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Review

Harnessing Nanomaterials for Enhanced Energy Efficiency in Transpired Solar Collectors: A Review of Their Integration in Phase-Change Materials

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Abstract: The building sector plays an important role in the global climate change mitigation objectives. The reduction of CO_2 emissions and energy consumption in the building sector has been intensively investigated in the last decades, with solar thermal energy considered to be one of the most promising solutions due to its abundance and accessibility. However, the discontinuity of solar energy has led to the study of thermal energy storage to improve the thermal performance of solar thermal systems. In this review paper, the integration of various types of phase-change materials (PCMs) in transpired solar collectors (TSC) is reviewed and discussed, with an emphasis on heat transfer enhancements, including nanomaterials. Thermal energy storage applied to TSC is studied in terms of design criteria, materials technologies, and its impact on thermal conductivity. This review highlights the potential of nanomaterial technology integration in terms of thermal performance improvements. The utilization of nanomaterials in solar walls holds the potential to significantly enhance their performance. The integration of diverse materials such as graphene, graphite, metal oxides, and carbon nanoparticles can pave the way for improving thermal conductivity.

Keywords: phase-change materials; nanomaterials; nano-enhanced phase-changing materials transpired solar walls; thermal energy storage; PCM; nePCMs

Citation: Croitoru, C.; Bode, F.; Calotă, R.; Berville, C.; Georgescu, M. Harnessing Nanomaterials for Enhanced Energy Efficiency in Transpired Solar Collectors: A Review of Their Integration in Phase-Change Materials. *Energies* **2024**, *17*, 1239. https://doi.org/10.3390/en17051239

Academic Editors: Umberto Berardi, Antonio Caggiano and Facundo Bre

Received: 12 January 2024
Revised: 20 February 2024
Accepted: 2 March 2024
Published: 5 March 2024

1. Introduction

The buildings and construction sectors are responsible for 30% of global final energy consumption and 27% of total energy sector CO_2 emissions, being considered one of the highest energy consumers [1]. Each year, CO_2 emissions increase around the world, and global warming threats become increasingly visible. Greenhouse gas emissions are a direct consequence of abrupt industrialization and urbanization, with citizens becoming both beneficiaries as well as victims. All these concerns have led to #climatestrike movements to raise climate change awareness. Finding and implementing solutions should be priority topics for research and development in the building and construction sectors.

Building envelopes serve as crucial thermal interfaces between the external environment and indoor spaces. Ensuring optimal thermal conditions is vital for the thermal comfort and well-being of the occupants. As a result, the energy needs of buildings are inseparably tied to the thermal performance of their structural components. Inadequate thermal performance in the building envelope results in either excessive heat buildup within the premises, causing increased energy consumption for cooling, or significant thermal losses, which directly affect the energy required for heating. This challenge becomes even more pronounced when striving to enhance the energy efficiency of buildings, moving them closer to the goal of achieving zero-energy buildings (ZEB) [2]. In this context, it is mandatory to use renewable energy sources (RES) in order to ensure indoor comfort with low energy consumption.

As the most widely available of all RES, solar energy is a natural choice in the attempt to reduce energy consumption due to its abundance and accessibility. However, since solar energy exhibits intermittent availability, solar thermal energy mandates its transformation and storage to ensure its uninterrupted availability [3]. Extensive research has been conducted with a primary focus on increasing the efficiency of both solar energy storage and conversion processes, with photovoltaic and solar thermal conversion technologies as cornerstones for efficient solar energy conversion to electricity and heat. However, using this solar energy throughout extended periods requires the integration of thermal energy storage systems in the building. This integration not only ensures the sustained availability of solar-derived thermal energy but also contributes significantly to the overall energy sustainability paradigm.

The solar collector is one of the most cost-effective pieces of equipment used to harvest solar thermal energy. Two main types can be identified: (1) water-based solar collectors (WSCs), an already popular solution for preparing domestic hot water and heating, and (2) air solar collectors (ASCs), used to preheat fresh air and to dry or heat the air inside a room. According to the manufacturer data, Reichl et al. [4] found that ASCs have the advantages of no frost risk in colder regions during the winter, a lower environmental impact, and a more cost-effective investment and operation.

TSCs are typically used for low-temperature applications with low operating costs [5]. TSCs, at their simplest, are perforated metal panels installed on the exterior of a building that absorb solar radiation and transfer this absorbed heat to the air drawn through the perforations and into the building. In theory, increasing the efficiency of TSCs is based on increasing the heat transfer from the perforated panels (the simplest thermal energy storage devices) to the air [6]. Using air solar collectors, the outlet temperatures can reach values of up to 65 °C, which is suitable for a variety of building applications [7–10].

Metal panels are efficient at absorbing and transferring heat, and thus, the first studies focused on panel designs (opaque or transparent, plate or corrugated) that would increase the heat transfer efficiency [10–14]. The problem is that metal panels are poor heat storage devices, and the discontinuity of solar thermal energy limits their long-term effectiveness. Combining this with the limited availability of solar thermal energy, it becomes clear that broader research into other efficiency-augmenting methods is necessary.

Thus, efforts to increase TSC efficiency have shifted to increasing their thermal energy storage (TES) capabilities through passive means, such as the implementation of phase-change materials (PCM) in the TSC [15]. PCMs have the capacity to absorb substantial heat during the daytime as they transition from a solid to a liquid state and then release this stored heat during the night as they shift from a liquid to a solid state. Thus, besides PCMs increasing the TES capabilities of TSCs, their release of thermal energy during the night also addresses the problem of intermittent solar energy availability.

PCM elements have attracted considerable attention as an efficient method for thermal energy storage due to their high thermal storage capacity, desirable fluidity, and thermal properties, allowing for efficient management of peak load demands [15] when incorporated in building envelopes. PCMs, however, are not a perfect solution. Their most important and glaring fault is their low thermal conductivity, which leads to low efficiency in transferring the considerable amount of stored heat to the airflow entering the building [15].

In order to address specific limitations associated with PCMs, the most important being low thermal conductivity, researchers have explored the integration of nanoparticles in PCM, which further elevates the thermal performance of the building envelope [16].

Thus, the implementation of nanomaterials and phase-change materials plays a vital role in enhancing the efficiency of solar energy use in the building energy balance, providing real benefits for the user's finances and health. PCM elements have attracted considerable attention as an efficient method for thermal energy storage due to their high thermal storage capacity, desirable fluidity, and thermal properties [17].

This paper presents the current state of research related to the integration of different types of nanomaterial-enhanced PCMS in TSCs for the purpose of optimizing solar thermal energy storage and usage in buildings. This paper is based on a comprehensive examination of over 100 research studies focused on increasing the energy efficiency of transpired solar collectors. Most of these studies are indexed in the Web of Science database, with publication dates spanning from 2009 to 2023. A quick review of the literature highlights the recent interest in the subject, as reflected in the growing number of articles on solar collectors, particularly after 2017 (an increase that is mirrored in this paper's bibliography).

Worldwide interest in TSC technology is centred in Asia, with Europe ranking as the second-highest contributor by a wide margin (the two continents account for more than 80% of the references examined in this paper). This statistic suggests that the majority of the solutions currently under discussion are likely geared toward urban locations in Europe and Asia and their respective climates.

An evaluation of the keywords of each research or review paper, based on their frequency of occurrence, has been undertaken to guide the paper's focus. The keywords for all references used in the present paper were extracted and processed (overly general keywords such as "buildings" or "renewable energies" were removed) and presented in a word cloud in Figure 1.

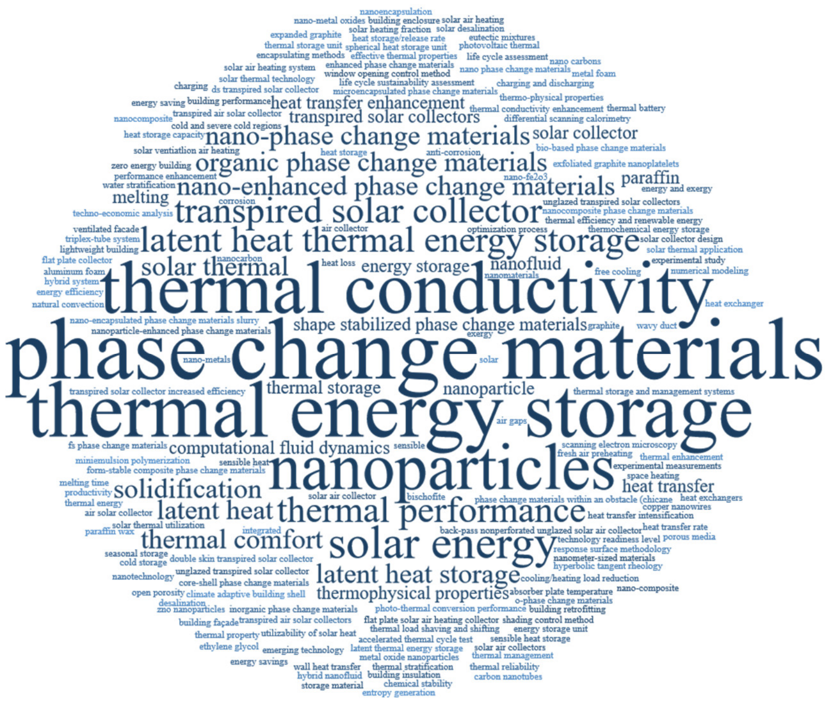


Figure 1. Keyword cloud for all the references considered in the present review article.

The results of the keyword analysis indicate that the most relevant research topics related to solar collectors concern (a) the use of PCMs as the primary means of energy storage and (b) the physics of thermal energy storage inside solar collectors through the study of different materials and techniques used to enhance materials' thermal conductivity, such as nanoparticle integration. Secondary areas of interest concern the economic viability of PCM-enhanced solar collectors or very niche methods and techniques for improving their performance.

This paper was structured in accordance with the overall objective of this work, which is to address the state of the art in TSCs using nanomaterial-enhanced PCMs (Figure 2).

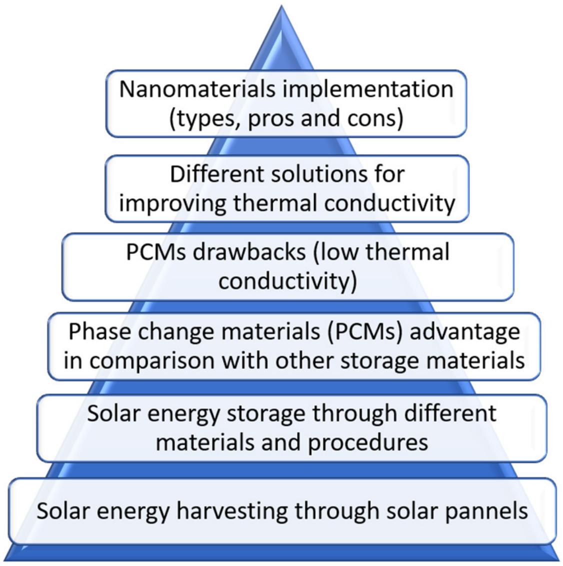


Figure 2. Paper's workflow.

The next sections will provide a qualitative description of common methods and techniques for PCM usage inside TSCs, as well as for the use of nanomaterials to enhance PCM performance. This will be followed by a quantitative evaluation of the aforementioned methods and techniques from the point of view of TES and heat transfer efficiency. Finally, the conclusion section of the present paper will summarize the most important findings and formulate recommendations for future research directions for the purpose of further enhancing TSC efficiency.

2. Thermal Energy Storage Systems Using Phase-Change Materials (PCMs)

The disparity between energy supply and consumption, along with the necessity to store excess energy that might otherwise go to waste, as well as the need to manage peak power demand, underscores the importance of thermal energy storage in various applications, including hot water, space heating, and air conditioning. Thermal energy storage systems facilitate more efficient utilization of fluctuating energy sources by aligning energy supply with demand. This has the potential to significantly reduce the reliance on fossil fuels, consequently mitigating the phenomena of Urban Heat Island and Urban Pollution Island and contributing to the development of sustainable urban areas.

There are several methods for storing thermal energy, with the main ones being sensible heat storage [18,19] and latent heat storage [20–23]. Sensible heat refers to the quantity of heat that is either added to or extracted from a material when its temperature changes. On the other hand, latent heat refers to the quantity of heat that is added to or removed from a substance during a phase change while maintaining a constant temperature. In the context of energy storage, latent heat storage represents a nearly isothermal process, offering significantly higher storage density and smaller temperature fluctuations compared to sensible heat storage systems. Furthermore, latent heat storage has the unique capability of storing the heat associated with a material's phase transition at a constant or nearly constant temperature, which corresponds to the phase transition temperature of the phase-change material.

While sensible heat storage is widely used in practical applications, latent heat storage, such as phase-change materials (PCMs), offers substantially higher energy storage density. PCMs exhibit minimal temperature variation during both charging and discharging processes, making them highly efficient for thermal energy storage [24–26].

An energy analysis for various collector types, along with the latest innovations to improve the heat collection efficiency of low-temperature solar collectors, has been provided in the study conducted by Gorjian S. et al. [27]. The methodologies discussed in this research cover a diverse set of strategies, including structural adjustments, absorber coatings, integration with reflectors, the use of alternative working fluids such as nanofluids, and the implementation of Thermal Energy Storage (TES) systems.

Instability and dependency on the outdoor climate are two of the main shortcomings when implementing RES. In order to eliminate or reduce the waste of surplus energy produced during periods with high-intensity solar radiation, the use of TES materials becomes essential [28]. In this way, the surplus energy can be stored for use during cloudy periods or during the night, thus increasing the solar collectors' overall efficiency, number of operating hours, and exterior air variation [9,29]. Moreover, incorporating PCMs into conventional building materials has shown significant promise for enhancing energy efficiency. Studies have indicated that such integration can result in a substantial 20% decrease in the cooling load for buildings, making it an interesting solution for hot climate countries, as Zahir, M.H. et al. noted in [30].

A comprehensive analysis of phase-change materials (PCMs) commonly employed in various applications was performed by Javadi, F.S. et al. in [31], revealing that paraffin waxes, salt hydrates, fatty acids, and eutectic organic/non-organic compounds are among the most frequently used PCMs. These PCMs are typically categorized into three primary groups: organic, inorganic (including salt hydrates and metallic compounds), and eutectic mixtures. Each group offers distinct advantages and disadvantages associated with their thermophysical properties.

Organic PCMs, for instance, undergo congruent melting without phase separation. Their non-corrosiveness and self-nucleation, as well as being chemically inert and thermally stable, make them desirable for certain applications like solar thermal energy applications, peak load shifting, or thermal management systems [32,33]. However, they tend to exhibit relatively low thermal conductivity, which can limit their overall efficiency. Notably, paraffin wax stands out as one of the most prevalent organic PCMs due to its narrow melting temperature range, spanning from −10 °C to 67 °C. This particular property enhances its suitability for a wide range of applications and technologies. Organic phase-change materials (PCMs) typically exhibit limited thermal conductivity, falling within the range of 0.1 to 0.4 W/mK. As an illustration, it can be considered n-octadecane, which displays a thermal conductivity of 0.35 W/mK in its solid state and 0.149 W/mK in its liquid state, a fact highlighted by Jegadheeswaran S. et al. [34].

Inorganic PCMs have gained attention for their exceptional capacity to maintain consistent thermophysical properties across numerous thermal cycles. Their specific feature is related to their increased thermal conductivity in comparison to organic PCMs, rendering them highly appealing for a wide array of applications. Furthermore, as Hinojosa J.F. et al. emphasize, inorganic PCMs boast an impressive volumetric latent heat density, typically around 350 MJ/m^3 [35]. This characteristic signifies their ability to efficiently store a substantial amount of energy. However, it is essential to recognize that inorganic PCMs are not without their challenges. One notable limitation is their corrosive nature, particularly in interactions with metals. This corrosiveness can give rise to concerns related to durability and compatibility, especially in specific applications, a problem yielded by Hua W. et al. [36]. Ushak S. et al. notice another potential issue is the occurrence of subcooling, where the PCM may fail to undergo a phase change at its designated melting point, instead remaining in a liquid state below that temperature [37]. Additionally, phase segregation, wherein components within the PCM may separate during phase transitions, can pose a significant concern [37].

In contrast, Singh P. et al. noted that eutectic PCMs present a distinct advantage by virtue of their well-defined melting and freezing points, guaranteeing a stable and predictable phase change without any component separation during transitions [38].

Cutting-edge technologies include PCMs derived from biomass, such as bio-based oils, which are being explored for their environmental sustainability. Research is underway for their potential use in TES systems, including solar thermal applications, like in the case of Jiang T. et al. [39].

Diverse melting temperatures must be tested and analyzed to cope with seasonal variability and different temperature requirements, or for applications such as drying (typically around 35 °C) or building heating (usually about 22 °C) [40].

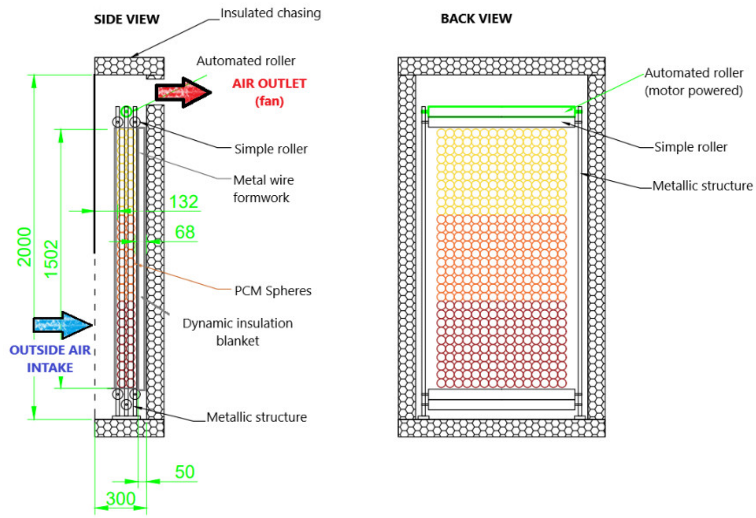
The primary areas of focus for PCM optimization are improving thermal conductivity and heat transfer in PCM thermal energy storage (TES) systems. Various techniques, such as adding fins and increasing the thermal conductivity of PCM, have been proposed to enhance heat transfer.

However, implementing these techniques, according to Khan M.I. et al., may lead to increased system costs and added complexity [41]. Enhancing thermal conductivity can be accomplished through several methods, one of which is to incorporate PCM into high-conductivity porous materials. For example, one approach involves embedding the PCM within porous materials known for their exceptional thermal conductivity, such as metal foam and porous graphite [42–44]. Adding high-conductivity metal structures or particles is another method of increasing thermal conductivity. This technique entails introducing high-thermal conductivity metal structures or particles, such as silver, aluminium, copper, or other materials, into the PCM, as Shah, K.W. states [45]. Another method of increasing the thermal conductivity of PCM is by encapsulating it with high-conductivity shell materials for their superior thermal conductivity. According to Peng G. et al., shell materials are categorized into three distinct groups, namely organic, inorganic, and hybrid materials, combining both organic and inorganic components [46].

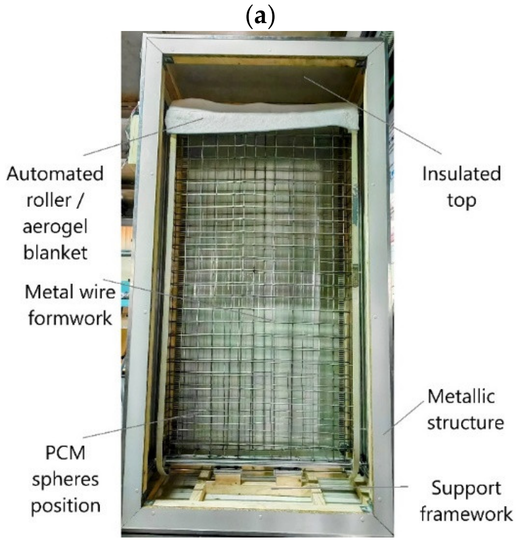
The thermal behavior of TSC equipped with PCM-based thermal storage was studied experimentally, and the results show that the latent heat thermal storage contributes to increased stability of the outlet air temperature of the collector and also a slight increase in the overall efficiency of the system, a fact suggested by Orzechowski T. et al. [47]. The use of PCM in solar collectors can increase the operating hours and thermal stability [3,48,49]. Recently, a team of researchers integrated thermal energy storage materials within the solar collector, and they used organic paraffin, a PCM with high latent heat suitable for building applications, obtaining a heat transfer efficiency of up to 38% and a higher number of operating hours of up to 800 min per 24 h compared to low-inertia TSC (the energy stored within the PCMs being released slowly during the night) [50]. Moreover, increasing the number of layers and introducing a separation plate influence the performance of the collector. The efficiency gradually increases when increasing the solar collector thickness until it reaches a value of 20 cm, according to Berville C. et al. [51].

Recent studies highlight the innovative integration of solar energy systems and thermal storage technologies to enhance the efficiency of domestic heating, food drying, and industrial applications, underscoring the potential for renewable energy solutions to address fuel poverty and contribute to sustainable development [52–60].

Several geometrical designs for PCM integration in TSC have lately been investigated. The incorporation of PCMs in spheres [22,51] is viewed as the optimum solution in terms of the unitary distribution of the flow and the size of the heat exchange surface. Furthermore, the TSC configuration can be refined with additional improvements by providing a mobile insulating blanket consisting of materials with very low heat conductivity, such as aerogel, as Calota R. suggests in a research grant report [61]. Throughout the day, during the cold season, the air is preheated as it passes over the transpired plate, which has a higher heat transfer rate due to the lobed perforations, and excess heat is stored in the highly efficient PCMs. During this operating mode, warm air is introduced inside the building. The dynamic insulation shifts to the exterior during the night, shielding the PCMs, which can now transfer heat to the interior via the conductive element. During the warm season, the process reverses, transferring heat out of the building, storing it in the PCM, and insulating as needed. The fresh, cool air may be used only at night and is bypassed during the day [61]. The process can be visualized in Figure 3 where one can observe the strategy for using Phase Change Materials (PCMs) arranged in a cascade, depicted in distinct colors (Figure 3a).



(**a**)



(**b**)

Figure 3. TSC with integrated PCMs and dynamic insulation [61]. (**a**) Side and back view; (**b**) real-scale experimental stand (with the front perforated plate removed).

Other research considered PCM incorporation in plates. According to Bejan et al. [9], after conducting experimental investigations, the performance of TSCs with lobed perforations can be substantially improved by adding 15 kg of organic PCM to the core structure. The results highlight that the maximum overall efficiency can be improved by nearly 6%, the maximum heating capacity by approximately 7.7%, and more than 17% supplementary energy was obtained during 9 h of operation.

A thermal energy storage unit made up of two plate coolers, each containing 40 kg of salt-hydrate-based PCM, was implemented in a TSC by Poole et al. [62]. The total storage capacity was 15 MJ.

Alternative geometries for PCM storage have been studied in order to identify the most energy-efficient structure. Abuska et al. [63] developed a novel solar air collector by combining the PCM with an aluminium honeycomb. The heat storage material having a mass of 26 kg was evaluated under the following conditions: PCM with honeycomb core in the first collector (type 1) and solely PCM in the second collector (type 2), as well as the third collector (type 3) with a flat absorber plate for comparison. The first one provided a usable energy output 70 min longer than the third one. Under daytime conditions, the thermal efficiencies were calculated to be 10.1%, 10.9%, and 13.6%, respectively.

Even though PCM integration in spheres, plates, and honeycomb structures is the most common, the PCMs can be embedded in complex materials' structures, such as gypsum plasterboard, like in the study performed by Bake M. [64]. The studies revealed that the construction envelope with PCM-gypsum plasterboard supplied an outlet temperature of 18 °C, which was 6 °C higher than the building envelope with simple gypsum plasterboard.

3. Integration of Nanomaterials in Thermal Energy Storage (TES) Systems

While the use of PCMs in solar collectors can increase the operating hours and their thermal stability, embedding nanoparticles in PCMs allows the improvement of thermal behavior related to melting and solidification rates as well as reducing the phase change period. Ma Z. points out that this is leading to increased benefits in the PCM's main area of weakness: their low thermal conductivity, especially in solid state [65].

3.1. Nanomaterials' Types

Existing nanomaterials used in TES have been grouped into three categories: nanometals, nanometal oxides, and nanocarbons.

Nanometals represent a class of materials wherein metallic particles are manipulated at the nanoscale, typically with dimensions below 100 nm. It is well known that metals have high thermal conductivities. This reduction in size imparts unique and enhanced properties to these materials compared to their bulk counterparts. Nanometals exhibit remarkable electrical, thermal, and optical characteristics, making them invaluable in various technological applications. They have a large surface area-to-volume ratio.

Silver exhibits the highest thermal conductivity among all metals, excelling in both heat and electricity conduction, with a thermal conductivity value of approximately 430 W/mK. Gold and copper are closely behind silver in terms of thermal conductivity, boasting values that are nearly equivalent. However, silver and gold are characterized by their high cost. In contrast, copper offers a more economical alternative and holds a competitive edge over silver and gold in various applications, as Leong K.Y. et al. notice in [66].

Nanometal oxides, composed of metal cations bonded with oxygen, are another fascinating class of nanomaterials. These materials exhibit diverse properties depending on their composition, size, and structure. They find extensive use in applications such as electronics, energy storage, environmental remediation, and catalysis. Nanometal oxides, like alumina and copper oxides, are good conductors of heat, with a thermal conductivity ranging from 30 to 40 W/mK. They are known for their exceptional surface area and reactivity, making them effective in various chemical processes.

Aluminium oxide nanoparticles (Al_2O_3) have been investigated for their potential to improve the thermal performance of phase-change materials (PCMs) used in low-temperature TES [66–68]. These nanoparticles can enhance heat transfer within the PCM, leading to more efficient energy storage and release.

Nano-titanium dioxide (TiO_2) is another metal oxide that has been studied for its applicability in low-temperature TES systems [68,69]. It can serve as a nucleating agent in PCMs, reducing subcooling effects and promoting more controlled phase transitions, thus improving overall TES efficiency. Nano-iron oxide nanoparticles (Fe_2O_3) have been explored as potential additives to enhance the thermal conductivity of PCMs used in low-temperature TES. Their presence can facilitate better heat transfer and temperature regulation within the storage medium, according to Chaichan M.T. et al. [70]. Nano-zinc oxide (ZnO) is known for its versatile properties and has been considered for low-temperature TES applications. Manoj Kumar P. et al. state that it can be integrated into PCMs to help manage temperature differentials and improve the overall thermal performance of the TES system [71]. Nano-copper oxide (CuO) particles have been investigated for their ability to enhance the thermal conductivity of PCMs in low-temperature TES applications. They can promote more efficient heat transfer and reduce temperature fluctuations [72]. Nano-cobalt oxide (Co_3O_4) is another example of a metal oxide that has shown promise in low-temperature

TES systems. Its use as an additive in PCMs can contribute to better temperature control and improved energy storage capabilities.

Nanocarbons encompass a family of carbon-based nanomaterials, including carbon nanotubes (CNTs), graphene, and fullerenes. These materials have garnered immense attention due to their extraordinary electrical, mechanical, and thermal properties. Carbon nanotubes, for example, exhibit exceptional thermal conductivity, knowing that individual carbon nanotubes can range from 1000 to 3000 W/m·K or even higher and are successfully used in this matter [66]. Graphene, a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice, boasts remarkable mechanical strength, electrical conductivity, and thermal properties and possesses extremely high thermal conductivity, with values exceeding 3000 W/mK. It has the potential to revolutionize various industries, including electronics and energy storage [68].

As a synthesis of the main advantages and disadvantages regarding each type of nanomaterial used in TES, nanometals have advantages such as high thermal conductivity, which leads to improved heat transfer within the storage medium, and increased heat capacity, allowing for more efficient thermal energy storage. The main disadvantages are related to agglomeration issues, which have an adverse effect on heat transfer qualities, as well as the increased cost. When compared to pure metals, nanometal oxides offer more stability and resistance to oxidation. Nevertheless, the thermal conductivity is lower, and the synthesis is more difficult, resulting in higher production costs. Nanocarbons, such as carbon nanotubes and graphene, have high heat conductivity and are lightweight, which might be useful in some applications, particularly if weight is an issue. Also, they show good chemical stability, reducing the possibility of reactions with the storage medium. Nonetheless, achieving uniform dispersion of nanocarbons in the storage medium can be challenging, affecting their performance.

The enhanced performance of nanomodified paraffins using carbon nanotubes was studied in [73,74]. These nanotubes significantly improved thermal conductivity, leading to increased efficiency in charge/discharge regimes. Moreover, the integration of carbon nanotubes enabled the development of robust thermal devices, demonstrating substantial heat flux through controlled thermal contact. Magnetically controlled heat storage materials, modified with carbon nanotubes, exhibited efficiency in practical applications like self-rescue devices.

The development of materials with thermo-optic switching properties, such as paraffin hosting carbon fillers, represents a significant advancement in the field of solar energy utilization. These materials exhibit the ability to alter their optical properties in response to temperature changes, making them valuable for applications in thermal energy storage [75,76]. The integration of nanomaterials, including carbon nanotubes and graphene, into paraffin enhances its thermal conductivity and allows for efficient absorption and release of thermal energy. Notably, nanometals, nanometal oxides, and nanocarbons bring unique characteristics to the composite material, such as enhanced thermal conductivity and adjustable properties, making them promising components for thermal energy storage systems.

The overview highlights the significant role of nanomaterials in overcoming challenges associated with traditional PCMs in solar collectors. The ability of nanomaterials to enhance thermal conductivity, regulate temperature differentials, and improve energy storage efficiency is a recurrent theme. The selection of specific nanomaterials, such as copper and graphene, reflects a consideration of both performance and cost-effectiveness.

Nanometals, nanometal oxides, and nanocarbons emerge as highly promising materials in TES applications. Their distinctive properties, including enhanced thermal conductivity and adjustable characteristics, position them as valuable components in the quest for efficient and effective thermal energy storage. This underlines the potential impact of nanomaterials on advancing the capabilities of solar collectors and expanding their applications in renewable energy systems.

3.2. Nanomaterials Integration

The present section delves into the diverse methodologies aimed at enhancing the heat transfer of phase-change materials (PCMs) in the context of thermal energy storage for buildings and renewable energies. Various techniques, ranging from macro and micro-encapsulation to the incorporation of metallic fins, materials with high thermal conductivity, and nanoparticles, are explored.

There are many methods that can be used in order to enhance the heat transfer of the PCM elements [77–79]: macro-encapsulation of the PCMs in steel cylinders or spheres, micro-encapsulation of the PCMs, the use of metallic fins to increase heat transfer surface, embedding materials with high thermal conductivity, and embedding nanoparticles with high thermal conductivity.

Nanoparticles represent a cutting-edge technological advancement aimed at enhancing heat transfer efficiency [80,81]. Nano-enhanced PCMs have been widely adopted in the fields of thermal energy storage for buildings and renewable energies [82,83]. Li [84] analyzed, via CFD simulations, the heat transfer inside a ventilation system for building heating based on paraffin RT30 integrated into sinusoidal encapsulations.

Alumina (Al_2O_3) nano-sized material was added to the paraffin with a fraction of 0.04 to enhance the conductivity of the latent heat storage. The most time-efficient method uses alumina nanopowders, with results showing a decrease in solidification time of 5.49%. The combination of Al_2O_3 nanoparticles with metallic fins in PCM storages [85,86] has shown even better results; indeed, solidification and melting time can be reduced by 12 and 6.4%, respectively. The findings from [70] indicate that the inclusion of nano-Fe_2O_3 at any mass fraction leads to a higher viscosity and density of the resulting mixture. The introduction of nano-Fe_2O_3 into paraffin wax results in a notable enhancement of thermal conductivity, with improvements of 10.04%, 57.14%, 76.19%, and 78.57% observed when mass fractions of 0.5%, 1%, 2%, and 3% are added, respectively. The outcomes of the study [71] demonstrated that the dispersion and distribution of zinc oxide nanoparticles within the paraffin did not disrupt its chemical structure. Additionally, the nanoparticles substantially improved the thermal stability of the paraffin and increased its thermal conductivity by up to 41.67% when incorporating 2% nano-ZnO particles. In [72], copper oxide (CuO) particles with a mean size of 40 nm were dispersed within the phase-change material (PCM) at three different weight percentages: 2%, 5%, and 10%. As a result of this dispersion, the thermal conductivity of the composite increased by 6%, 6.7%, and 7.8% in its liquid state. Simultaneously, the dynamic viscosity showed enhancements of 5%, 14%, and 30% as the mass fraction of CuO nanoparticles increased. During the solidification process, the heat transfer coefficient exhibited an increase of approximately 78% at the maximum flow rate [72].

Several types of materials have been investigated, but continuous research is needed. The integration of nanocarbon and nanococonut shells has been investigated by Sun Liu et al. [87]. Oleic acid and span 80 have been used to mitigate the agglomeration of nanoparticles during melting phases. The optimal concentration of nanoparticles was 0.02 wt%, and combined with oleic acid, a shorter melting time of 21% was reached compared to pure paraffin. Despite a more sustainable profile, the nanococonut shell was less effective than the nanocarbon. A challenging problem that arises in this domain is the design of more sustainable PCM and nanoparticles. Xie et al. [88] fixed one of these two issues using an organic PCM; nevertheless, they still used expanded graphite to improve the thermal characteristics of thermal energy storage. A new approach is therefore needed to develop more sustainable thermal energy storage.

Integrating nano-enhanced phase-changing materials (nePCMs) into solar walls offers a promising strategy [65]. Several studies conducted emphasize that using fins, metallic foams, or nanoparticles increases heat transfer efficiency and thermal backup time [3,48,89] in the case of integrating PCMs within solar collectors. There are several types of nanoparticles that can be used: metal, metal oxides, metal foams, carbon nanotubes, carbon nanoparticles, graphene, and graphite, and the current nanotechnology has led to the production of even more materials of various types at the nanoscale level [66]. Different types of micro/nano-PCMs for solar thermal applications are presented in research conducted by Qiu L. et al. in [90], and a comprehensive image indicating nanomaterials with high conductivity for increasing the thermal performance of latent heat thermal energy storage systems can be seen in the Jegadheeswaran S. study [91]. The main implications of using different types of nanomaterials are presented in Figure 4.

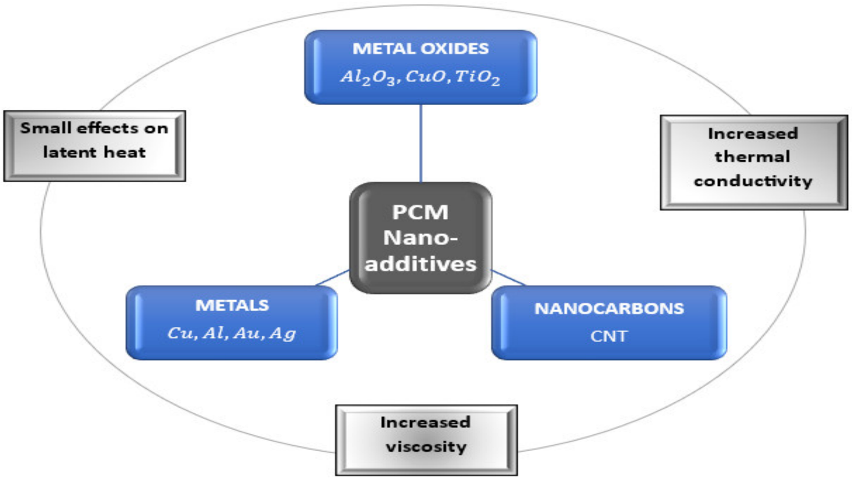


Figure 4. Nanomaterials with high conductivity for increasing the thermal performance of latent heat thermal energy storage systems.

In [92], a composite bio-phase-change material (PCM) was investigated by Yu S. et al. by incorporating carbon nanoparticles at varying mass fractions of 1%, 3%, and 5%. The findings revealed a substantial enhancement in the thermal conductivity of the composite PCM with the inclusion of carbon nanomaterials. Moreover, the composite PCM exhibited impressive latent heat properties, featuring suitable phase change temperatures and robust thermal durability. Notably, the highest increase in thermal conductivity, reaching 336%, was observed at a concentration of 5.0 wt%, while a substantial increase of 166% was recorded at 1.0 wt%.

The utilization of nanomaterials in solar walls holds the potential to significantly enhance their performance. The integration of diverse materials such as graphene, graphite, metal oxides, and carbon nanoparticles can pave the way for improved thermal conductivity. Research has shown that even small concentrations, like 3 wt% of graphene and graphite, can lead to a remarkable 101.2% increase in thermal conductivity [93], according to Dsilva Winfred Rufuss D. et al. [93].

According to the same author, the thermal conductivity of the nePCM (nano-enhanced phase-changing materials) is affected by particle concentration, dispersion, size, shape, and temperature. Moreover, using graphite nanomaterials with concentrations between 0 and 10 wt%, the thermal conductivity of PCMs can be improved by about 540 to 1000%, but the incorporation of metal foams may also be a promising technique [94]. According to Mumtaz et al. [3], nanoparticles were first used in solar applications in 2009 and can lead to an overall efficiency increase. In a study conducted by Saw et al. [95], by using nano-enhanced PCMs, a flat plate collector's efficiency was improved by 8.4%. Moreover, adding 1 wt% and 2 wt% copper nanoparticles in organic PCM improved the thermal conductivity of a pure PCM by up to 24% and 46.3%, respectively [96].

Despite advancements in developing new PCMs and improving their characteristics for use in solar walls, some limitations persist. The incorporation of nanoparticles into PCMs has shown promise in addressing these challenges. According to Kasaeian et al. [48], by embedding nanoparticles in PCM, the melting and solidification rate can improve, and the phase change time period can be reduced. As can be observed from the previous state-of-the-art survey, researchers have been concentrating on investigations mainly concerned with developing new PCMs or improving their characteristics and implementation into building components [48]. These advancements, however, have not overcome some major limitations, including the reduced potential for solidification and melting in order to discharge the accumulated heat indoors.

Nano-structuring the PCM could provide better thermal conductivity. However, other factors related to the geometry, quantity, and size of the implemented materials could have an impact on the properties of the mixture. Thus, the thermal characteristics of nePCMs should be measured, factoring in different geometries and loading ratios. By implementing various techniques, the nePCMs' thermal properties can be controlled [97,98]. However, the non-homogeneous distribution due to high concentrations of the nanoparticles in the PCMs could reduce the melting performance, as Amidu, M.A. et al. observe, and the thermal performance overall [99]. The literature data suggest that the use of PCMs and nePCMs in buildings could increase energy storage efficiency and building performance. A reduction in temperature fluctuations and internal thermal stability can also be achieved with the implementation of these materials.

On the other hand, active walls with PCM and nePCM are inefficient in very hot climates where a higher temperature gradient is required and when the differences at high temperatures are significant. Therefore, additional solutions are required.

Several studies emphasize the application of nanoparticles in solar collectors, indicating that the incorporation of PCMs within these systems can lead to increased heat transfer efficiency and extended thermal backup time. Table 1 presents a brief synthesis of the results collected from various studies about the impact of adding nanoparticles to PCM.

Table 1. Results regarding nano-enhanced phase-changing material (nePCM) properties.

Author	Investigation	Results
Keshteli et al. [85], Chen et al. [86]	Combination of Al_2O_3 nanoparticles with metallic fins in PCM storage	Solidification and melting time can be reduced by 12 and 6.4%, respectively.
Sun Liu et al. [87]	Integration of nanocarbon and nanococonut shell	Shorter melting time of 21% was reached compared to pure paraffin. The nanococonut shell was less effective than the nanocarbon.
Li W et al. [78]	Metal foam or nanoparticle integration in PCM	Increased heat transfer efficiency and thermal backup time.
Jegadheeswaran S. [91]	Nanomaterials integration in PCMs	Enhanced thermal performance of latent heat thermal energy storage systems.
Yu S. et al. [92]	Incorporate carbon nanoparticles at varying mass fractions of 1%, 3%, and 5% in PCMs	The highest increase in thermal conductivity, 336%, was observed at a concentration of 5.0 wt%, while a substantial boost of 166% was recorded at 1.0 wt%.
Dsilva Winfred Rufuss D. et al. [93]	Integration of diverse materials such as graphene, graphite, metal oxides, and carbon nanoparticles in solar walls	At concentrations of 3 wt% of graphene and graphite, a 101.2% increase in thermal conductivity was identified.
Saw et al. [95]	Use of nano-enhanced PCMs in a flat plate collector	Efficiency was improved with 8.4%
Al-Kayiem, H.H. [96]	Addition of 1 wt% and 2 wt% copper nanoparticles in organic PCM	The thermal conductivity of the pure PCM improved by up to 24%
Amidu M.A. et al. [99]	High concentrations of the nanoparticles in the PCMs	Melting performance and the thermal performance reduction

Although progress has been achieved, challenges emerge, such as the non-homogeneous distribution in high-concentration nanoparticle integration. The importance of a detailed understanding of the thermal properties of nePCMs should be investigated further, taking into account varied geometries and loading ratios.

4. Conclusions

High thermal energy density materials, such as PCMs (phase-change materials), have been widely used as storage for important quantities of energy, finding an application in the field of harvesting solar thermal energy. A PCM thermal buffer can fill the gap between solar energy availability and demand. Experimental research shows that, for transpired solar collector (TSC) systems, PCMs can increase outlet air temperature stability and overall efficiency.

This article offers both quantitative and qualitative evaluations of common methods and techniques for PCM usage inside TSCs. It not only addresses the efficiency of these methods in terms of thermal energy storage (TES) and heat transfer but also discusses the implications of incorporating nanomaterials into PCMs, providing a critical overview of the current state of research in this area.

A shortcoming of the PCMs is their low thermal conductivity, which prevents adequate heat transfer intensity. A common approach to overcoming this disadvantage is the inclusion of nanoparticles within the PCM.

The review clearly demonstrates the significant advancements in thermal energy storage (TES) and heat transfer efficiency within transpired solar collectors (TSC) through the integration of phase-change materials (PCMs) with nanomaterials. The incorporation of nanomaterials such as graphene, graphite, metal oxides, and carbon nanoparticles leads to a substantial improvement in the thermal conductivity of PCMs, thereby enhancing the overall efficiency of solar thermal systems. Researchers embedded Al_2O_3 nano-sized material in paraffin wax, decreasing solidification time by 5.49%. Other materials that increase thermal conductivity are nanocarbons, nanococonut shells, nanotubes, graphene, and graphite. These improvements determine the emergence of a new range of PCMs called nano-enhanced phase-change materials.

Several factors impact the efficiency of the use of nanoparticles: concentration [wt%], dispersion, size, shape, and temperature. Using graphite nanoparticles, the thermal conductivity can be improved by up to 1000%, depending on the concentration. In the case of copper nanoparticles, an improvement in conductivity between 24% and 46.3% was reported when incorporating the nanoparticles within a concentration range of 1–2 wt%. It was also reported that the efficiency of flat plate collectors was increased by 8.4% by incorporating nano-enhanced PCMs.

While plenty of research is dedicated to the improvement of PCMs and their thermal characteristics, as well as the development of novel PCMs, the limited potential for thermal charging and discharging, which is heavily linked to climatic conditions, should also be one of the main research topics. In the literature, concepts of dynamic systems that adapt the position of the PCM based on demand for building wall systems have been proposed.

Nanometals, nanometal oxides, and nanocarbons have emerged as exceptionally promising materials within thermal energy storage (TES) applications. Their distinctive attributes, marked by heightened thermal conductivity and the capacity for controlled adjustments, render them valuable constituents in TES systems. However, it is important to note that ongoing research and development efforts are aimed at fully unleashing their true potential. Scientists and engineers continue to explore innovative ways to harness the exceptional properties of these nanomaterials to optimize TES solutions, improve energy efficiency, and contribute to sustainable energy practices. As the field of nanotechnology advances, we can anticipate even more groundbreaking discoveries that will further elevate the role of nanometals, nanometal oxides, and nanocarbons in the realm of thermal energy storage.

The utilization of nanomaterials in TSCs (transpired solar collectors) holds the potential to significantly enhance their performance. The integration of diverse materials such as graphene, graphite, metal oxides, and carbon nanoparticles can pave the way for improved thermal conductivity. Integrating nano-enhanced Phase-Changing Materials (nePCMs) into solar walls offers a promising strategy.

Various innovative techniques for improving thermal conductivity and heat transfer in PCM-based TES systems were presented as well. Among these, the utilization of fins, high-conductivity porous materials, and the embedding of PCM in materials with high thermal conductivity stand out. These methods significantly contribute to the enhancement of heat transfer, addressing one of the critical challenges in the practical application of PCMs in TSCs.

A comprehensive analysis of different types of nanomaterials used in TES, including nanometals, nanometal oxides, and nanocarbons, is provided. This review sheds light on how these nanomaterials improve the thermal properties of PCMs, offering a detailed examination of their impact on the efficiency of solar energy storage and conversion processes.

PCMs have the capacity to contribute to increasing the overall energy efficiency of buildings that employ RESs (renewable energy sources). The development of novel PCMs with enhanced thermal properties to increase heat transfer intensity is necessary to further the knowledge in the field and facilitate practical implementation. The challenges regarding the direction of the following scientific research are related to the finding of techniques to counteract the particle agglomeration effect in the mixture with phase-change materials, followed by the problems of inhomogeneous distribution that can appear after multiple cycles of melting and solidification.

Author Contributions: Conceptualization, F.B. and C.C.; methodology, F.B. and R.C.; formal analysis, F.B. and C.B.; investigation, R.C.; writing—original draft preparation, F.B. and R.C.; writing—review and editing, F.B., M.G. and R.C.; visualization, M.G. and C.B.; supervision, F.B.; project administration, R.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the following grants of the Executive Agency for Higher Education, Research, Development, and Innovation Funding (UEFISCDI), project number PN-III-P2-2.1-PED-2021-1903, within PNCDI III; by a grant of the Ministry of Research, Innovation, and Digitization, CCCDI-UEFISCDI project number PN-III-P1-1.1-PD-2021-0342, within PNCDI III; and by a grant of the Ministry of Research, Innovation, and Digitization, CCCDI-UEFISCDI, project number PN-III-P2-2.1-PED-2021-4137, within PNCDI III-CT 714PED/2022.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

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