



INVESTIGATING COLLOIDAL STABILITY OF NANO-ENHANCED PHASE CHANGE MATERIAL UNDER THERMAL CYCLING

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1. ABSTRACT

We investigate the role of rationally selected surfactant and nanoparticle surface treatment on the stability of a Al_2O_3 /Eicosane nanosuspension as a phase change material. The resulting better dispersion of Al_2O_3 led to superior stability of the nanosuspension under multiple heating/freezing cycles, and suggesting excellent thermophysical properties. The nanosuspension with functionalized nanoparticles and sodium dodecylbenzene sulfonate (SDBS), as a surfactant showed better stability compared with pristine Al_2O_3 . The present work provides a route to enhance the performance of nanosuspensions as phase change materials (PCMs) for thermal management.

2. INTRODUCTION

Phase change materials (PCMs) have attracted considerable attention in the last few years due to their enormous potential for passive thermal management [1]. Therefore, adding the nanoparticles to the PCM has a noteworthy potential for intensification of the thermophysical properties of PCM. However, owing to the high surface energy of commonly employed thermally conductive nanoparticles, they tend to self-aggregate. This can alter both hydrodynamic size and morphology, occasionally accompanied by changes in volume fraction through settling, affecting the inherent stability of the colloidal system, thereby counteracting the benefits of adding nanoparticles in the first place [2]. Thus, investigating the colloidal stability of nanosuspensions under multiple heating/cooling cycles is of paramount importance towards realization of nano-PCM as a viable alternative. Numerous investigations have been conducted to synthesise a suspension characterized by enhanced stability and improved heat transport capabilities of PCMs. Two main routes can be employed to improve the dispersion characteristics; the use of surfactants and surface treatment of nanoparticles. Surfactants are commonly employed for achieving homogeneous dispersion of nanoparticles within the base fluids. The inclusion of surfactants is intended to modify the surface characteristics of suspended particles, thereby mitigating the formation of particle clusters and facilitating the attainment of stable suspensions. However, they also influence the physical properties of PCM, such as thermal conductivity and viscosity. The impact of surfactants on nanosuspensions has been explored, yielding intricate and varied outcomes in reported studies [3], [4]. These studies have focussed on surfactant altered thermophysical properties of nanosuspensions without explicitly studying their colloidal stability, especially under thermal cycling. Surface treatment, on the other hand, plays a key role in tuning particle interactions and enhancing stability with inherent enhancement in the thermophysical properties of the nanosuspensions. However, in previous studies on PCM-based nanosuspensions, detailed investigation into the stability of the colloidal system after melting/solidification cycle has been lacking or even neglected, often in favour of emphasizing enhancements in thermophysical properties. This study aims to address this gap by exploring both strategies of surfactant infusion and surface modification of nanoparticles on the stability of an Al_2O_3 /Eicosane nanosuspension.

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3. METHODOLOGY

3.1 Materials

In the present study, the *n*-Eicosane was used as a PCM with phase-transition temperature of 35-37 °C, 13 nm Aluminium oxide (γ -Al₂O₃) nanoparticles, sodium dodecylbenzene sulfonate (SDBS), *n*-Hexane, and Trichloro(octadecyl)silane (OTS) were purchased from Sigma-Aldrich, UK. All materials are used as received without further chemical treatment.

3.2 Preparation of surface modified Al₂O₃

The surface modified Al₂O₃ nanoparticles were prepared by the following protocol. First, 1 g of dried Al₂O₃ was dissolved in 60 mL Hexane. Then, the solution was sonicated for 30 minutes. Afterwards, 1 vol.% of OTS was added to the solution with providing mechanical stirring at room temperature for 2 hours. Finally, the nanoparticles were washed with Hexane several times to remove the excess silane and then dried at vacuum oven for 24 hours at 70 °C. 1.0 wt.% of modified Al₂O₃ was added into pristine liquid Eicosane.

3.3 Preparation of PCM nanosuspension

A precise two-step preparation method, involving 60 minutes of mechanical stirring followed by 30 minutes of sonication, was carried out to synthesize PCM nanosuspension, which has been used extensively in preparation of nanofluids [5]. The surfactant was added into the liquid PCM with mass fraction of 0.1 wt.% to enhance the dispersion of nanoparticles. Thereafter, a constant amount of 1.0 wt.% of pristine Al₂O₃ was added into the solution.

3.4 Thermal stability of nanosuspension

All suspensions are observed through a quartz cuvette on a hot plate (temperature of \cong 50 °C) for 2 hours. This is referred to as the liquid phase. A 1.6 MP, CMOS camera (Thorlabs) fitted with a 6x zoom lens (MVL7000) was used to visualize settling of suspension. Images were acquired every 30 s. After 2 hours, the hot plate was turned off and the images were acquired every 10 s till the suspension solidified. Subsequently, the hot plate was turned on to melt the suspension, thus completing one thermal cycle.

4. RESULTS

Four cases were tested to understand colloidal stability as shown in **Fig. 1**. The first case is the pristine Al₂O₃/Eicosane. A thin layer of particle-free region near to the sidewall is observed in **Fig. 1(a)** after 2 hours, indicating early signs of aggregation induced particle settling. This is exacerbated after the 1st thermal cycle. The investigation of stability in the solid phase presents challenges due to the similarity in colours between solid Eicosane and nanoparticles. However, transparent regions observed in the upper portion after the first thermal cycle suggest phase separation between nanoparticles and Eicosane. The second case involved adding 0.1 wt.% of SDBS to the suspension and followed by pristine Al₂O₃. As a result, the particle-free region is avoided as shown in **Fig. 1(b)**. After undergoing the first thermal cycle, the suspension again shows similar particle separation as shown in **Fig. 1(a)**. The results indicate that mechanical dispersion via stirring and sonication with presence and absence of surfactant is insufficient in altering the interfacial energies between nanoparticles and Eicosane under multiple melting/solidification cycles. Consequently, the sustainability of well-dispersed colloidal systems is compromised. Building upon these findings, a third case involving surface modification of Al₂O₃ nanoparticles using OTS to enhance their dispersion within Eicosane was explored. Significant sedimentation of functionalized nanoparticles was observed during the liquid phase of the suspension, as depicted in **Fig. 1(c)**. However, at the end of the thermal cycle, the severity of phase separation is relatively less as observed from the cloudy appearance of cuvette. Based on this finding we hypothesize that both surfactant addition and particle modification are necessary to stabilize the suspension during thermal cycling.

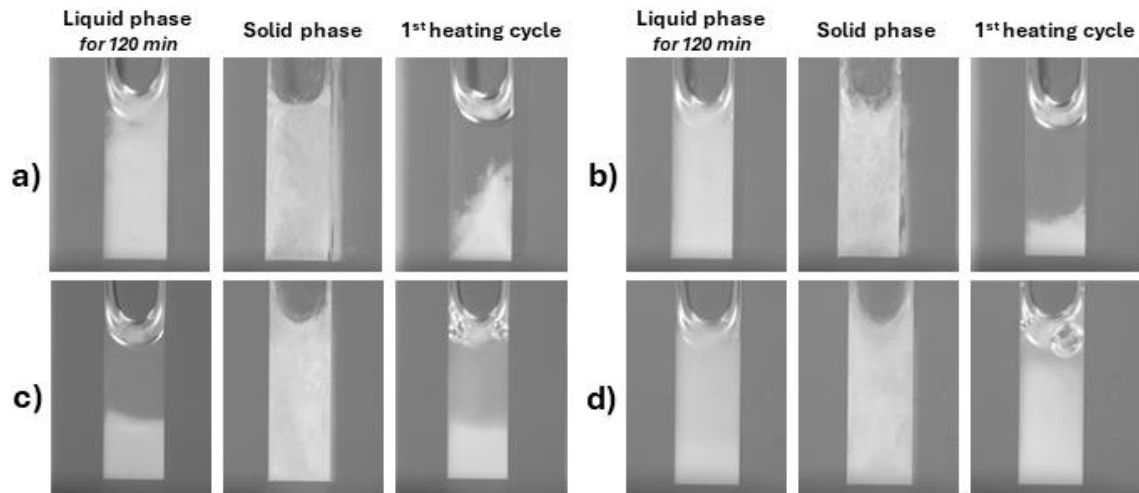


Figure 1: stability observation of PCM nanosuspension at liquid phase, solid phase and liquid phase after cooling/heating cycle, of **a)** pristine $\text{Al}_2\text{O}_3/\text{Eicosane}$, **b)** pristine $\text{Al}_2\text{O}_3/\text{Eicosane}/0.1 \text{ wt.}\% \text{ SDBS}$, **c)** modified $\text{Al}_2\text{O}_3/\text{Eicosane}$, and **d)** modified $\text{Al}_2\text{O}_3/\text{Eicosane}/0.1 \text{ wt.}\% \text{ SDBS}$.

Thus, a fourth case involving the addition of 0.1 wt.% of surfactant to surface modified Al_2O_3 nanoparticles based nanosuspension was tested. **Fig. 1(d)** illustrates that the addition of surfactant improves the stability of the colloidal system during the liquid phase. The pristine nanoparticles, both in absence and presence of surfactant, are excluded during solidification. We believe that particle treatment prevents this exclusion and complements the surfactant in nanosuspension stabilization.

5. CONCLUSION

The study investigated the impact of surfactants and surface treatments on the stability of Al_2O_3 -based Eicosane PCM-based nanosuspensions. Although surfactants are commonly employed to enhance the dispersion of colloidal systems, they fail to do so under thermal cycling for the concentrations studied here. Equally, surface functionalisation of the nanoparticles alone cannot ensure stability following one heating cycle of the suspension. However, combining surfactants with nanoparticle functionalisation exhibiting superior stability performance. Further work is currently underway to characterize the thermophysical properties of tested suspensions and experimentally investigate their heat transfer performance within a heat sink.

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