



Research paper

Preparation and control mechanism of nano-phase change emulsion with high thermal conductivity and low supercooling for thermal energy storage



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ABSTRACT

In order to investigate the control mechanism of composite phase change materials (PCM), a series of composite nano-phase change emulsion (NPCE) were prepared in this paper with high thermal conductivity, high heat storage and low supercooling using hexadecane, octadecane, hexadecanol, octadecanol and various metal nano-particles. Through the control mechanism, it is expected to adjust the phase transition range of NPCE to a desirable range. The NPCEs were characterized by particle size analyser, cryogenic transmission electron microscope (Cryo TEM), differential scanning calorimeter (DSC), thermal conductivity meter and rheometer. The results showed that the NPCEs were successfully prepared with uniform dispersion, great stability, low viscosity and narrow particle size distribution. DSC results showed that the latent heat of NPCE with 20 wt. % hexadecane was 55.86 kJ/kg. The supercooling degree of prepared NPCEs using 1.25 wt. % of hybrid nucleating agents was reduced by 81%. Metal oxides effectively improved the thermal conductivity of NPCEs. The thermal conductivity of the NPCEs with 1wt. % nano Al₂O₃ was 0.70 W/(m · K), which was increased by 21%. The viscosity of the NPCEs increased with the increase of metal oxide concentrations and decreased with the increase of temperature. Importantly the NPCEs presented a shear thinning effect and can be considered as Newtonian fluid after shear rate of 2 s⁻¹, which had great potential in the thermal energy storage system.

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1. Introduction

In order to control the trend of global warming and improve the energy structure, various renewable energy sources have been developed and applied (IPCC AR6). Energy storage systems are often combined with renewable energy power systems such as solar and wind energy (Jordehi et al., 2021; Barnoon, 2021a). Thermal energy storage technologies mainly include sensible heat storage, chemical heat storage and latent heat storage (Sahan and Paksoy, 2018; Vahid-Ghavidel et al., 2022). NPCEs can absorb or release a large amount of latent heat during the phase transition (Barnoon, 2021b; Barnoon et al., 2021; Zhang et al., 2012), thereby it is widely used in electronic product heat dissipation (Monfared et al., 2021; Li et al., 2020; Jaguemont et al.,

2018), building energy conservation (Köse Murathan and Manioğlu, 2020), indoor thermal insulation (Kishore et al., 2021), biological tissue thermal management (Barnoon and Bakhshandehfard, 2021), cold chain transportation (Tong et al., 2021), etc. In recent years, the popularity of electronic products has led to an increase in the energy consumption (Yang et al., 2021). Although intensive researches on the cooling process of electronic products were carried out, the cooling method using traditional heat transfer fluid cannot achieve desirable effect. Therefore, seeking appropriate heat transfer medium for cooling electronic products has become a popular research topic (Kumar et al.) The cooling mode of micro-electronic equipment can be divided into active cooling and passive cooling. When phase change nano-emulsion (NPCE) is employed as a passive cooling medium, the phase change material can absorb a large amount of heat and keep the temperature of device within a safe range. NPCEs is an effective coolant with high heat transfer performance compared to pure water and other refrigerants (Solangi et al., 2015; Zhang et al., 2020).

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The heat transfer performance of a heat transfer medium is determined by its thermophysical properties (Zhang and Zhao, 2017). Zhang and Zhao (2011) investigated thermophysical properties of microencapsulated phase change slurries, such as latent heat, thermal conductivity and thermal gravimetric analysis. They also investigated rheological properties of slurries and found out the relationship between the shear stress, shear rate and dynamic viscosity of slurries. Therefore, improving the thermophysical properties of the heat transfer medium can significantly enhance the heat transfer effect (Hayat et al., 2022). The usage of nanoparticles with concentration of 2% caused lower thermal resistances in comparison to the case of pure water (Ho et al., 2021a). Compared with the traditional fluid, adding phase change materials and high thermal conductivity particles in the nanofluids improved energy storage and heat transfer of the fluids. Sahoo et al. (2016) showed that the viscosity of NPCE increased with the increase of particle mass fraction, which affected the convective heat transfer. Zhang et al. (2019) employed SiO₂ nano-particles as an effective nucleating agent to reduce the degree of supercooling. Raam Dheep and Sreekumar (2014) indicated that metals and carbon based nanomaterials were incorporated with PCM to achieve efficient phase change properties. Singh et al. (2022) investigated the comparative effects of Al₂O₃, MgO, and SiO₂ nano-doping on the thermal performance and the overall thermal behaviour of PCM based thermal energy storage systems. The result explicated that the optimum volume concentration of SiO₂ was 0.3 wt. %. Cherecheş et al. (2021) investigated thermophysical properties of Al₂O₃/ PEG 400 nanoparticle enhanced fluids and they demonstrated that both temperature variation and nanoparticle mass concentration were the main factors for influencing the viscosity and heat capacity of nanofluids. Liu et al. (2021) used n-octacosane as a nucleating agent to reduce the supercooling of NPCE to 2.4 °C. Shoebi et al. (2021) indicated that adding CuO and Al₂O₃ nanoparticles at 0.1 wt. % could reduce the supercooling degree by 2.1 °C and 1.8 °C, respectively. Ibrahim et al. (2022) mixed nano-TiO₂ and MgO with paraffin and the thermal conductivity of nano-composites improved with a maximum value of 24.92%. The melting and solidification temperatures decreased by 1 °C for addition of nano-TiO₂ and MgO and by 2 °C for addition of the hybrid nanoparticles. Najafi et al. (2021) dispersed TiO₂ and Fe₃O₄ nanoparticles to the pure paraffin for enhancing the heat-sink cooling ability. Shafee et al. (2020) prepared a novel nano-phase change emulsion consisting of paraffin and multiwall carbon nanotube (MWCNT). The result explicated that the efficiency of the nanofluid with MWCNT were better than paraffin. Lu et al. (2022) prepared paraffin/nano-Fe₃O₄ composite PCMs to enhance the thermal conductivity of PCM. Results showed that when the mass fraction of nano-Fe₃O₄ was 5 wt%, the thermal conductivity of nano-composite PCM could be enhanced by 53% at the solid state and 79% at the liquid state compared to that of pure paraffin.

According to the above background and knowledge of the authors, limited attempts have been made to propose a control mechanism of the thermophysical properties for NPCEs. The control mechanism intended to regulate the phase transition range of NPCEs to a desirable range. This will expand the potential applications of NPCEs to a broader vision. Therefore, the aims of this study was to propose a new concept to improve the thermophysical properties of nano-phase change emulsion based on a control mechanism. In the current work, a series of NPCEs with high heat of fusion, high thermal conductivity, high stability, low viscosity, and low supercooling were prepared with various concentrations of hybrid alkanes, metal oxide nanoparticles and hybrid nucleating agents. Through the control mechanism regulation, the prepared NPCEs are expected to achieve the desirable thermophysical properties and they will have potential application in the thermal systems.

2. Materials and methods

2.1. Materials

Hexadecane (98%, melting point: 20 °C), octadecane (98%, melting point: 31 °C), hexadecanol (99%), octadecanol (99%), OP-10 emulsifier, ZnO (99.0%, 1 µm), nano-ZnO (99.9%, 30 nm) and nano-Al₂O₃ (99.9%, 30 nm) were all purchased from Shanghai Maclean Biochemical Technology Co., LTD. All chemicals were used as received from the suppliers.

2.2. Preparation of NPCE

Samples A, B, C and D nano-phase change emulsions were prepared by the sonication method. Type A, nano-phase change emulsions prepared with various concentrations of phase change materials (5 wt. %, 10 wt. %, 20 wt. %); Type B: nano-phase change emulsions prepared with various concentrations of hybrid phase change materials (hexadecane and octadecane). Type C, nano-phase change emulsions prepared with hybrid phase change materials (10 wt. %) and various concentrations of metal oxide particles (ZnO, nano-ZnO, nano-Al₂O₃). Type D: nano-phase change emulsions prepared with hybrid phase change materials (10 wt. %), nano-Al₂O₃ (10 wt. %), and various concentrations of nucleating agents (0.25 wt. %, 0.75 wt. %, 1.25 wt. %), the mass ratio of hexadecanol and octadecanol was set as 1:1. Fig. 1 shows the preparation process diagram of NPCEs. Table 1 shows all the samples prepared, it should be pointed out that the control mechanism of composite phase change materials refers to that the alkanes with different melting points are proportioned in order to obtain the desirable melting points and latent heats.

The preparing procedure is taken sample C1 (5 wt. % hexadecane + 5 wt. % octadecane + 0.1 wt. % nano-Al₂O₃) as an example. Firstly, an electronic balance was used to weigh 2.5 g hexadecane, 2.5 g octadecane, 0.5 g OP-10 and 0.05 g ZnO, respectively. Hexadecane and octadecane were then added to 44.45 g of deionized water, and a magnetic agitator was used to stir the mixture for 30 min at 40 °C with a rotating speed of 800 r/min, nano-Al₂O₃ particles were added while stirring. Then, the mixture was placed in an ultrasonic water bath at 40 °C for 60 min. The mixture was finally sonicated with a tip sonicator (Type JY92-IIN, LNB Instrument, Shanghai) in a water bath at 85% (650 W) amplitude for 25 min (with 2 s probe on and 3 s probe off) while the mixture was gently stirred by a magnetic stirrer. The above preparation method is able to prepare NPCEs within 200 nm. Therefore, the NPCEs prepared in this paper can be applied to the cooling process in the microchannel.

2.3. Particle size and stability analysis of NPCE

Zeta-sizer nano series (Malvern Zetasizer Nano ZS 90) was utilized to characterize the particle size distribution. The specified accuracy of the instrument is ±2%. The samples were well shaken before measurements and sampled with a pipette gun and diluted with deionized water at a ratio of 1:1000. Each sample was measured three times at 25 °C after preparation. The sensitivity of the particle size and PDI measurements is 0.1 mg/ml.

2.4. Morphology analysis of NPCE

In this study, a cryogenic transmission electron microscope (Talos F200C G2) was used to characterize the two-dimensional structure of the nano-emulsion at an accelerating voltage of 200 kV and −196 °C. By freezing the sample, the damage of electron beam to the sample and the deformation of the sample were avoided, thereby the original morphology of the sample were

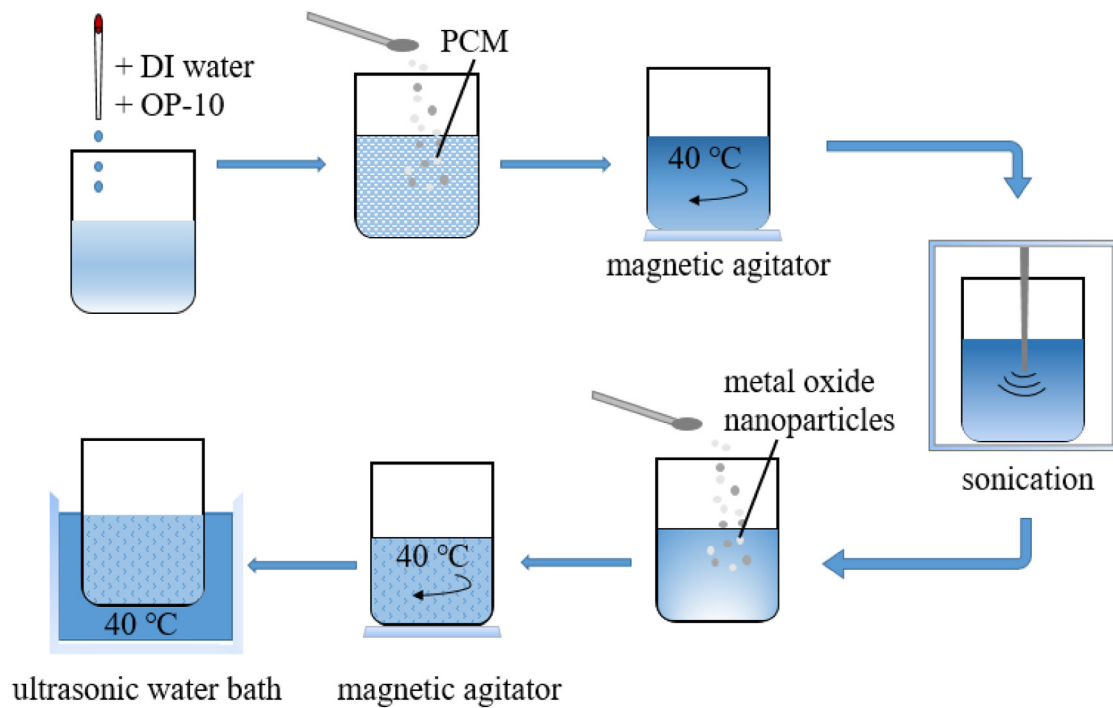


Fig. 1. The preparation process diagram of NPCEs.

Table 1

Prepared nano-emulsions with various concentrations of hybrid alkanes, metal oxide nanoparticles and hybrid nucleating agents.

Sample	Hexadecane/g	Octadecane/g	ZnO/g	Nano-ZnO/g	Nano-Al ₂ O ₃ /g	Hexadecanol/g	Octadecanol/g	OP-10/g	DI water/g
A1	2.5	0	0	0	0	0	0	0.5	47
A2	5	0	0	0	0	0	0	0.5	44.5
A3	10	0	0	0	0	0	0	0.5	39.5
A4	0	2.5	0	0	0	0	0	0.5	47
A5	0	5	0	0	0	0	0	0.5	44.5
A6	0	10	0	0	0	0	0	0.5	39.5
B1	1	4	0	0	0	0	0	0.5	44.5
B2	1.75	3.25	0	0	0	0	0	0.5	44.5
B3	2.5	2.5	0	0	0	0	0	0.5	44.5
B4	3.25	1.75	0	0	0	0	0	0.5	44.5
B5	4	1	0	0	0	0	0	0.5	44.5
C1	2.5	2.5	0.05	0	0	0	0	0.5	44.45
C2	2.5	2.5	0.25	0	0	0	0	0.5	44.25
C3	2.5	2.5	0.5	0	0	0	0	0.5	44
C4	2.5	2.5	0	0.5	0	0	0	0.5	44.45
C5	2.5	2.5	0	0	0.5	0	0	0.5	44.45
D1	2.5	2.5	0	0	0.5	0.0625	0.0625	0.5	43.9375
D2	2.5	2.5	0	0	0.5	0.1875	0.1875	0.5	43.8125
D3	2.5	2.5	0	0	0.5	0.3125	0.3125	0.5	43.6875

observed. A 5 μ L of sample was diluted with 5 mL deionized water and then a 5 μ L of diluted sample was placed on a 200-mesh copper lacy formvar carbon coated EM grid. The sample was blotted using a filter paper after sitting at room temperature for 1 min. The grid was then plunged into liquid ethane and stored with liquid nitrogen for imaging.

2.5. DSC analysis of NPCE

Differential scanning calorimeter (DSC, 200F3 Maia, Netzsch) was used to characterize the thermal properties of nano-phase change emulsions. The specified accuracy of the instrument is $\pm 1\%$ with standard metal measurement. The sample was well shaken before measurement, 20–30 mg phase change nano-emulsion was put into an aluminium crucible by pipette gun and sealed well. The differential scanning calorimeter was preheated for 30 min. All the measurements were carried out in nitrogen atmosphere at a heating or cooling rate of 2 $^{\circ}$ C/min.

2.6. Thermal conductivity measurement of NPCE

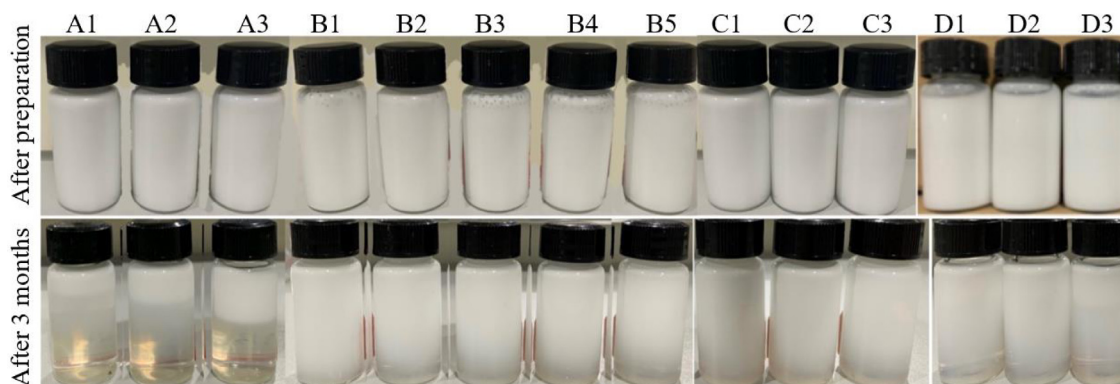
Thermal conductivity instrument (DZDR-S, NANJING DAZHAN) was used to characterize the thermal conductivity of nano-phase change emulsions. The specified accuracy of the instrument is $\pm 3\%$ depending on the sample size, conductivity and reproducibility. The instrument was calibrated with water before the experiment. The sample measurement interval was set as 10 min and each sample was measured 5 times at 20 $^{\circ}$ C after preparation. The average value with standard deviation was taken to reduce the experimental error.

2.7. Rheology analysis of NPCE

The dynamic viscosity of NPCE was measured by a rheometer (Malvern instruments, Kinexus Ultra). Cup lower and bob upper geometries were employed for measurements. As the viscosity of

Table 2
Particle size distribution and particle dispersion index (PDI) of prepared NPCEs.

Sample	T (°C)	After preparation		After 3 months		After 10 months		After 100 cycles	
		Size (nm)	PDI	Size (nm)	PDI	Size (nm)	PDI	Size (nm)	PDI
A1	25	139	0.101	201	0.177	333	0.162	312	0.168
A2	25	142	0.109	211	0.214	384	0.101	354	0.208
A3	25	162	0.110	239	0.023	399	0.193	400	0.146
A4	25	135	0.102	199	0.132	341	0.117	308	0.183
A5	25	145	0.104	214	0.183	398	0.131	353	0.179
A6	25	166	0.113	240	0.207	421	0.122	469	0.201
B1	25	141	0.203	217	0.149	385	0.200	319	0.197
B2	25	144	0.076	220	0.019	393	0.155	336	0.190
B3	25	140	0.112	212	0.132	391	0.142	330	0.193
B4	25	148	0.118	216	0.113	389	0.107	351	0.191
B5	25	144	0.107	210	0.109	401	0.201	389	0.062
C1	25	146	0.168	220	0.110	323	0.132	312	0.143
C2	25	149	0.105	231	0.062	319	0.099	323	0.147
C3	25	144	0.112	219	0.191	320	0.121	310	0.129
C4	25	151	0.109	222	0.183	353	0.127	334	0.109
C5	25	149	0.157	201	0.201	336	0.013	320	0.193
D1	25	146	0.186	222	0.155	336	0.136	336	0.110
D2	25	153	0.132	217	0.142	351	0.201	333	0.166
D3	25	148	0.070	219	0.099	340	0.153	327	0.125

**Fig. 2.** Image of NPCEs (sample A1 to sample D3), 3-month storage.

nano-phase change emulsion has significant influence on the application, the dynamic viscosity of nano-phase change emulsions were analysed under various temperatures and concentrations. The instrument was calibrated with air and standard oil before measurement. The specified accuracy of the instrument is $\pm 1\%$. Each sample was well shaken and 1.2 mL of sample was placed in the cup geometry for measurement.

3. Results and discussion

3.1. Particle size and stability of NPCE

Stability is one of the most important factors affecting the application of NPCE. The NPCE has the following unstable forms: emulsification and sedimentation, flocculation, merger and Ostwald maturity (Taylor, 1998). Fig. 2 shows the results of the static experiment for samples A1–D3 after preparation and 3-month storage. For all samples, PCM and metal oxide nanoparticles were well dispersed in water after preparation. Apparently, three months later, sedimentation and flocculation phenomena occurred in some NPCEs. This is attributed to the density of the PCMs is lower than that of water, leading to the upward movement of the droplet, while the sedimentation was caused due to the density of the metal oxide nanoparticles is greater than that of water. However, mechanical agitation can easily solve sedimentation and flocculation issues of NPCEs in real practice.

Table 2 shows particle size distribution and PDI of prepared NPCEs after preparation, 3-month storage, 10-month storage and

100 heating and cooling cycles, respectively. With the increase of time, the particle size of NPCE shows an increasing trend. The heating and cooling experiment of NPCE was performed 100 times at 25 °C. The NPCE was heated by an electric heating plate (50 W) and then crystallized naturally for one heating and cooling cycle. The particle size of NPCEs increased after 100 heating and cooling cycles. The reason for this phenomenon is that small droplets cluster might be gathered to form large clusters. It further demonstrates that the metal oxide particles and nucleating agents have little or no effect on the particle size distribution and PDI of prepared NPCEs. As shown in Table 2, low PDI of NPCEs are observed after preparation, long storage and 100 heating and cooling cycles, indicating that prepared NPCEs have low polydispersity and great colloidal stability.

Fig. 3 shows the particle size distribution of sample B3 (5 wt. % hexadecane + 5 wt. % octadecane) after preparation, 3-month storage, 10-month storage, and 100 heating and cooling cycles. As shown in Fig. 3, three lines represent three measurement results of each sample respectively. The average particle size of the newly prepared emulsion is 140 nm, and the average particle size is 212 nm after standing for three months. The average particle size of NPCE standing for ten months is 391 nm, and the average particle size is 330 nm after 100 heating and cooling cycles. Nanofluid is a multiphase system with interfacial energy and unstable internal energy. Nano-emulsion is a thermodynamically unstable system due to its large interface area. The instability of nano-emulsion is characterized by the decrease in the number of emulsion droplets caused by flocculation or coalescence, and

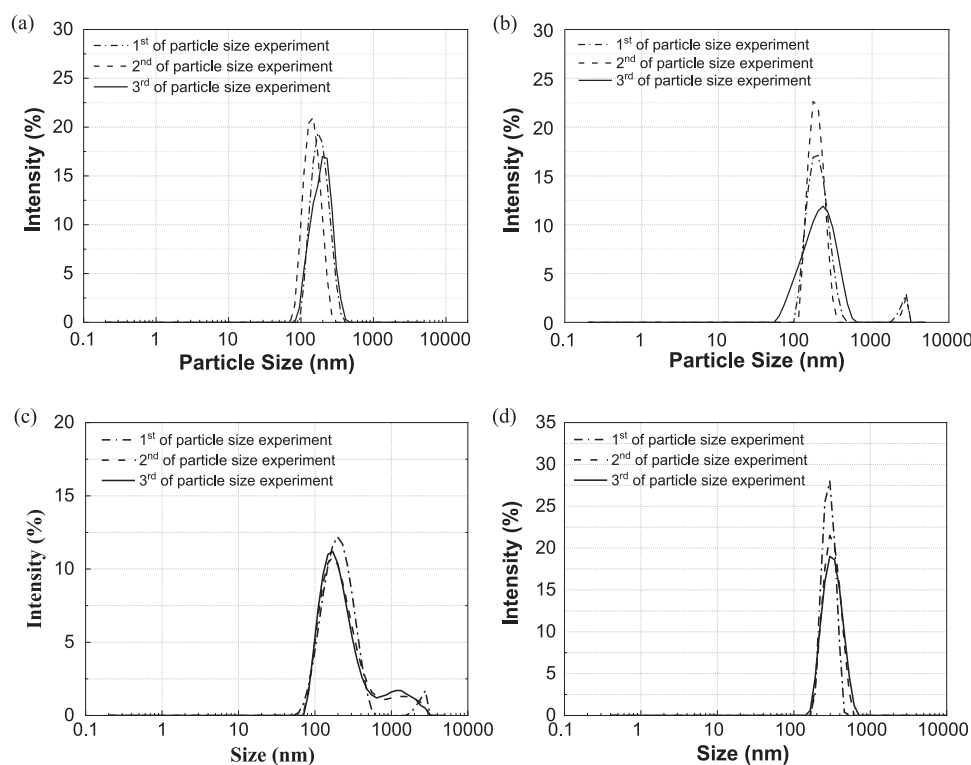


Fig. 3. Sample B3 (5 wt% hexadecane + 5 wt% octadecane): (a) after preparation, (b) after 3 months, (c) after 10 months, (d) after 100 heating and cooling cycles.

instability rate is defined as the product of collision frequency and collision efficiency. Individual droplets collide can be caused by Brownian motion, gravitational field (buoyancy), and other mechanical forces (Zhang et al., 2019). The smaller droplet of nano emulsion, the less the phenomenon of emulsification and deposition appear, as the dispersion rate caused by Brownian motion is greater than the sedimentation or emulsification rate (Solans et al., 2005).

3.2. Morphology of NPCE

Fig. 4 shows the morphology of samples A2, B3, C5 and D3 under the Cryo-TEM. It can be seen that most of particles are in spherical shape. According to the images from the TEM, the average particle size of nano-emulsion is around 200 nm, which agrees well with the results from DLS analysis. Figs. 4c and 4d show that those long shape particles are nano- Al_2O_3 particles. It is interesting to note that nucleating agent particles are appeared as black agglomerated particles in Fig. 4d. The particle size is an important parameter in the nano-emulsion. In general, the smaller the particle size is, more stable the nano-emulsion will be. In addition, for the nano-emulsion with a certain mass fraction, the smaller the particle size, the greater the viscosity, the greater the supercooling (Walstra, 1993). Therefore, the particle size will also affect the viscosity of the nano-emulsion.

3.3. Thermal properties of NPCE

Differential scanning calorimeter was utilized to characterize the thermal properties of pure phase change materials and composite nano-phase change emulsions. Fig. 5 shows the DSC curves of hexadecane and octadecane. The peaks of melting are 20.8 °C & 31.5 °C and the peaks of crystallization are 12.1 °C & 21.6 °C, respectively. According to Fig. 5, Fig. 6 and Table 3, the melting temperature of the nano-emulsion is higher than that of pure hexadecane and octadecane. This is caused by the large specific

surface area of the emulsion will lead to a large percentage pre-melting of the phase change material. The decrease of droplet size leads to the decrease of melting enthalpy, the dissolution of surfactants in the PCM will lead to the decrease of the melting temperature and enthalpy of the PCM itself (Chen et al., 2020).

As shown in Fig. 6 and Table 3, samples A1-A6 all present high supercooling degree. For instance, the initial temperature of melting and solidification for NPCE with 10 wt. % hexadecane (sample A2) is 28.4 °C and 9.3 °C, respectively, and the supercooling is 19.1 °C. The supercooling degree of pure hexadecane is 8.7 °C, the supercooling degree of pure hexadecane is 10.4 °C lower than that of NPCE with 10 wt. % hexadecane. The degree of supercooling is the temperature difference between the melting peak and solidification peak of phase-change material. Nucleation is the initial phase of phase transition, which consists of two methods, one is homogeneous nucleation, the other is heterogeneous nucleation (Golemanov et al., 2006). Generally, the core is formed first on the surface of the particle, i.e. the solid particles in the solution can promote nucleation and crystallization. This is attributed to most of the crystal nuclei are formed on the surface of the particle during the initial nucleation stage of the solidification process, which is favourable for nucleation and even solidification. The phase change materials are dispersed in the emulsion for NPCE and they are in the form of droplets, which reduces the contact with the wall surface and therefore increases the degree of supercooling. In addition, the number of nuclei in each droplet decreased as the droplet size reduced, resulting the crystallization temperature of nano-droplet lowered with reducing their diameters.

The test results of DSC are shown in Fig. 7 and Table 3, T_m and T_c are the melting point and freezing point of PCM respectively, ΔH_f and ΔH_c are the heat of fusion and crystallization respectively, ΔT is the supercooling degree of NPCEs, which was calculated by the temperature difference between the freezing point and melting point. The crystallization point and melting point of the mixture are between the two pure alkanes. The latent

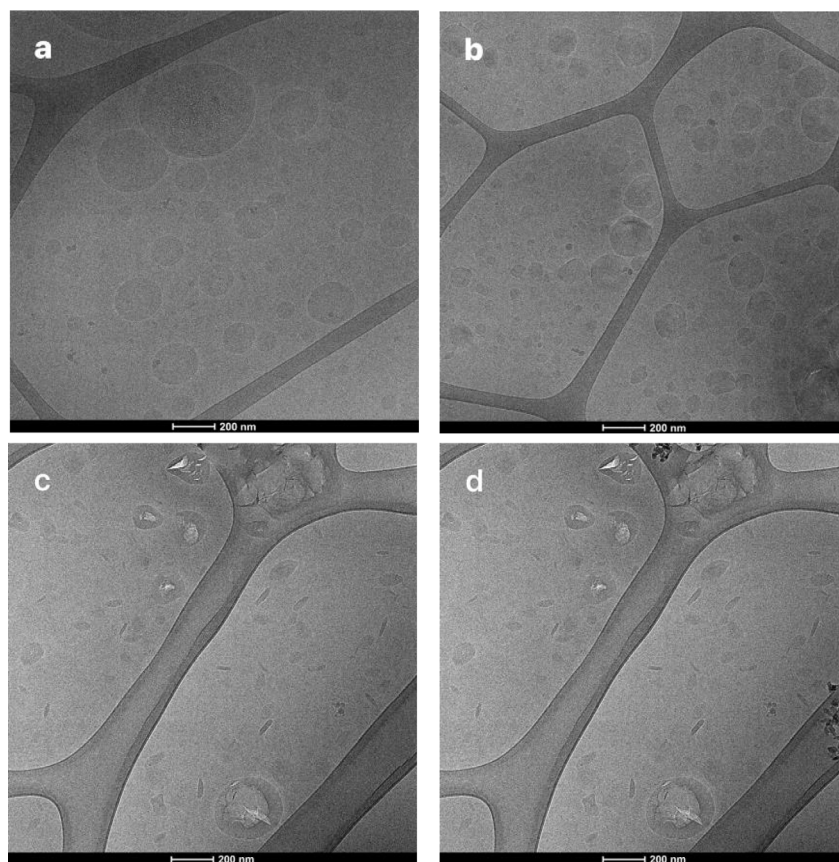


Fig. 4. Cryo-TEM images of NPCEs: (a) sample A2, 10 wt% hexadecane; (b) sample B3, 5 wt% hexadecane + 5 wt% octadecane; (c) sample C5, 5 wt% hexadecane + 5 wt% octadecane + 1 wt% nano- Al_2O_3 ; (d) sample D3, 5 wt% hexadecane + 5 wt% octadecane + 1 wt% nano- Al_2O_3 + 0.625 wt% hexadecanol + 0.625 wt% octadecanol.

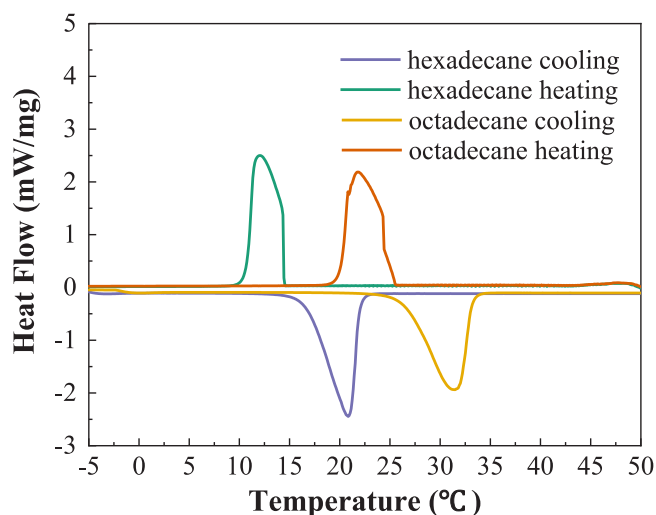


Fig. 5. DSC curves of hexadecane and octadecane.

heat of the mixed NPCE is between the latent heat of the two pure alkanes in the same proportion. As shown in Table 3, it is also interesting to note that the phase change temperatures of NPCEs prepared by the control mechanism (sample B1–B5) were tailored to desirable temperature range for thermal system application, especially for crystallization temperature. Therefore, the control mechanism proposed in this study is an effective method to

tailor the thermal properties of NPCEs in terms of phase change temperature and latent heat.

There are many limiting factors for the development of nano-phase change emulsions, among which the main factors are low thermal conductivity and high supercooling. In order to solve these issues, adding different concentrations of metal oxide particles cannot only improve the thermal conductivity, but it also can reduce the degree of supercooling. In the current work, composite nano-phase change emulsions (samples C1–C5) with metal oxide concentrations of 0.1 wt. %, 0.5 wt. % and 1 wt. % were prepared using sample B3 as the base solution. As shown in Fig. 8 and Table 3, in comparison with sample B3, the supercooling degree of sample C1, C2, C3, C4 and C5 were reduced by 14%, 15% and 15%, 10% and 11% respectively. Importantly, the melting temperature of sample C1–C5 was not changed after adding metal oxide nanoparticles, compared with sample B3.

As shown in Fig. 9, the thermal conductivity decreases with the increase of phase change materials content at room temperature. The thermal conductivity of NPCE with 5 wt. % octadecane is 0.591 W/ (m K), while the thermal conductivity of NPCEs with 10 wt. % octadecane and 20 wt. % octadecane are 0.578 W/ (m K) and 0.531 W/ (m K), respectively. Fig. 10 presents the thermal conductivity increases gradually with the increase of the content of metal oxide nanoparticles. The thermal conductivity of base solution B3 at room temperature is 0.581 W/ (m K). The thermal conductivity of sample C1 is 0.592 W/ (m K) with 0.1 wt. % ZnO, which increases by 1.1%. The thermal conductivity of sample C2 with 0.5 wt. % ZnO is 0.632 W/ (m K), which increases by 8.8%. After adding 1 wt. % ZnO, the thermal conductivity of sample C3 is improved to 0.689 W/ (m K), which increases by around 18.6%. After adding 1 wt. % nano-ZnO and nano- Al_2O_3 , the

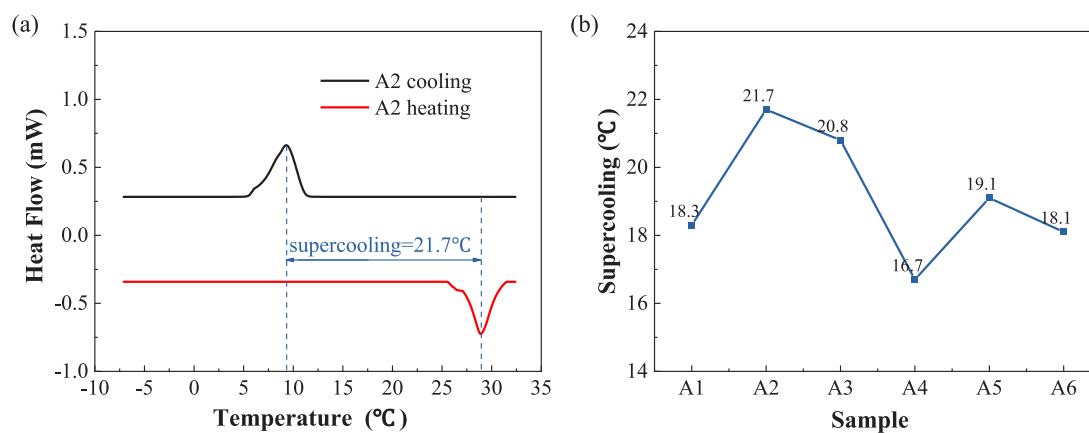


Fig. 6. (a) DSC curves of A2; (b) supercooling degree of NPCEs prepared by the control mechanism: sample A1, 5 wt% hexadecane; sample A2, 10 wt% hexadecane; sample A3, 20 wt% hexadecane; sample A4, 5 wt% octadecane; sample A5, 10 wt% octadecane, sample A6, 20 wt% octadecane.

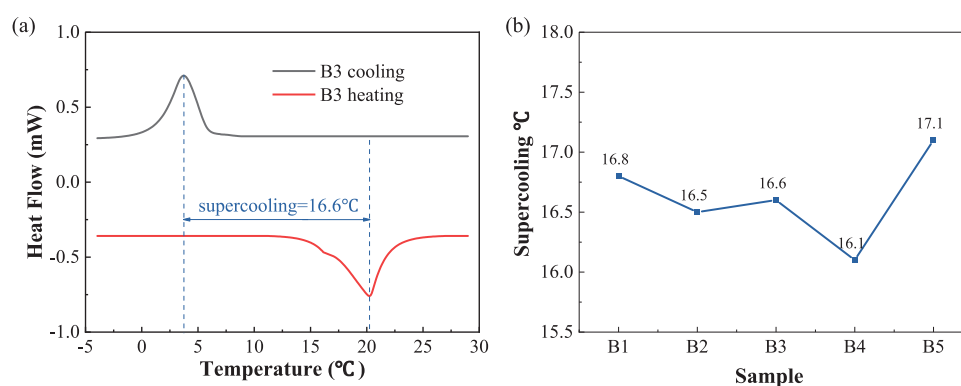


Fig. 7. (a) DSC curves of B3; (b) supercooling of NPCEs prepared by the control mechanism: sample B1, 2 wt% hexadecane + 8 wt% octadecane; sample B2, 3.5 wt% hexadecane + 6.5 wt% octadecane; sample B3, 5 wt% hexadecane + 5 wt% octadecane; sample B4, 6.5 wt% hexadecane + 3.5 wt% octadecane; sample B5, 8 wt% hexadecane + 2 wt% octadecane.

Table 3

DSC measurements results of prepared NPCEs with various concentrations of hybrid alkanes, metal oxide nanoparticles and hybrid nucleating agents.

Sample	After preparation					After 100 heating and cooling cycles		
	$T_m/^\circ\text{C}$	$T_c/^\circ\text{C}$	$\Delta H_f/^\circ\text{C}$	$\Delta H_c/^\circ\text{C}$	$\Delta T/^\circ\text{C}$	$\Delta H_f/^\circ\text{C}$	$\Delta H_c/^\circ\text{C}$	$\Delta T/^\circ\text{C}$
Hexadecane	20.8	12.1	225.7	224.3	8.7	–	–	–
Octadecane	31.5	21.6	234.4	238.2	9.9	–	–	–
A1	17.8	–0.5	13.34	9.01	18.3	–	–	–
A2	19.5	–2.2	17.53	15.49	21.7	–	–	–
A3	19.4	–1.4	55.86	33.81	20.8	–	–	–
A4	26.6	9.9	9.7	10.46	16.7	7.1	8.11	16.7
A5	28.4	9.3	13.61	17.53	19.1	11.1	11.92	19.1
A6	27.2	9.1	41.62	45.36	18.1	38.43	39.11	18.1
B1	23.3	6.5	14.36	16.90	16.8	12.97	12.77	14.9
B2	21.8	5.3	13.28	15.77	16.5	12.21	12.33	14.1
B3	20.3	3.7	14.07	16.72	16.6	12.87	11.95	14
B4	18.4	2.3	13.92	15.32	16.1	12.01	12.23	14.2
B5	17.3	0.2	14.41	16.59	17.1	12.44	12.4	14.5
C1	19.1	4.8	16.21	16.93	14.3	12.35	11.93	14.8
C2	19.0	4.9	15.97	16.74	14.1	11.71	11.42	14.3
C3	19.2	5.0	14.03	16.45	14.0	12.34	12.41	14.1
C4	19.05	5.05	14.57	15.99	14.0	–	–	–
C5	19.37	4.98	15.88	16.23	14.39	–	–	–
D1	19.6	15.3	14.51	12.39	4.3	12.21	12.31	3.5
D2	20.05	16.25	13.06	14.43	3.8	12.5	11.87	3.3
D3	19.8	16.7	13.36	14.16	3.1	12.38	11.45	3.3

thermal conductivity of sample C4 and C5 is 0.695 W/ (m K) and 0.70 W/ (m K), which is increased by 19.6% and 20.5%. Therefore, metal oxide nanoparticles have great effect on the improving the thermal conductivity of nano-phase change emulsions.

Although the supercooling was reduced by adding metal oxide nanoparticles to nano-phase change emulsion, it is still too high

for NPCE to be applied in the thermal systems as a heat transfer fluid. Nucleating agent can be employed to effectively reduce the supercooling degree of nano-PCM emulsions (Agresti et al., 2019). In this work, as sample C5 has the highest thermal conductivity among others reduced the supercooling degree by 15%, different concentrations (0.25 wt. %, 0.75 wt. %, 1.25 wt. %) of hybrid

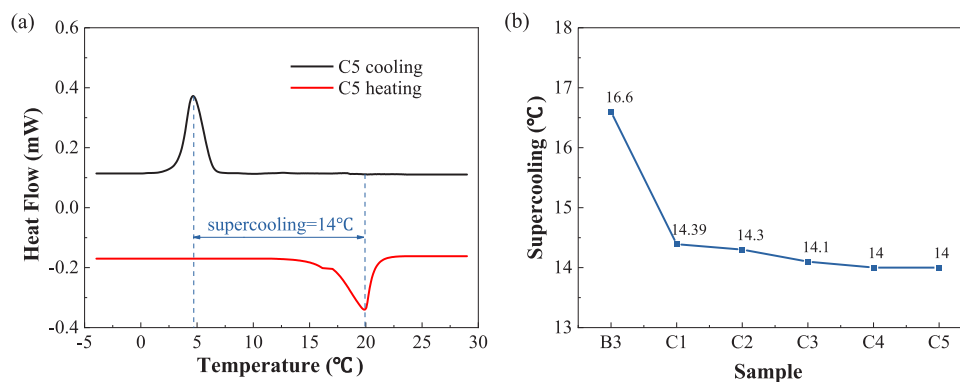


Fig. 8. (a) DSC curves of C5; (b) supercooling of NPCEs prepared with various concentrations of metal oxide particles added to sample B3 (5 wt% hexadecane + 5 wt% octadecane): sample C1 with 0.1 wt% ZnO; sample C2 with 0.5 wt% ZnO; sample C3 with 1 wt% ZnO, sample C4 with 1 wt% nano-ZnO, sample C5 with 1 wt% nano- Al_2O_3 .

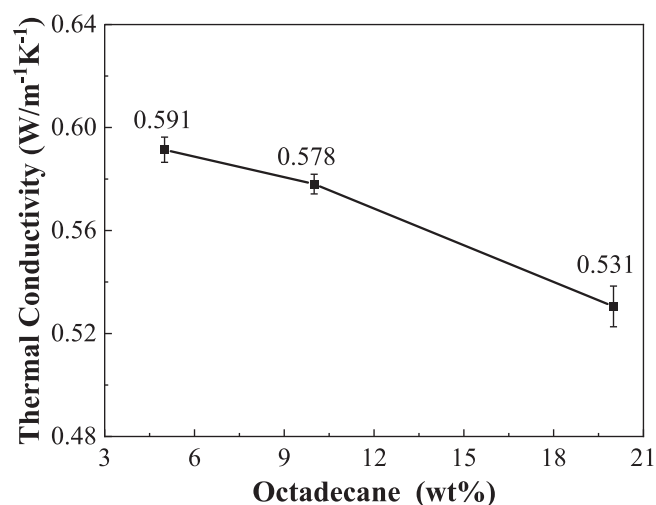


Fig. 9. The thermal conductivity of NPCEs with various concentrations of pure octadecane.

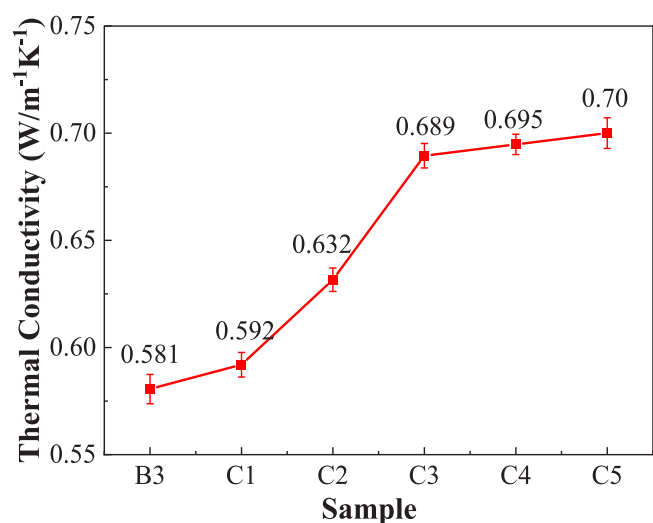


Fig. 10. Thermal conductivity enhancement of NPCEs: sample B3, 5 wt% hexadecane + 5 wt% octadecane; sample C1, 5 wt% hexadecane + 5 wt% octadecane + 0.1 wt% ZnO; sample C2, 5 wt% hexadecane + 5 wt% octadecane + 0.5 wt% ZnO; sample C3, 5 wt% hexadecane + 5 wt% octadecane + 1 wt% ZnO; sample C4, 5 wt% hexadecane + 5 wt% octadecane + 1 wt% nano-ZnO; C5–5 wt% hexadecane + 5 wt% octadecane + 1 wt% nano- Al_2O_3 .

nucleating agents were added to sample C5 (5 wt. % hexadecane +5 wt. % octadecane +1 wt. % nano- Al_2O_3) to further reduce the degree of supercooling, sample D1, D2 and D3 were prepared as shown in Table 3. As it can be seen from Fig. 11, in comparison with sample C5 the supercooling degree of sample D1, D2 and D3 are significantly reduced. In addition, with the increase of nucleating agent concentration, the cooling curves move to the right, and the heating curves coincide. The supercooling degree of sample D1 was 4.3 °C when adding 0.25 wt. % nucleating agent, and the supercooling degree decreased by 74%. The supercooling degree of sample D2 was 3.8 °C with the addition of 0.75 wt. % nucleating agent, and the supercooling degree decreased by 77%. When 1.25 wt. % nucleating agent was added, the supercooling degree of sample D3 was 3.1 °C and it was reduced by 81%. Nucleating agent has great effect in reducing the supercooling and the supercooling degree decreases with an increase of nucleating agent concentration. It is also important to note that adding hybrid nucleating agent did not significantly change the melting temperature and latent heat of samples D1–D3 compared with sample C5, as shown in Table 3 and Fig. 11.

3.4. Thermal stability of NPCE

The poor stability is one of main challenges for the development and application of NPCE in the thermal systems. In this study, the thermal stability of NPCE was evaluated based on repeated 100 heating and cooling cycles. Fig. 12 shows the DSC results of samples B3, C3 and D3 after 100 heating and cooling cycles. As shown in Fig. 12 and Table 3, it is noteworthy that samples C3 and D3 present great thermal stability with respect to the phase change temperature and latent heat. It can be seen that no obvious phase change temperature and latent heat changes are observed in samples C3 and D3 after thermal cycling experiment. It indicates that metal oxide particles and nucleating agent can maintain and improve the thermal stability of NPCEs.

3.5. Rheology of NPCE

The viscosity of a fluid is the resistance of the fluid to deformation due to external shear forces, which are expressed in the form of internal friction. In order to be better applied in the microchannel thermal management system, the viscosity of nano-phase change emulsion should be controlled appropriately. A rheometer was employed to measure the dynamic viscosity of samples C1, C2 and C3 at different temperatures and concentrations of metal particles. As shown in Fig. 13, the viscosity is higher with higher concentrations of metal particles and a shear thinning effect is observed before a low shear rate of 1 s^{-1} , the

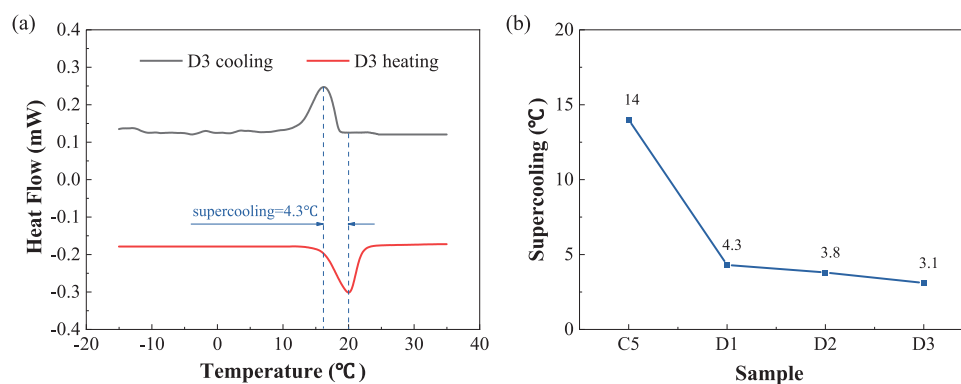


Fig. 11. (a) DSC curves of D3; (b) supercooling of NPCEs prepared with different concentrations of nucleating agent added to sample C5 (5 wt% hexadecane + 5 wt% octadecane + 1 wt% nano- Al_2O_3): sample D1 with 0.25 wt% nucleating agent; sample D2 with 0.75 wt% nucleating agent; sample D3 with 1.25 wt% nucleating agent.

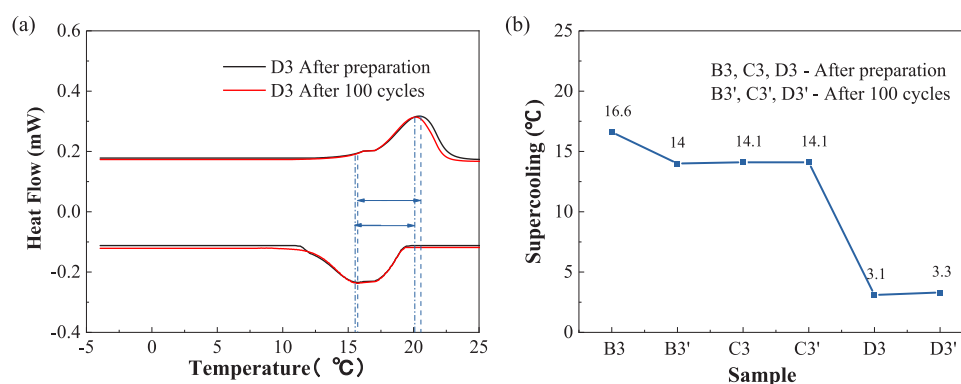


Fig. 12. (a) DSC curves of D3; (b) supercooling of NPCEs (sample B3, C3 and D3) after 100 thermal cycling.

concentrations of metal particles have no obvious effect on the viscosity of NPCEs after shear rate of 1 s^{-1} . This phenomenon can be attributed to the entanglement nodes between molecular chains are in equilibrium and orderly arrangement at low shear rates. With the increase of stress and shear rate, the entanglement of molecular chains is greater than reconstruction, thereby there is no entanglement between molecular chains at last. NPCE is difficult to flow with high entanglement of molecular chains and greater viscosity. In addition, when the shear rate is low, the droplets tend to gather together, which implies that the emulsion is a non-Newtonian fluid. This aggregation structure is easy to be destroyed when the shear rate increases. As shown in Fig. 13, samples C1, C2 and C3 can be a Newtonian fluid after shear rate of 2 s^{-1} .

Temperature also has a strong effect on the viscosity of NPCEs. Fig. 14 shows the relationship between the viscosity and temperature of 10 wt. % NPCE with 0.1 wt. % ZnO, 0.5 wt. % ZnO and 1 wt. % ZnO at 5 °C, 10 °C, 15 °C, 20 °C and 25 °C, respectively. It can be seen that the viscosity decreases with the increase of temperature. The viscosity of emulsion with larger mass fraction decreases faster as the temperature rises. For instance, the viscosity of NPCE with 1 wt. % ZnO decreased from 89.21 mPa·s at 5 °C to 70.49 mPa·s at 25 °C. The viscosity of NPCE with 0.5 wt. % ZnO decreased from 78.31 mPa·s at 5 °C to 73.66 mPa·s at 25 °C. The dynamic viscosity of nano-emulsion is higher during the cooling process compared with the heating process. The reason for this phenomenon can be that the droplets in the emulsion tend to stick together at lower temperatures, leading to a higher viscosity. With the increase of temperature, the movement of nanoparticles in the base fluid increases, resulting in a decrease in the intermolecular force between the base fluid and nanoparticles, which leads to a decrease in the viscosity of the nanofluid at higher temperatures (Ho et al., 2021b).

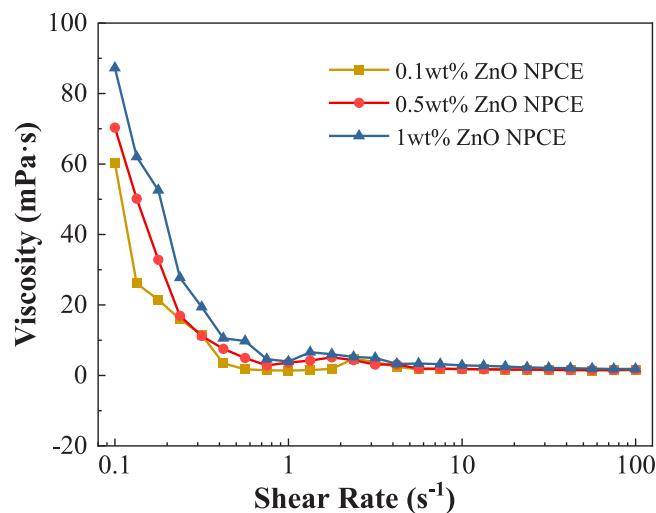


Fig. 13. Effects of different concentrations of metal oxide particles on the viscosity of samples C1, C2 and C3 at 25 °C.

4. Conclusions

In this paper a series of phase change nano-emulsion with desirable phase change temperature, low supercooling, low viscosity, high thermal conductivity, high heat of fusion and high stability were prepared based on a control mechanism method. The thermophysical properties of nano-phase change emulsions were significantly improved by the control mechanism process.

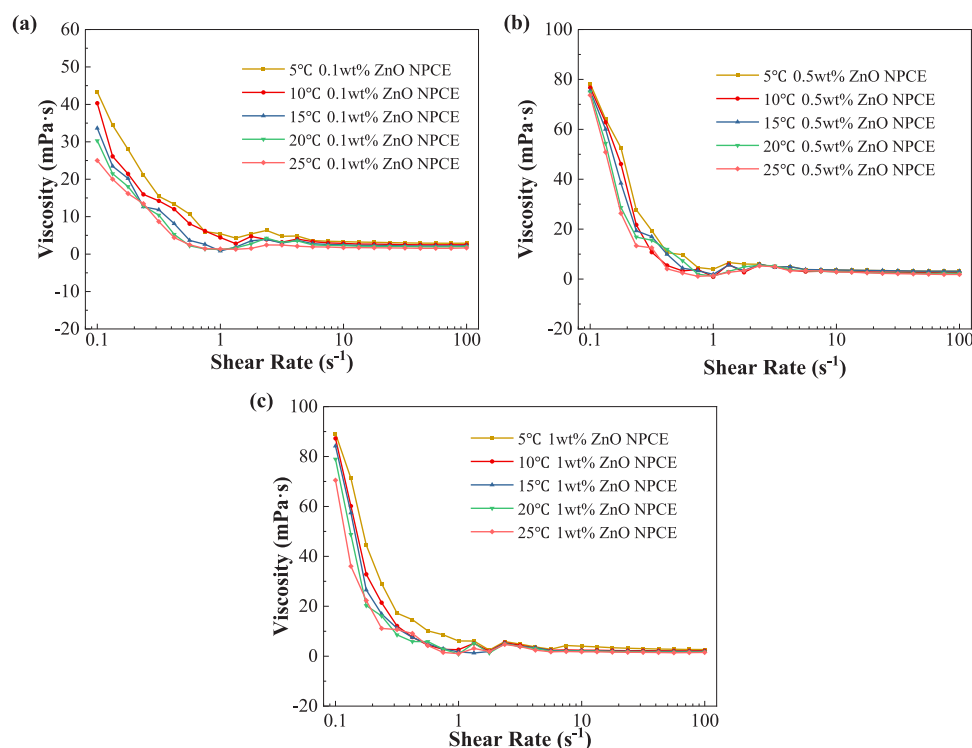


Fig. 14. The effect of temperature on the viscosity of NPCEs: (a) shear rate vs. viscosity of NPCE with 0.1 wt. % ZnO (C1) at various temperatures; (b) shear rate vs. viscosity of NPCE with 0.5 wt. % ZnO (C2) at various temperatures; (c) shear rate vs. viscosity of NPCE with 1 wt. % ZnO (C3) at various temperatures.

It was proposed to have great potential application in the thermal management for active thermal energy storage systems. The following conclusions can be drawn:

- (1) The static, particle size, Cryo-TEM and thermal stability analysis showed that prepared NPCEs presented narrow particle size distribution and great stability.
- (2) The test results of DSC showed that the prepared NPCEs had high heat storage capacity. The peak value of DSC results showed that the addition of metal oxide particles and nucleating agent effectively reduced the supercooling of NPCEs. When 0.1 wt. %, 0.5 wt. % and 1 wt. % ZnO were added to samples C1–C3, the supercooling degree was reduced by 14%, 15% and 15% respectively. The supercooling of samples C4 and C5 with 1 wt% nano-ZnO and nano- Al_2O_3 decreased by 10% and 11%, respectively. In addition, adding 0.25 wt. %, 0.75 wt. % and 1.25 wt. % of hybrid nucleating agent reduced the supercooling degree of samples D1, D2 and D3 by 74%, 77% and 81%, respectively.
- (3) The concentrations of PCM and metal oxide particles have great influence on the thermal conductivity of NPCEs. The thermal conductivity of NPCEs increased with the increase of metal oxide concentration and decreased with increase of PCM concentration. The thermal conductivity of base solution B3 was 0.58 W/ (m K). When 0.1 wt. %, 0.5 wt. % and 1 wt. % ZnO were added to sample B3, the thermal conductivity of NPCEs increased by 2%, 9% and 19% respectively. The thermal conductivity of NPCEs with nano-ZnO and nano- Al_2O_3 increased by 19% and 21% respectively.
- (4) The viscosity of NPCEs increased with the increase of metal oxide concentration and decreased with the increase of temperature. Prepared NPCEs presented shear-thinning effect and can be considered as Newtonian fluid after shear rate of 2 s^{-1} .

CRedit authorship contribution statement

Guanhua Zhang: Conceptualization, Writing – original draft, Supervision, Project administration, Funding acquisition, Writing – review & editing. **Yuqian Guo:** Experiment, Formal analysis, Data curation, Writing. **Bin Zhang:** Experiment, Formal analysis, Data curation, Writing. **Xiaoyu Yan:** Review, Resources. **Wei Lu:** Review, Resources. **Guomin Cui:** Review, Resources. **Yanping Du:** Conceptualization, Supervision, Project administration, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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