Agglomeration of Nanoparticles in Organic Phase-Change Materials for PV/T Systems: Causes, Effects, and Mitigation

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Abstract: Nanoparticle-enhanced phase-change materials (NePCMs) have been widely explored to improve thermal management in photovoltaic/thermal (PV/T) systems by raising PCM thermal conductivity. However, nanoparticles tend to cluster or settle out over time (agglomeration), degrading performance and stability. This review examines how and why nanoparticles agglomerate in organic PCMs used with PV/T, the consequences for thermal and PV/T performance, and methods to prevent or mitigate agglomeration. We summarize mechanisms of nanoparticle clustering (e.g. surface forces and poor dispersion), document impacts on heat storage capacity and system efficiency, and outline experimental strategies (surfactants, sonication, functionalization, etc.) shown to enhance NePCM stability. A comprehensive literature survey highlights recent studies on organic NePCMs in PV/T and reveals remaining challenges (e.g. long-term reliability and optimal formulations) and future research directions. By integrating findings from 31 sources, this article provides an in-depth resource on nanoparticle agglomeration in organic PCMs for PV/T applications.

Keywords: *Nanoparticles, Phase change materials, agglomeration,*

1.0 Introduction

Photovoltaic/thermal (PV/T) systems are able to integrate solar generation with heat generation, although they are inefficient due to high temperatures of modules. The use of passive cooling based on the phase-change materials (PCMs) has become the promising solution: PCMs soak up latent heat as they are melting and cause the temperature of the solar cells to drop ; (Rahman et al., 2015; Soltani et al., 2017). The most common usage is of organic PCMs (usually paraffins or fatty acids) due to their attractive melting characteristics and chemical stability. These organic PCMs are however usually low thermal conductivity, which slows the accumulation and dissipation of heat (Ling et al., 2015). To overcome this, research has focused on *nano-enhanced PCMs (NePCMs)* in which high-conductivity nanoparticles (e.g. metal oxides, carbon materials, metal particles) are dispersed in the PCM. Many studies report that adding a small fraction (usually 1–5 wt%) of nanoparticles can substantially boost thermal conductivity and improve heat transfer in PCM modules(Dambhare et al., 2021; Said et al., 2024). For example, Yu and Tao added expanded graphite to paraffin and achieved conductivity increases (Yu & Tao, 2022).

Despite these gains, the benefits of NePCMs are often limited by poor nanoparticle dispersion. Nanoparticles have high surface energy and tend to attract each other, forming clusters or settling out of suspension during melting/solidification cycles (Khan et al., 2023). This agglomeration reduces the effective surface area of the particles and can even block heat transfer paths, negating the thermal enhancement(Huang et al., 2024; Song et al., 2019; Tamayo-Vegas et al., 2022). In PV/T systems, agglomeration is especially problematic because long-term reliability is required for solar deployment. Clustering can diminish the PCM's heat storage capacity, reduce cycling stability, and ultimately lower the thermal regulation of the PV module(Huang et al., 2024). This review focuses on agglomeration in organic NePCMs used for PV/T: its causes, its effects on system performance, and strategies to mitigate or prevent it.

2. Nanoparticles and Organic PCMs in PV/T

Organic PCMs such as paraffin waxes and fatty acids are used in PV/T systems to passively cool PV panels. These materials typically melt in the range 20–80°C(Dash & Anna Mahanwar, 2021), matching PV operating temperatures. However, their thermal conductivity (≈0.2–0.3 W/m·K for paraffin) is poor, which slows the uptake and release of heat(Fauzi et al., 2025; Xu et al., 2022). To enhance heat transfer, high-conductivity nanoparticles are dispersed into the PCM. Common nanoparticles include metal oxides (Al_2O_3, CuO, TiO_2), metals (Ag, Cu), and carbonaceous materials (graphite, graphene, carbon nanotubes). These particles can form thermal bridges through the solidifying PCM, increasing thermal conductivity many-fold in ideal cases (Sadiq et al., 2023; Venkitaraj & Suresh, 2019).

In PV/T applications, researchers have experimented with various nano-PCM composites. For example, adding graphene or silver nanoparticles to paraffin can raise conductivity by >50% (Babapoor et al., 2022)(Kalidasan et al., 2022). Hybrid PV/T studies have shown that a system using nanoparticle-enhanced PCM (NePCM) can achieve much higher heat extraction and efficiency than PCM or nanofluid alone. In one outdoor experiment under Malaysian conditions, a PVT-NePCM system delivered a water outlet temperature increase over 46 °C and reached ~85% overall energy efficiency, far surpassing standard PV or PV+PCM setups (Islam et al., 2021). These results show the potential of NePCMs in PV/T by improving PCM conduction, more heat is removed from the panel and usable energy is recovered as desired.

2.1 Causes of Agglomeration of Nano Particles

The basic physical and chemical forces that cause agglomeration of nanoparticles in PCMs include

(i) **Surface Energy and Van der Waals Forces**

High specific surface area and number of unsaturated chemical bond
s means that nanoparticles possess strong attractive van der Waals forces between them. These forces combine the particles into clusters in the liquid PCM (melted state). In the absence of repulsive stabilization, agglomeration of particles is inevitable to reduce the total energy of the system [10].

(ii) **Low Wettability/Dispersion Stability**

The majority of nanoparticles are naturally hydrophilic or hydrophobic as compared to organic PCMs . Incompatible (wettability) surfaces of the particle to the PCM fluid phase result in resistance to dispersion of particles. The result of this mismatch in the long run, or in thermo-mechanical cycling, is that the particle-mainstream interaction is overwhelmed by the particle-particle interaction to cause aggregation.

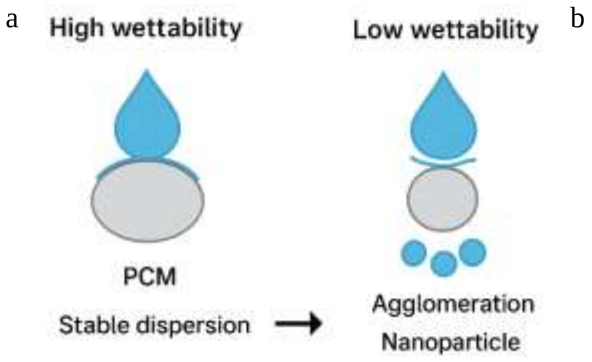

Figure 1: Wettability of Nanoparticles in PCM

For the high wettability Figure 1(a), PCM spreads and adheres to NP surface while for the low wettability shown in Figure 1(b), PCM does not spread well on NP surface (high contact angle, poor adhesion).

(iii)**Thermal Cycling and Density Effects**

Multiple melting and freezing can enhance clustering. It is possible that the PCM solidifies when it expels or pushes nanoparticles together. When the PCM is in liquid form, metal particles or dense particles can also settle due to gravity to cause sediment. Even initially dispersions which are stable can be separated over many cycles, as observed with hybrid PCM systems in which nanoparticles slowly formed clumps and settled during testing (Arifin et al., 2022).

(iv)**Surface Charges and Zeta Potential:**

The surface charge of the particles in the melted PCM determines the tendency to agglomerate (Hussain & Hussain, 2025). When the zeta potential of particles is low (tends to be near the isoelectric point), there is poor electrostatic repulsion and agglomeration would ensue. This has been observed in nano-PCM dispersions, where the lack of stabilization of particles, due to poor charge stabilization, results in grouping up of particles (Ofir et al., 2007).

Overall, in an organic PCM medium, nanoparticles will spontaneously cluster with no countermeasures(Thirumalaivasan et al., 2024). These clusters disrupt the homogeneous thermal network which neat nanoparticles would construct, thereby limiting the thermal conductivity which is achievable. The experimentally determined concentration at which the conductivity levels off and begins to decrease is due to agglomeration because adding 2 wt% graphene following a significant increase in conductivity, but at the point where 2% of the conductivity is reached, according to studies, the sheets will be largely agglomerated conductivity plateaued then dropped by agglomeration (Azizi et al., 2022).

2.2 Effect of Agglomeration

The thermal and PV/T performance of the NePCM systems are highly influenced by agglomeration: Some of the effect of agglomeration include:

Clumping of particles reduces the effective thermal conductivity compared to well dispersed particles. Large agglomerates act as more micro sized particulates and offer fewer conductive pathways. This directly constrains the extent to which the heat transfer of the PCM can be enhanced particularly at the higher nanoparticle loadings. According to Kalidasan et al., the agglomeration of graphene nanoplatelets of more than approximately 1 wt% to paraffin was extremely intense and hampered the establishment of a steady thermal network[7].

Agglomerates decrease the proportion of PCM material that is in the free (melting) state. Minute crystals are widely clumped together to form inert solids, which substitute PCM volume. This has the ability to reduce the total latent heat storage capacity of the composite. Practically, the majority of NePCM works report a small decrease in latent heat measurement (because some mass is not PCMs), yet clustering may be of great magnitude. Nevertheless, when particles are not segregated, the latent heat can be significantly maintained (Kalidasan et al. obtained less than 3% loss of latent heat of well-dispersed Gr/Ag particles.

Stability and Reliability in cycling Agglomeration is usually built up gradually through numerous thermal cycles. When subjected to prolonged testing, researchers have observed that nanoparticles slowly develop larger agglomerates that can be removed out of the PCM matrix. This causes progressively more causing mismatch between cycles. After some time, the composite performance (heat uptake rate, discharge rate, temperature uniformity) decreases. In case of PV/T, it will reduce the cooling effect with time and minimize the increases in electrical efficiency. Therefore, agglomeration compromises long-term thermal reliability.

The net benefit of NePCM in a PV/T system requires keeping the heat removed. In the event of nanoparticles agglomeration, the PCM layer cools the PV panel to a lesser degree. Using field tests (or simulations) would indicate that PV temperatures would be higher and electrical output would be less. By way of example, any benefit observed in the initial PVT-NePCM studies would be decreased by the onset of agglomeration effect because the PCM would not be able to maintain the panel at the same cool temperature during the brightest sunlight. Agglomerated NePCM, in quantitative terms, could only provide a fraction of the efficiency benefit laid out by a well-dispersed one.

In a nutshell, agglomeration defeats the rationale of using nanoparticles as it decreases the conductivity gain, and may degrade the phase-change advantages of PCM. This causes reduced temperature drops, heat recovery and efficiency of PV/T.

2.3 Mitigation of Agglomeration in Nano Particles in PCM

Numerous strategies have been worked out in order to reduce the agglomeration of nanoparticles in PCMs. They are categorized into physical and chemical:

Preliminary agglomerates and the dispersal of the particles can be done by high- shear mixing (e.g. ultrasonic bath, magnetic stirring, ball milling, etc.). As an illustration, ultrasound introduces cavitation pressures which disturb particle agglomerations and promote homogenous dispersion. Care should be taken though: too much sonication power or milling energy may heat the PCM or re-agglomerate particles. Preparation of NePCM composite is often done by a combination of stirring and a few minutes of ultrasonication.

Surface coat on nanoparticles can be added by adding a surfactant (wetting agent) which can sterically or electrostatically stabilize the nanoparticles. In non-polar organic PCMs, particles can be adsorbed by suitable surface-active molecules (e.g. polymeric surfactants with hydrophobic tails) so that the particles do not come into close contact. The principle behind this technique is that the surfactant develops a thin film around each nanoparticle and enhances the repulsion between the nanoparticles. Nevertheless, the use of surfactants is a tradeoff since they can decrease the overall heat capacity of the composite or even change the phase change.

Nanoparticles can be chemically functionalized to include organic PCMs (e.g. grafting of organic functional groups) in the surface. An example is the case of silane-based coupling agents, which are able to bind to metal or oxide particles, and the organic-compatible moieties are projected outwards. This increases the dispersion of particles in paraffin or fatty-acid mediums. Significant sedimentation and clustering of nanoparticle-PCM composites have been observed to be reduced by many coupling chemistries (e.g. oleic acid, stearic acid functionalization, etc.).

(i) Polymer Coating or Encapsulation

It is possible to enhance dispersion by polymer or inorganic coating of the nanoparticles. Indirectly, direct particle to particle contact can be eliminated by coating particles of carbon or metal with silica or polymer. Correspondingly, by encapsulating the whole PCM (nano-PCM capsules) the nanoparticles remain suspended in micron-scale beads although the PCM delivery form will be altered.

(ii) Optimized Particle Selection

It can assist with the use of some nanoparticle shape or support. Indicatively, the agglomeration of 2D materials (such as graphene or MXenes) is not easily predicted as compared to the agglomeration of spherical particles. They can be physically separated, by supporting the particles on a lightweight scaffold (metal foam or graphite foam). Agglomeration can also be disrupted by steric hindrance with particles of different sizes (hybrid nanofillers) being combined with each other.

(iii) Additive Approaches

On a practical basis, mixtures (e.g. hybrid nanoparticles blends) can at times be less clustering than a single kind. In one study [12] for example, dispersion was maintained by mixing graphene and silver nanoparticles. Likewise, the nano-porous media (such as fumed silica) can be added in order to trap the particles.

The most common applications of mechanical dispersion and surfactants in the NePCM preparation in the laboratory setting are used in the NePCM preparation. As an example, Kalidasan et al. obtained a stable Gr:Ag-paraffin dispersion with the help of water-bath sonication (Asgharian & Baniasadi, 2019). Practically, long term stability requires a mixture of these techniques (vigorous mixing, selected surfactant, and surface treatment).

Some of the recent researches investigated organic NePCM performance and agglomeration. For example, (Islam et al., 2021) in an experiment conducted outdoor in real-time in five configurations (PV, PVT, PV+PCM, PVT+PCM, PVT+NePCM). The PVT-NePCM system (PCM containing both CuO and TiO2 nanoparticles) provided much higher heat recovery. The temperature of the water outlet increased to approximately 46 degC and the total energy efficiency was approximately 85. This research emphasizes the benefit that may be realized when NePCM is dispersed peoperly. Furthermore, PCM Nanoparticle Synergies: Lab studies have shown both negative and positive effects of the incorporation of carbon or metal particles owing to agglomeration. As an illustration, further researches have noted some percent rise in lauric acid PCM conductivity using the addition of graphene (Jin et al., 2021), though they also reported that beyond some loadings particle networks would be destroyed. Nada et al. (2018) established that nano-PCM beneath PV modules increased cooling, but there was no evaluation of cyclic stability.

Hybrid NP Formulations: Hybrid nanofillers have also been suggested by different authors in order to exploit the properties of the various particles. In paraffin, a 1:1 mixture of graphene and Ag nanopowder was used by Kalidasan et al.,[7] which has lead to the enhancement of conductivity without any substantial drop in the latent heat, to which the authors attribute the success to improved dispersion of the composite particles.

Agglomeration Observations: Agglomeration effects have been found in studies on cycle testing. Deshpande et al.[19] (Int. J. Sustain. Energy 2025) took 500 cycles of a PEG-based solid-solid PCM using CuO and TiO2 NPs. They stated that latent heat capacity (117-123 J/g) increased following cycling, indicating that it remained stable. Nevertheless, there are also cases in the literature in which thermal performance declined with cycles as a result of NP clustering (e.g. layers of sediment of different melt cycles, in a variety of lab tests).

Techniques of dispersion in literature Nepcm studies often involve the use of sonication and surfactants. As an illustration, mixing PCM and NPs with ultrasonic agitation or addition of Sodium Dodecyl Sulfate (SDS) to the mixture are reported in many papers. The need of such actions is usually underscored by the outcome obtained that without these actions, the thermal improvements intended are not achieved.

Modeling and Theory: Some literature has modeled agglomeration. Although it is specific to PV/T, general NePCM reviews[10] observe that high particle fractions, as well as the absence of stabilizers, result in extensive clustering. Most numerical methods neglect agglomeration effects, as it is often simpler to do. A few more recent studies have tried to model particle settling or clustering as a source of heat transfer in NePCM.

In conclusion, it is stated in the literature that the dispersion of nanoparticles is essential. A report of high efficiency gain with PV/T and cooling of buildings is only made when the NePCM is well prepared. Agglomeration is cited as a factor limiting many experimental articles although it is rarely quantified. All in all, combined physical/chemical dispersion methods are the best way to go in order to gain long-term benefits, as most authors help to understand.

3. Issues and Future Projections

Despite serious advances in this field, a number of issues still persist for example

The number of cycles done is tens to hundreds of cycles, whereas PV/T systems need stability that is years-long. Very little information is available as to whether NePCM dispersions can really be stable in actual outdoor conditions (changing temperature, exposures to moisture and mechanical loads). The long-term testing procedures require standardization to determine the agglomeration according to decades of operating period of solar panels.

Additionally, the ideal nanoparticle choice is still an issue There is research to be done to determine what nanoparticles (material, size, shape) and loadings provide the balance between conductivity gain and stability. It has been demonstrated that carbonaceous particles (graphene, CNTs) are more readily dispersed than dense metal particles, whereas a combination of the two can utilize their synergies. Machine learning or high-throughput experiments can be used in the future to identify ideal nanoformulations.

The need for surface active agents and dispersants is also a challenge. Although surfactants and dispersants are beneficial, they may change PCM phase behavior or provide impurities. It is an open space to find new stabilizers that can be directly combined with the organic PCMs (e.g. polymeric additives that are tailored to PCMs). Also possible could be the in-situ forming dispersants (activated by temperature).

Furthermore, environmental and degradation factors are also pertinent issues: The effect of UV exposure, oxidation of the nanoparticles or chemical degradation of the surfactants on outdoor PV/T environment is not well investigated. Additional agglomeration triggers could be determined in long-term studies in realistic sunlight and weathering.

Altogether, the perspectives look promising, yet pay a lot of attention to the work of NePCM composite engineering. The physics of nanoparticles dispersion in the organic melts will be better understood so that the next-generation PV/T thermal batteries can be designed. The cooperation of material scientists with solar engineers and chemical modelers will be important. This can be followed by emerging methods like nano encapsulation of nano-PCMs or smart PCMs, which will not cluster.

4. Conclusion

Organic PCMs enhanced with nanoparticles are promising technique of increasing the overall performance of PV/T systems through improving thier thermal conductivity and heat storage. Nonetheless, nanoparticle agglomeration is a significant challenge. During phase change, groups of particles may develop and become deposited, and the expected thermal enhancements are minimized. This review has thus discussed the reasons why agglomeration occurs (surface forces, poor compatibility), why it is harmful to heat transfer, and PV/T efficiency, and some of the mitigation strategies have been proposed. To prevent agglomeration, it is necessary to employ a combination of techniques such as ultrasonication, surfactants, and surface treatment of particles. The reviewed literature supports the notion that properly dispersed NePCMs have the ability to greatly increase PV/T output (e.g. far greater energy efficiency of NePCM-cooled PVT systems. It is recommended that future research should look into the long-term stability and scalability of organic NePCMs. The solution of these issues will result in dependable, high efficiency PV/T systems utilizing all solar energy.

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