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THE ROLE OF ALUMINIUM NITRIDE AS REINFORCEMENT MATERIAL FOR PHASE CHANGE MATERIALS (PCMs)

A Review on Synthesis, Characterization and Applications in Thermal Energy Storage

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Abstract. The improvement of thermal energy storage and management has become a significant focus in various industrial applications, including EV battery thermal management, solar energy storage, and high-power electronics. Phase Change Materials (PCM) are widely used for thermal energy storage due to their capacity to absorb and release latent heat. However, organic-based PCMs like paraffin have limited heat conductivity (~0.2 W/mK), limiting their efficiency. This research investigates the potential of Aluminum Nitride (AlN) as a reinforcing material to improve the thermal conductivity and stability of PCM composites. AlN has strong thermal conductivity (~300 W/mK), chemical stability, and oxidation resistance, making it a promising material for increasing PCM thermal performance. Several synthesis methods, including Carbothermal Reduction Nitridation (CRN), sol-gel, hydrothermal, and thermal plasma procedures, have been investigated to produce AlN nanoparticles with appropriate characteristics for integrating into PCM matrices. Furthermore, multiple dispersion strategies, including ultrasonication, surface functionalization, and surfactant-assisted dispersion, are studied to ensure uniform distribution and prevent sedimentation. The use of surfactants like Sodium Dodecyl Sulfate (SDS) and Sodium Stearoyl Lactylate (SSL) further improves dispersion and stability, preventing phase separation and maintaining long-term efficiency. In applications such as EV battery thermal management, AlN-enhanced PCMs demonstrate superior heat dissipation, reducing battery peak temperatures by 19.4% compared to conventional air-cooled systems. Further research is recommended to explore hybrid nanocomposites, optimize AlN particle size and morphology, and develop advanced dispersion techniques to maximize the efficiency of PCM-AlN composites.

Keywords : PCM, Aluminium Nitride, Synthesis, Characterization, Thermal Energy Storage.

1. INTRODUCTION

Improving the efficiency of thermal energy storage and management is becoming a major focus in various industrial applications, including battery thermal management systems for electric vehicles (EV), solar energy storage, HVAC systems, and high-power electronic equipment that require optimal heat management [1]. Phase change material (PCM) is a thermal energy storage mechanism that utilizes materials that can store and release energy through a phase change process. PCM is part of the energy storage method, where in general, there are three (3) types of thermal energy storage systems, namely latent heat, latent sensible, and thermochemical. Latent heat energy storage using PCM is the most widely developed, due to its advantages in terms of ease of operation, and has a similar energy storage density [2]. When a material changes from a solid to a liquid, or from a liquid to a gas, or vice versa, latent heat storage occurs as a result of heat absorption or release. [3]. The following equation expresses the storage capacity of the latent heat system with PCM:

$$Q = \int_{T_i}^{T_m} mCp\,dT + ma_m\Delta h_m + \int_{T_m}^{T_f} mCp\,dT \quad (1)$$

$$Q = m[C_{sp}(T_m - T_i) + a_m\Delta h_m + C_{lp}(T_f - T_m)] \quad (2)$$

Where: Q denotes the amount of energy stored in joules (J). Ti, Tm, and Tf are the initial, melting, and final temperatures (in °C). The specific heat (Cp), average specific heat between Ti and Tm (Csp), and average specific heat between Tm and Tf (Clp) are all expressed in kJ/kg.K, m is the mass of the heat storage media (kg), a_m and Δh_m both are the liquid fraction and heat of fusion per unit mass (J/kg). However, a major challenge in the use of organic-based PCM, such as paraffin, is their low thermal conductivity (~0.2 W/mK), which limits the heat transfer rate and overall performance of the thermal energy storage system [4]. Furthermore, PCMs' long-term thermal degradation and mechanical stability must be considered in practical applications [4].

A common method to improve the performance of PCM is to add reinforcing materials, including carbon-based materials (CNTs, graphene), boron nitride (BN), and metal oxides [5]. Aluminium Nitride (AlN) is a popular reinforcing material due to its exceptional thermal conductivity (~300 W/mK), thermal stability, compatibility with organic PCMs, and great electrical insulation qualities [6]. AlN has an advantage over other materials because of its resistance to oxidation at high temperatures and ability to maintain PCM stability in long-term applications. The addition of AlN nanoparticles to organic PCM can significantly increase its thermal conductivity, and a small concentration of AlN nanoparticles can also help maintain the PCM composite's latent heat value [7].

Although several studies have explored the performance improvement of PCMs with AlN addition, there are still gaps in the understanding of its dispersion method, the effect of the addition ratio on thermal performance, and its application in electric vehicle battery cooling systems [8]. Another challenge that needs to be considered is the processing method of AlN so that it can be homogeneously dispersed in PCM and how variations in AlN particle size can affect the improvement of heat transfer [9]. Therefore, this review aims to analyze the role of aluminum nitride as a reinforcement material in PCM, i.e., the structure and thermal properties of AlN, the synthesis and dispersion method of AlN into PCM, the effect of AlN addition on improving thermal performances of PCM, and its prime potential in the thermal management system of battery electric vehicles (EV).

2. METHODS

The method used in this review includes collecting literature from reputable articles and analyzing and determining research gaps that can be used in the development of further research. The paper used in this literature review focusing on the use of AlN as reinforcement material for PCMs, includes the scope of material science, thermal energy storage, and renewable energy. The selected paper is from a highly reputable journal with an impact factor of more than 0.1 and a publication date of about 10 years, used as primary literature. The research gap for further research is conducted from the gap research about the synthesizing process of nano AlN, the mixing method of nanomaterials into composite PCMs, and the application of PCMs in thermal energy storage.

2.1 Aluminium Nitride: Synthesis and characterization methods

AlN is a promising material with a broad energy bandgap that can be used in high-temperature and high-power electrical and optoelectronic devices. With a binding energy of 4.2 eV, which is higher than the C-C binding energy in diamond (3.8 eV), AlN is ionic and also has extremely strong bonds. At high temperatures (2792 K), AlN starts to break down. The typical deposition temperatures for AlN thin films are 700°C to 1080°C [10]. The challenge of using aluminum nitride nanomaterial is its limited availability and relatively high price. This has led to numerous studies on the synthesis of aluminum nitride using different materials and techniques. Research on the materials and processes used in the synthesis of aluminum nitride is given in Table 1.

Table 1. Synthesis and characterization of AlN

Methods	Materials	Characterization	Results and Highlights	Reference
Gas-reduction–nitridation	$Al(OH)_3$, NH_3, C_3H_8	XRD, TGA, FTIR, SEM	AlN conversion of over 70% at temperatures above 1200°C	[11]
Direct nitridation (with and without additives)	Aluminum Powder, N_2	XRD, SEM, Raman Spectroscopy	Additives enhance the nitridation rate of Al to AlN, accelerating the formation of pure phases	[12]

CRN	Sodium Aluminate ($NaAlO_2$), Carbon Black	XRD, SEM, BET	AlN with an average particle size of 0.50 ± 0.18 µm at 1400°C	[13]
CRN	Al_2O_3, NH_3,, glucose, SF	XRD, SEM, FTIR, BET	Smaller AlN particles, better distribution, no agglomeration	[14]
CRN in-situ nitridation	Al_2O_3 and carbon	XRD, Raman, SEM	AlN nanopowder with good size distribution	[15]
CRN – sol-gel	Al_2O_3/Phenol Resin	XRD, SEM, FTIR, BET	AlN synthesis with more uniform grain size and better particle distribution	[16]
CRN - slurries	$Al(OH)_3$, Carbon Black, PVB	XRD, SEM, TEM, FTIR	PVB improves mixing homogeneity and nitridation efficiency	[17]
CRN - hydrothermal precursor	Al_2O_3, NH_3,, glucose, PEG	XRD, SEM, TEM, FTIR	AlN nanofibers with diameters of 90-110 nm at 1400°	[18]
Hydrothermal synthesis	Aluminum-based precursor	XRD, TEM, FTIR, UV-Vis	Particle size is controlled by hydrothermal pressure and temperature	[19]
Electrical Explosion of Wire (EEW)	Aluminum Wire	XRD, TEM, EDS	Al/AlN nanoparticles with controlled size through explosion parameters	[20]
Thermal Plasma Reactor (TPR) synthesis	Aluminum 1100 discs	XRD, SEM, TEM, EDS	High-purity nanocrystalline AlN with a thin carbon layer, enhancing oxidation resistance	[21]
RF Induction Thermal Plasma synthesis	Aluminum powder, N_2	XRD, SEM, TEM, FTIR, BET	AlN nanoparticles (20–60 nm) with high purity, controlled via plasma power and gas flow rate	[22]

2.2 Method of Aluminum Nitride Dispersion in PCMs

The thermal conductivity of organic PCM can be enhanced by adding the nanomaterial AlN, but integrating nanomaterials with PCM leads to challenges due to density differences that cause a propensity for agglomeration and sedimentation. To prevent this phenomenon, a variety of methods of PCM mixing with various nanomaterials are employed to produce uniform and even PCM composites. Table 2 shows several mixing methods of nanomaterial addition into PCM.

Table 2. Methods of nanomaterial addition

PCM Material	Dispersion Method	Added Nanomaterial	Results and Highlight	Reference
Paraffin	Mixing with Sodium Stearoyl Lactylate (SSL) surfactant	Nano-Al_2O_3	Thermal conductivity increased by 31% (solid phase) and 13% (liquid phase); melting rate improved by 27%.	[23]

PCM Material	Dispersion Method	Added Nanomaterial	Results and Highlight	Reference
Bio-based PCM (PureTemp PCM)	Addition of surfactants SDS, SDBS, and SSL	Graphene nanoplatelets (GnPs)	Thermal conductivity increased up to 1.03 W/mK.	[24]
Nano-emulsion water-based PCM	Phase Inversion Temperature (PIT) method using dual surfactants	n-Hexadecane, Brij L4, Tween 60	High stability for 120 days and 300 thermal cycles with droplet size below 80 nm.	[25]
PCM with carbon additives	Direct mixing with stabilizer (PVP)	Carbon nanotubes, Graphite, Graphene	Heat transfer rate increased up to 3.35 times at 5.0 vol% Graphite.	[26]
PCM A70	Dispersion of graphene nanoplatelets with surfactant	Graphene nanoplatelets with SDBS surfactant	Thermal conductivity increased by 122.26% compared to conventional PCM.	[27]
PCM PT-58	Dispersion with copper foam	Graphene nanoplatelets (GNPs), Magnesium oxide (MgO)	Maximum temperature reduced by 16% with 0.02 wt.% GNPs addition.	[28]
Stable-form composite PCM	Adsorption of aluminum nitride into the matrix	Aluminum nitride (AlN)	Thermal conductivity increased by 2903% compared to pure PCM.	[29]
Aluminum nitride-based PCM	Vacuum adsorption and nano-encapsulation	Aluminum nitride (AlN), nano-encapsulated PCM	Thermal conductivity increased up to 3.5 W/mK, approximately 17.5 times higher than pure PCM.	[30]
Nanocomposite PCM	Blending, encapsulation, and impregnation	Al, Cu, Al_2O_3, TiO_2, Fe_2O_3, CNT, Graphene nanoplatelets	Improved energy storage efficiency and thermal conductivity depending on the method used.	[31]
Paraffin wax	Dispersion of various nanoparticles	Fe_3O_4, Al_2O_3, CNT	Enhanced PCM stability with carbon-based and metal oxide additives.	[32]
Paraffin-based PCM	Mechanical dispersion (stirring & sonication)	Al_2O_3, BN, CNTs	Improved thermal conductivity and stability over multiple heating cycles.	[33]
PEG-based PCM	Functionalization with acid treatment	MWCNTs	Enhanced dispersion stability and increased heat transfer performance.	[34]
Organic PCM	Microencapsulation via spray drying	Nano-SiO_2, Graphene oxide	Improved leakage prevention and long-term stability.	[35]

3. RESULTS AND DISCUSSION

3.1 Aluminum Nitride: Structure, Properties, and Potential as Reinforcement Material

Aluminum Nitride (AlN) is a ceramic material with remarkable thermal conductivity, high electric insulation, and chemical stability. Its crystal structure is classified under the wurtzite phase, which explains its high thermal conductivity at about 300 W/mK. Due to its high thermal conductivity and chemical stability, AlN is an ideal reinforcement material for PCM in use for energy storage.

Aluminium Nitride (AlN) has a limitation in terms of availability and very high prices. This has led to research in synthesizing aluminium nitride using various methods and materials. In recent years, the methods used in synthesizing AlN are: Direct Nitridation, Carbothermal Reduction Nitridation (CRN), Sol-Gel, Thermal Plasma, and hydrothermal, as shown in Table 1. The results in particle size and phase purity from Table 1 are shown in Figure 1:

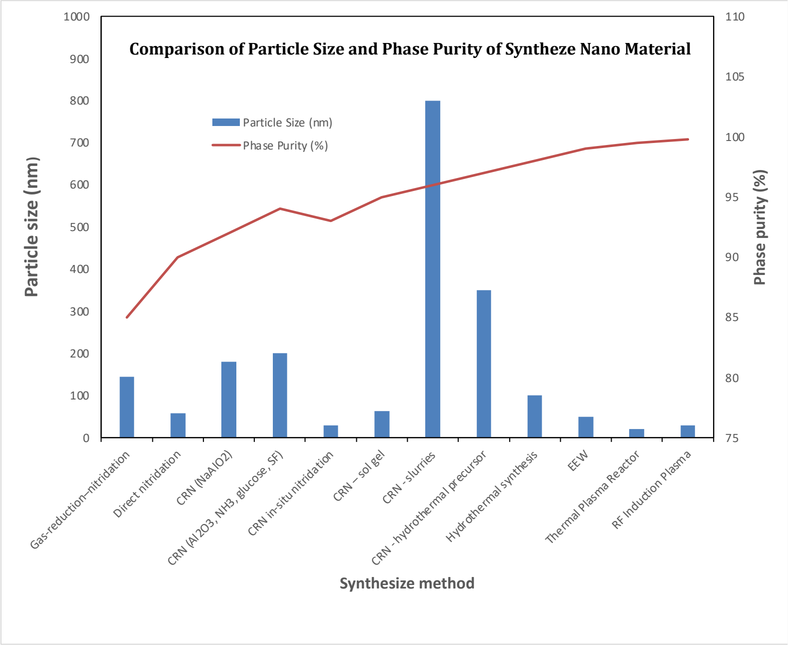

Figure 1. Particle size and phase purity of AlN from different methods of synthesizing

The most common methods used in synthesizing nano-AlN were direct nitridation of aluminium and the use of carbon as a reduction agent (CRN methods). CRN-based AlN synthesis using carbon precursors leads to improved thermal conductivity due to better phase purity and controlled particle size distribution; this caused the CRN methods to become major methods used in synthesizing AlN [13], [14], [15], [16], [17]. From Figure 1 it can be known that the gas-reduction nitridation and direct nitridation methods produce aluminium nitride in lower phase purity (80% and 90%) compared to the other methods. The CRN method, which has an advantage in simpler processes than the plasma methods, became a major method that is used on an industrial scale to produce nano AlN. In addition, AlN synthesis through plasma-based techniques exhibits finer grain structures and enhanced dispersion properties, making them more effective for integration into PCM matrices, but this process requires a high operating temperature in the reactor [21], [22]. The smaller particle size of AlN nanoparticles can improve the thermal conductivity of PCM because it can be homogeneously mixed in the composite matrix because it is well distributed and prevents agglomeration.

To confirm the structure and properties of synthesized AlN, several characterization techniques are employed:

a. Fourier Transform Infrared Spectroscopy (FTIR): Identifies chemical bonds within the material. Peaks at ~600 cm^{-1} indicate Al-N stretching vibrations, confirming AlN formation.
b. Scanning Electron Microscopy (SEM) & Transmission Electron Microscopy (TEM**)**: Provide insights into the morphology, grain size, and distribution of synthesized AlN. Nanoparticles with uniform size and minimal agglomeration exhibit better dispersibility in PCM.
c. X-Ray Diffraction (XRD): Used to determine the crystallinity and phase purity of AlN. The presence of sharp diffraction peaks corresponding to the wurtzite AlN phase confirms successful synthesis.
d. UV-Vis Spectroscopy & Photoluminescence (PL)**:** Used to measure the optical properties and bandgap energy. A bandgap around 6.1 eV is typically observed for high-purity AlN.
e. Thermogravimetric Analysis (TGA)**:** Evaluates the thermal stability and weight loss behavior of AlN.
f. Raman Spectroscopy**:** Used to detect vibrational modes and assess the structural integrity of AlN. Raman peaks corresponding to E2(high) and A1(LO) modes indicate high crystallinity and phase purity. The presence of additional peaks or shifts can signal structural defects, impurities, or stress in the lattice.
g. Particle Size Analysis (PSA): Determines the size distribution of AlN nanoparticles, which significantly affects their dispersion and performance in PCM. A uniform and narrow particle size distribution enhances the stability and thermal conductivity of the composite material.

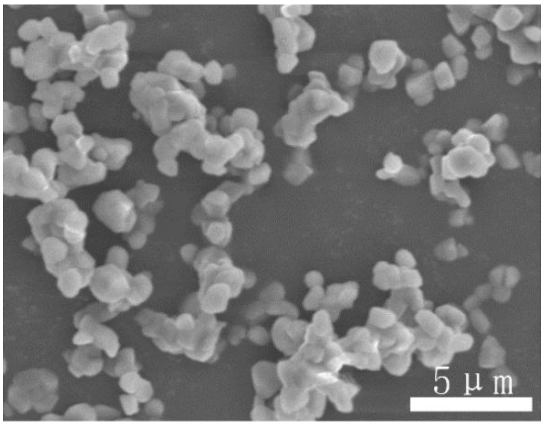

Figure 2. SEM morphology of AlN synthesized using CRN-slurries method [17]

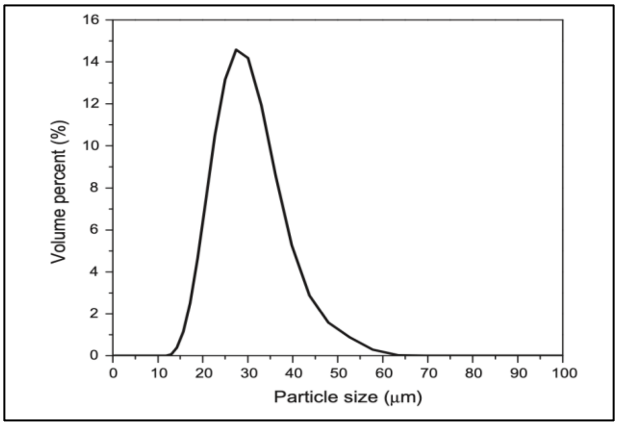

Figure 3. The particle size of AlN using PSA analysis [36]

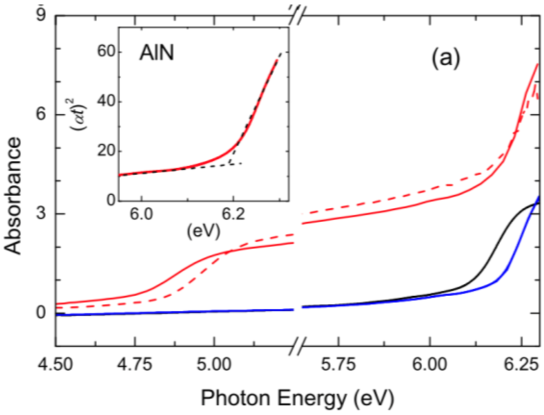

Figure 4 Photon energy of AlN using UV-vis diagram analysis [37]

Figure 2 shows the SEM image of aluminum nitride at 5 um scale. The AlN was synthesized using the CRN-slurries method. The results show that the AlN particles have a granular morphology with a non-uniform size distribution. Particles with non-uniform morphology can have a larger specific surface area, which could potentially improve the thermal contact between PCM and AlN. To ensure homogeneous distribution in PCMs, it is necessary to modify the particle morphology or use better dispersion methods to avoid aggregation and sedimentation in PCM-based heat storage systems.

Figure 3 shows the particle size analysis of AlN using PSA, with an average size of about 30 µm. AlN particle sizes in the 30-40 µm range can still increase the thermal conductivity of PCM but are less effective than nanoparticles. For PCM-based thermal energy storage applications, it is more advisable to use AlN on a nanoscale (<100 nm) so that the increase in thermal conductivity is more optimal and the dispersion stability in PCM is better.

From the UV-vis spectrograph in Figure 4 known that aluminium nitride has a wide band gap (6.0 – 6.2 eV) and photon energy of about 6.0 eV. With a wide band gap (6.0 - 6.2 eV), AlN has excellent thermal resistance, which prevents degradation of the material structure when used in repeated heating-cooling cycles in PCMs. The high energy absorption of AlN enables more uniform heat distribution in the PCM, reducing the risk of hot spots and improving thermal management efficiency in thermal energy storage applications.

3.2. Thermal Conductivity Enhancement and PCM-AlN Efficiency

The addition of AlN into PCM improves both thermal conductivity and heat storage efficiency. The dispersion method is the most important in determining AlN's efficiency as a reinforcing agent. From Table 2, there were several methods used in the dispersion of nanomaterials into PCM, including vacuum adsorption and nano-encapsulation technologies, which resulted in excellent integration, enhancing the thermal performance of PCM-AlN composites [30], [35]. The thermal conductivity of pure PCM is around 0.2-0.3 W/mK. AlN-reinforced PCM can reach values of up to 3.5 W/mK, marking a nearly 17.5-times improvement compared to conventional PCM. This improvement ensures faster heat transfer rates during phase transitions, reducing the risk of overheating and improving overall energy efficiency. In addition, the nanoencapsulation of AlN in the PCM matrix minimizes phase separation issues and ensures stable cycle performance over long operational periods.

The use of surfactants in the dispersion of nanomaterials into PCM also plays an important role. The study of addition surfactants such as sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), and sodium stearoyl lactylate (SSL) shows results that using SDS surfactant in PCM composites leads to maximum thermal conductivity across all PCM mass fraction variations. The addition of 3% SDS increases the thermal capacity of PCM composites while adding SSL increases the PCM enthalpy value [24]. Another result using SSL as a surfactant in dispersing nano-Al_2O_3 into paraffin has a similar finding where the effective thermal conductivity of paraffin increased from 0.20 to about 0.28 and 0.29 W/mK (enhancement of more than 43%) [23].

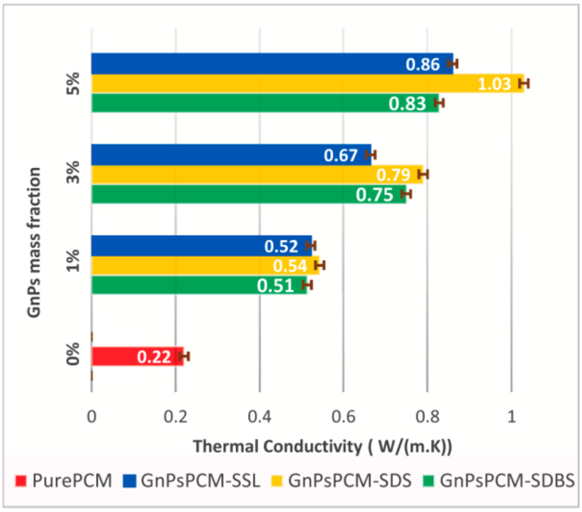

Figure 5. Thermal conductivity of nanocomposite PCM- Graphene Nanoplatelets and surfactants [24]

From Figure 5 we can see clearly that the addition of surfactant (SDS, SSL, SDBS) into nano-enhanced PCM-GnP significantly increases the thermal conductivity compared to pure PCM. According to the study of literature, it is known that a combination of ultrasonication, surface functionalization, and surfactant-assisted dispersion yields the highest enhancement in thermal conductivity of PCM. This is because the combination methods can ensure that AlN remains well-distributed within PCM without excessive sedimentation or aggregation. The optimization of these dispersion methods is crucial for maintaining the long-term stability and effectiveness of PCM-AlN composites.

3.3 Application of PCM-AlN for Thermal Energy Storage

The addition of nanomaterial AlN to PCM can significantly increase the thermal conductivity and stability of composite PCM. This makes the nanocomposite PCM/AlN a promising application in the thermal management system of battery electric vehicles (EV). Efficient heat dissipation is crucial for maintaining battery temperature within an optimal range, preventing thermal runaway, and extending battery lifespan.

The integration of nano-AlN into paraffin increased the thermal conductivity, mechanical strength, and volume resistivity, of which the addition of 20 wt% AlN is the most effective. The result in the battery module shows better heat dissipation and temperature uniformity compared to an air-cooled battery module, leading to a

19.4% decrease in the maximum temperature and a less than 1°C temperature difference at a high discharge rate of 3C. This indicated that the AlN-enhanced composite PCM thermal management system has significant temperature control and balancing capability for the battery module. [38]. Similar research in the addition of AlN in organic PCM polyethylene glycol (PEG) was also done, and the result shows that increasing AlN nanopowder into composite PCM polyethylene glycol (PEG) will increase the thermal conductivity of composite PCM, and the latent heat of composite PCM will decrease. [39]

Another research is also done to improve the solar panel output by adding composite PCM (NePCM) for passive cooling in surface solar panels. Solar panel efficiency has increased from 10.11% to 13.19%. The maximum power produced was 46.22 W when the PV working temperature reached 52.62°C. It has been demonstrated that using the NePCM system improves simple PCM's capacity to absorb heat [40].

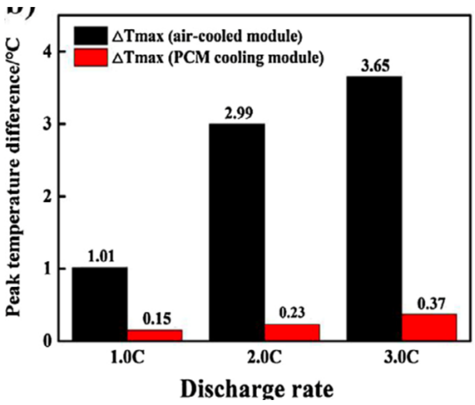

Figure 5. Temperature of battery module using air-cooled and nanocomposite PCM [38]

3.4 Potential Research and Development: Sustainability and Recyclability Aspects

While significant advancements have been made in PCM-AlN composites, several areas still require further research and development to optimize their performance, sustainability, and recyclability, ensuring long-term viability in thermal management and energy storage systems:

a. Optimization of AlN nanoparticle size and morphology:
   Research into the impact of nanoparticle size on PCM performance can lead to enhanced thermal stability, efficiency, and durability. Smaller, well-dispersed AlN nanoparticles improve thermal conductivity while minimizing sedimentation and phase separation in PCM composites. From a sustainability perspective, optimizing particle size can reduce material waste, improve heat cycle stability, and extend the lifespan of thermal storage systems, decreasing environmental impact.

b. Hybrid nanocomposite approaches**:**
   Research of the effects of combining AlN with various materials, i.e graphene nanoplatelets (GnPs), expanded graphite (EG), and carbon nanotubes (CNTs) could enhance thermal performance, mechanical strength, and stability of PCM-AlN composites. This hybrid approach can lead to more durable and high-performance thermal storage materials, reducing material degradation over multiple heating cycles.

c. Dispersion methods for enhanced stability and recyclability:
   Research on efficient dispersion techniques—such as functionalization, surfactant-assisted methods, and ultrasonic dispersion—can improve nano-PCM stability and reusability. Ensuring long-term dispersion stability is essential for achieving recyclable and sustainable PCM-AlN composites, allowing for multiple thermal cycles without loss of performance.

By integrating sustainable synthesis techniques, optimized dispersion strategies, and recyclable hybrid nanocomposite materials, future research can significantly contribute to green energy solutions in thermal management applications for battery electric vehicles (EVs), buildings, and renewable energy storage.

4. CONCLUSION

From the result of this study, it can be concluded that aluminum nitride (AlN) in the form of nanometers has great potential as a reinforcement material for PCM. Its high thermal conductivity, chemical stability, and high oxidation resistance can increase the thermal performance of PCM, which is suitable for application in energy storage and thermal management systems of battery EVs. The method of dispersing AlN into PCMs plays a major role in the optimal performance of composite PCMs. This is because the differences in density between AlN and PCM can lead to agglomeration and sedimentation, which can reduce the characteristics of AlN in PCM. According to this conclusion, more studies may be conducted by optimizing the size and morphology of nano-AlN, hybrids, or combinations of nano-AlN and other materials to optimize the thermal performance and also optimize the methods of dispersion of AlN into PCM.

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