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Simultaneous decrease in supercooling and enhancement of thermal conductivity of paraffin emulsion in medium temperature range with graphene as additive

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ABSTRACT

As a promising functional latent-heat fluid, phase change emulsion suffers from high supercooling and low thermal conductivity, yet no satisfactory solution for both problems has been reported. We firstly proposed a solution to the problems of 20 wt% paraffin emulsion(PE) in medium temperature range (40–80 °C) with graphene as additive. After adding graphene, the supercooling degree dropped from 14.23 to 0.27 °C, while the latent heat changed by less than 2J g^{-1}(3%), and the thermal conductivity increased by 20.22%. The size of the emulsion particles with or without graphene, which was originally between 200 and 1500 nm, only changed within 5% after 300 melting/freezing cycles. DSC test showed the graphene-added composite PE(GPE) had good stability with only changed 1.53%, 3.14% in latent heat and 1.45% in phase change temperature after 300 cycles. Therefore, this new emulsion with high heat storage capacity, good thermal performance, and high stability, will exhitat remarkable potential in thermal energy storage.

1. Introduction

With the development of society, the energy consumption is increasing. While energy consumption leads to energy shortages. To solve the energy shortage problem, more efficient methods to store energy are urgently needed. Thermal storage is a way to collect and store excess redundant heat, then reuse it when needed [1]. As an important part of energy storage, the thermal storage system can be divided into two categories. One is stored by reaction heat named chemical storage. Another is the physical storage which is further divided into sensible heat storage and latent heat storage. Sensible heat storage has obvious disadvantages, such as low heat capacity, large volume, and difficult control of temperature change [2]. Latent heat storage with phase change materials, in contrast, utilizes the high latent heat values during the process of phase transition. Therefore, compared with sensible heat storage, latent heat storage has larger storage capacities in the same temperature range [3]. In such systems, a phase change material with high latent heat is used to absorb or release heat during the phase transition to achieve the purpose of heat storage [4]. The phase change materials can be divided into four categories according to the nature of phase change: solid-to-solid, solid-to-liquid, solid-to-gas, and liquid-to-gas [5]. Especially, solid-liquid phase change material has been widely studied because of its wide applications. It can be either directly diffused in the liquid (called phase emulsion), or encapsuled with inorganic or organic materials and then dispersed in the fluid (called phase change microcapsule suspension).The microcapsule suspension suffers from complicated preparation process, easy demulsification during usage, and poor thermal conductivity. In comparison, phase change emulsions have the advantages of simple preparation and easy operation. Further, when the emulsion broken, the homogeneity can be quickly restored by slightly stirring. Therefore, in recent years the phase change emulsion has become the focus as a latent heat functional fluid in practical engineering.

Phase change emulsions can be used in low-, medium-, and high-temperature regions. There are many studies for the low- and medium-temperature regions, but few studies in the high-temperature region due to the evaporation and volatilization of conventional based fluids (water). The low-temperature (0–20 °C) phase change emulsion can be used as a medium for heat transfer in air conditioning system to replace traditional fluoride refrigerants, so as to meet the environmental standard while maintain the required heat transfer capacity. While high viscosity causes a large energy consumption and high supercooling degree may lead to a delay of solidification. The following researches focus on improving these two problems. Huang [6] studied the effects of paraffin content on the performance of 15–75% RT10 emulsion. For the phase change range 2–12 °C, the 30% PE has an equivalent heat

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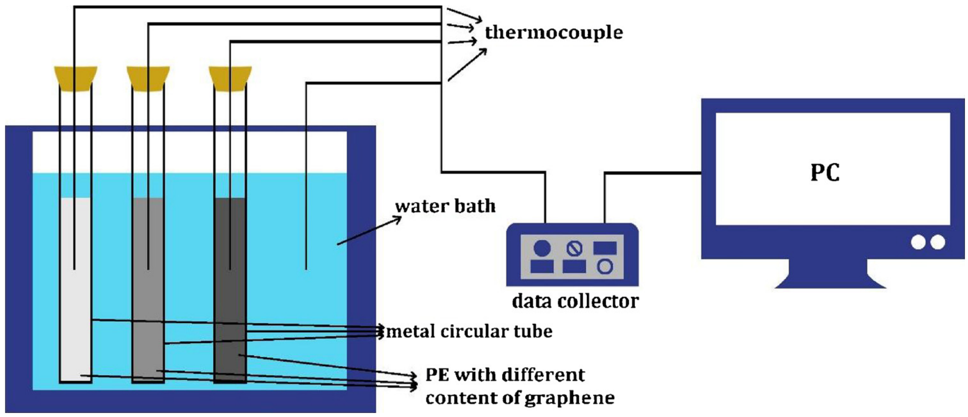

Fig. 1. Schematic diagram of heat storage experiment.

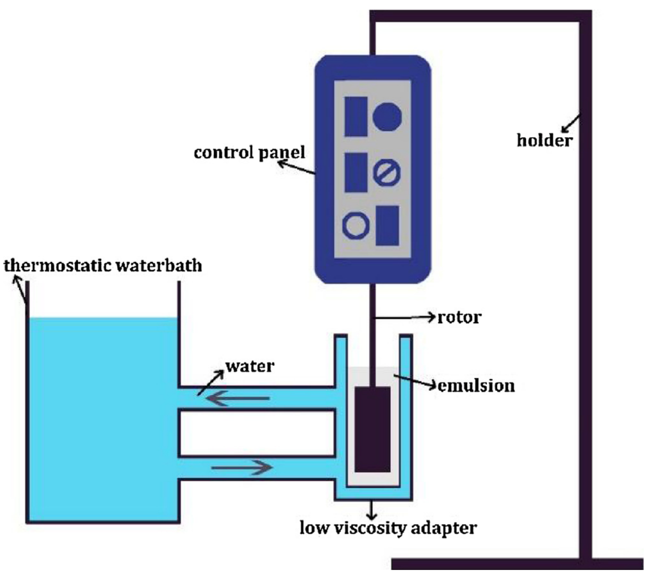

Fig. 2. Schematic diagram of viscosity measurement.

Table 1
Measurement range and accuracy of the instruments.

Instruments	Measurement range	Accuracy
laser particle size analyzer	particle size 0.3–10 μm concentration 0.1 ppm-40%(w/v)	accuracy ± 1 repeatability ≥ 1%
DSC	–	accuracy ± 0.1% reliability ± 1%
Hotdisk	thermal conductivity 0.005–500 $W\,m^{-1}\,K^{-1}$ temperature 10 K–1000 K	accuracy ± 3%
rotational rheometer	viscosity 1–2^6cp(mPa s)	accuracy ± 1% repeatability ± 0.2%

capacity of 50 $kJ\,kg^{-1}$, which is twice than that of water. The equivalent heat capacity of 50% PE, meanwhile, is 2.7 times as large as that of water. Liu [7] prepared a new phase change microcapsule suspension with graphene nanosheet and brookite TiO_2 as the shell, *n*-eicosane as phase change material. Study shows that the thermal conductivity of new system is increased from 0.64 to 0.98 $W\,m^{-1}\,K^{-1}$, and TiO_2 have a good photocatalytic effect. Yang [8] prepared 5 °C phase change microcapsule suspension and phase change emulsion by in-situ polymerization and hybrid synthesis method to obtain a latent functional fluid with low viscosity. However, there is still a certain degree of supercooling in these suspensions and emulsions. A series of studies have been conducted to solve the high supercooling degree in preparation of phase change emulsions. Huang [9] prepared PEs with *n*-tetradecane, hexadecane, and commercial paraffin RT20, and studied the supercooling properties of these emulsions. Also studies have shown that the type of surfactant has no influence on the supercooling degree. Meanwhile, the nucleating agent has an effect on the melting and solidification temperatures, thus can effectively reduce the supercooling degree. Zhang [10] used carbon nanotubes as a nucleating agent to effectively reduce supercooling degree in the phase change emulsion, but an oil layer was separated from the emulsion after the heating-cooling cycles. Wang [11] prepared 30% PE with OP10E, and improved its supercooling property by adding 2.0% nano-graphite. A higher graphite content could increase the thermal conductivity of PE. Zhang [12] prepared a 10–25 °C phase change emulsion with hexadecane. Then, carbon nanotubes were modified by concentrated sulfuric acid and nitric acid to attach the COOH group. When used as a nucleating agent at 0.1 wt%, these carbon nanotubes reduced the supercooling degree of the emulsion by 43%.

Medium-temperature (40–80 °C) phase change emulsions can be used as heat transfer medium in solar energy systems in place of the traditional medium such as water and ethylene glycol. Thus, the sensible heat and latent heat can be stored and used at the same time. Wang [13] used 58–60 °C paraffin as the phase change material and PVA, PEG600 as dispersants to prepare the emulsion, whose thermal storage density is double the value of water after adding 0.05% or 0.1% nano-graphite, together with low viscosity. Salla [14] prepared nanofluids with stearic acid, lauric acid and paraffin as phase change materials. The melting temperature of the obtained emulsion is lower than the pure oil phase by 3 °C. The latent heat is consistent with the theoretically calculated value, and the specific heat value has ± 3% diviation from the theoretical result. Nevertheless, fatty acid emulsions suffer high viscosity despite their higher latent heat than PEs. As Zhang [15] prepared emulsions with stearic acid, lauric acid, capric acid, myristic acid. The results show that for the composite fatty acid emulsion, the maximum value of viscosity can reach up to 1 Pa·s. Due to the high viscosity, the application of fatty acid emulsions remains to be further researched [16]. Zou [17] conducted experiments on the convection heat transfer characteristics of PE, finding the equivalent specific heat of high concentration PE was higher than that of low concentration. However the convective heat transfer coefficient decreased with the increase of concentration. Then Zou [18] studied the pumping power consumption rates of phase change emulsion compared to water. The results show that using PE as flow medium effectively reduce the quantity of mass flow and pump power. And 20% PE could reduce the same pump consumption as 30% emulsion. But in [19] the author draw a different conclusion that using the same pumping powers, the nanofluids show a poorer heat transfer performance than that of water due to the higher viscosity of nanofluid.