\phi^2 + 0.00273 \exp(16.6\phi) \quad (18)$$

ePCM-S viscosity values were calculated using Equations 16, 17, and 18 and compared for reference purposes. However, since ePCM-S remains within the high-fit region at low volume concentrations, the values obtained were quite close to each other.

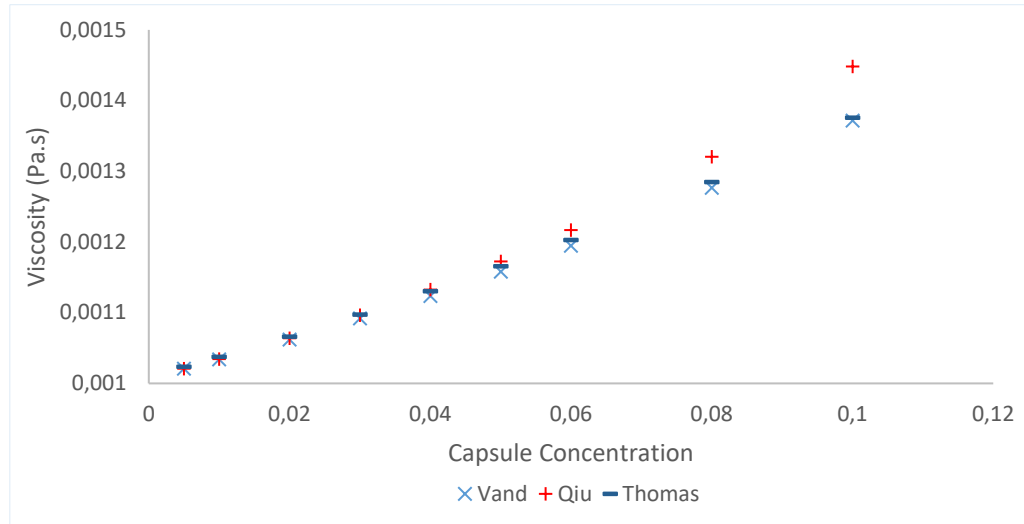


Figure 11. Values of viscosity models for MF/LA ePCM-S at 293K versus capsule concentration

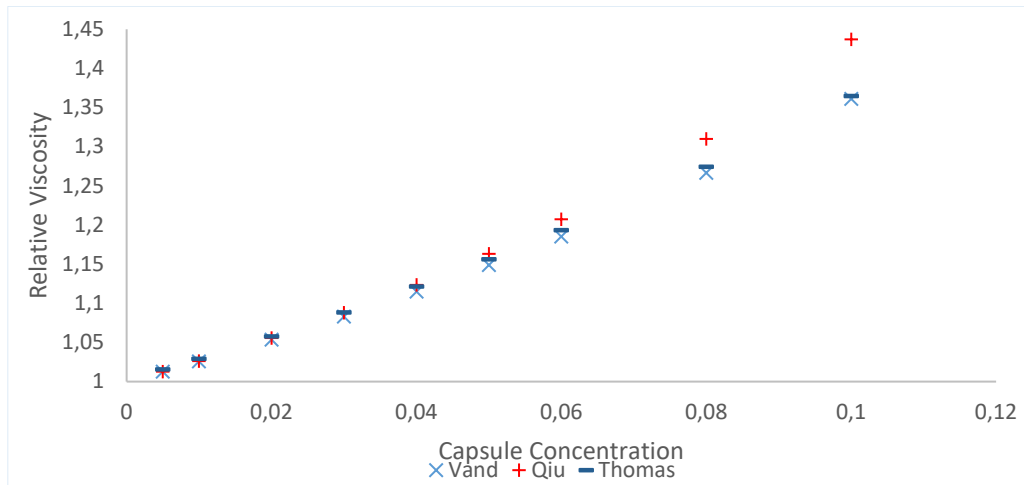


Figure 12. Relative viscosity of MF/LA ePCM-S at 293K versus capsule concentration

The results of the three correlations for this study are presented as absolute and relative viscosity in Figure 11 and Figure 12. As previously mentioned, the correlation proposed by 86[86] is a variant of the correlation by 83 [83], aiming to provide a better fit at higher concentrations. Although all correlation values showed good agreement with experimental measurements, the Vand correlation, updated with a corrected shape factor for commercial ePCMs (63), and[63], was found to exhibit the highest agreement. Furthermore, the difference between experimental and theoretical values was assessed to be small enough to fall within the error margin of the viscometer.

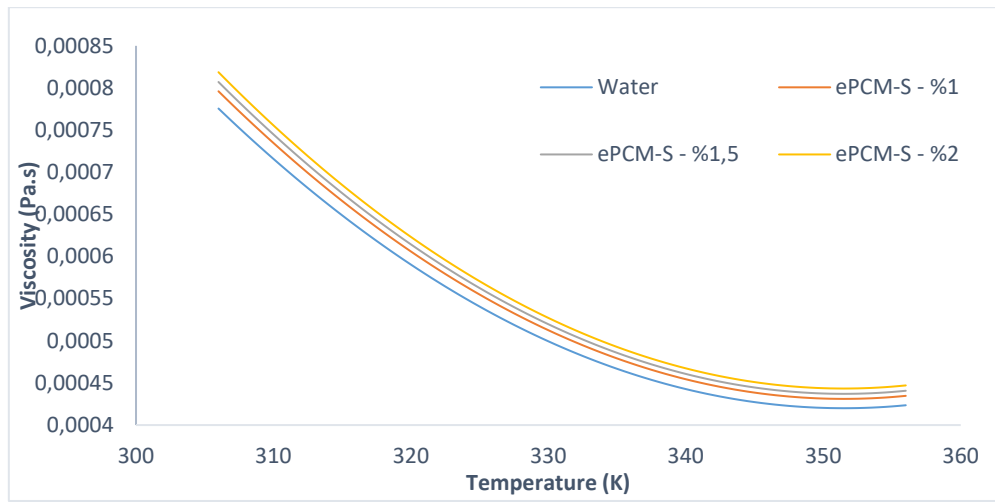


Figure 13. Temperature-dependent viscosity change of MF/LA ePCM-S

The change in viscosity of ePCM-S with concentrations of 1%, 1.5%, and 2% and water with temperature is shown in Figure 13.

3.3.5. Pressure drop and pumping power

Using the Darcy-Weisbach correlation, the theoretical pressure drop is calculated as follows [85,87,88] :

$$\Delta P = f_D \frac{L}{D} \frac{\rho v^2}{2} \quad (23)$$

Here, f_D is the friction coefficient, L is the total length of the circulation circuit, D is the pipe diameter, ρ is the bulk density, and v represents the average flow velocity of the HTF, and is expressed by:

$$v = \frac{\dot{m}}{\rho_{\text{ePCM-S}} \cdot \left(\pi \frac{D^2}{4} \right)} \quad (19)$$

Equation (Hata! Başvuru kaynağı bulunamadı.) is substituted into (v) and adjusted to account for the elevation differences between the inlet and outlet:

$$\Delta P = \rho g (L \sin \theta) + \frac{8 \dot{m}^2}{\pi^2 g \rho^2 D^5} \left(f_D \frac{L}{D} + K \right) \quad (20)$$

[89]. Here, K represents local losses, and θ represents the slope angle between the inlet and outlet.

According to the Hagen–Poiseuille equation, the correlation between f and Re is defined in three different flow regimes: laminar flow ($Re < 2000$), transitional flow ($2000 < Re < 3000$), and turbulent flow ($Re > 3000$) [90]. The friction coefficient can also be calculated based on Re depending on which region the flow is in.

$$f_D = \begin{cases} 64/Re & Re < 2300 \text{ (laminar)} \\ 0.3164 Re^{-0.25} & Re > 4000 \text{ (turbulent)} \end{cases} \quad (21)$$

Additionally, the friction factor can also be calculated using the Colebrook correlation, where ϵ is the relative roughness value of the channel [91].

$$\frac{1}{\sqrt{f_D}} = -2 \log \left(\frac{\epsilon/D}{3.7} + \frac{2.51}{Re \sqrt{f_D}} \right) \quad (22)$$

Here, Re :

$$Re = \frac{4 \dot{m}}{\pi D \mu_{\text{ePCM-S}}} \quad (23)$$

The increase in viscosity and the associated pressure drops also bring about a relative increase in pumping power. However, when the improvement achieved through heat transfer is compared to the increase in pumping power, it is seen that, as is the case with many nanofluids, but to a more significant extent, a relatively negligible increase in pumping power is offset by a significant improvement.

The pumping power required to circulate ePCM-S through the system based on pressure drop (Δp) and the pump's mechanical efficiency (η_p):

$$P_{\text{pump}} = \frac{\dot{m}\Delta p}{\rho_{\text{ePCM-S}}\eta_p} \quad (24)$$

is calculated as follows:[89,92,93].

Additionally, the electrical power required for the pump to circulate ePCM-S in the system is empirically calculated as [94]:

$$P_{\text{pump}} = \frac{1.2465 \times 10^4 A_{\text{PVT}} h_f^{3.5} \mu^{1.83} D_h^{0.5}}{k^{2.33} C_p^{1.17} \rho^2 \eta_p} \quad (25)$$

With δ being the pipe length, hydraulic diameter, D_h is calculated by:

$$D_h = \frac{4\delta D}{2(\delta + D)} \quad (26)$$

While the additional pumping power required for ePCM content below 30% is generally negligible, [62], the pumping power required for ePCM content above this level increases parabolically.

4. Conclusions

Research on renewable energy is important within the framework of sustainable development and clean energy strategies. PVT systems are becoming increasingly widespread among solar energy applications, which have the highest potential and widest range of applications among renewable energy sources. Efforts to increase both the electrical and thermal efficiency of PVT systems continue with different approaches on different parameters of the system. In this context, this study aimed to extract more heat from the system with lower pumping power and to achieve a more stable operating temperature by using ePCM-S as HTF.

Within the scope of this study, MF/LA ePCMs incorporated into water in 1%, 1.5% and 2% were characterized as a slurry HTF. The properties obtained from the chemical, physical, and thermal characterization of ePCM and ePCM-S, as well as the properties calculated using empirical formulas and correlations, were found to be largely consistent and verifiable with the outputs obtained from the experiments.

- It has been shown that even at low ratios, the addition of ePCM provides a significant increase in the heat capacity of the carrier fluid.
- It has been observed that the heat transfer capacity increases significantly during the phase change process and that, as a result of heat extraction at a constant temperature, the local average temperature values on the plate surface become closer to each other, thus providing more uniform cooling.

Future Research

The selection, synthesis, and use of ePCM-S require expertise in a number of areas or extensive background knowledge and interdisciplinary collaboration, as well as comprehensive research.

Future research should be deepened to improve capsule size, capsule shell and core materials, or develop new materials, taking advantage of new developments in the field of nanotechnology. The narrow phase change temperature window acts as a constraint on flow velocity, forcing it to be low enough to allow PCM to melt within short circuits, but this, on the other hand, can cause problems in other parts of the cycle. On the other hand, in long circuits, phase change will occur in a shorter section of the exchange circuit and cause noticeable heat storage in the rest of the circuit. Research on the application of ePCM as a working fluid in thermal systems, as a HTF or thermal storage medium in dilute solutions of water or other fluids, aim to design and develop binary, ternary, or even quaternary (quaternary) ePCM-S can be promising.

Furthermore, studies can be conducted to improve the low thermal conductivity and average convective heat transfer coefficient of ePCM-S due to the organic composition of PCM.

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Declaration of Conflict of Interests

The authors declare that there is no conflict of interest. They have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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