Study on the Rheological Properties of MPCS with Isopropanol/Water as Base Fluid

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Abstract. In order to obtain a good stability of micro-encapsulated phase change suspension, then study its rheological properties, herein formulated a phase change micro-capsulated suspension and utilized isopropanol/water mixed solution as the base fluid. The particle size distribution, viscosity and rheological properties of micro-encapsulated phase change suspension were measured at different concentrations. The effects of mass fraction, temperature on viscosity were discussed. Based on the classic viscosity formula, a correction factor was introduced to get higher precision viscosity formula. The results show that: a volume ratio of 1:1.75 of isopropanol/water suspension, suspension stability is up to 48h. It is also found that the viscosity decreases with the increase of temperature, but it increases with the increases of mass concentration. The fitted Tomas viscosity formula is reliable when the volume concentration is less than 15.58%, the error could be controlled within 5.7%.

1. Introduction

With the development of energy storage technology, phase change emulsions and micro-encapsulated phase change suspensions, acting as latent thermal functional fluid, have gained concerns in various energy related sectors. Compared to the traditional single-phase fluid, the latent thermal functional fluid, with higher heat storage density and smaller fluctuation range of temperature difference during use, has a widely application prospect in the fields of heat exchanger, HVAC and electronic system heat dissipation. Numerous researches of the phase change emulsion have been done by scholars worldwide. Inaba et al. [¹] from Japan, Zhao Zhennan et al. [²] of Tianjin University and Yang Rui et al. [³] of Tsinghua University, prepared phase change emulsions with a phase change material of tetradecane, and that thermophysical parameter of particle size distribution, viscosity, and latent heat of phase change had been tested, then in depth study on stability and rheological properties. However, the research on micro-encapsulated phase change suspensions is not deep enough, especially the stability and viscosity calculations of suspensions. Water is used as a carrier fluid on traditional micro-capsulated phase change suspensions generally, and is added various additives (emulsifier, suspending agent, dispersant, etc.) to improve the dynamic stability [⁴-⁵]. However, the operation of these methods is relatively complex, and the addition of additives often leads to the increase of viscosity [⁶] and poor fluidity of suspension. The viscosity of micro-capsulated phase change suspension is mainly obtained through experiment and it is difficult to calculate due to the lack of corresponding calculation formula.
In this study, the traditional method of increasing the viscosity of micro-capsulated phase change suspension to improve the stability was abandoned, and the density difference between liquid and solid was minimized to suppress the layer separation by changing the density of carrier fluid. The micro-capsulated phase change suspension with isopropanol/water mixed solution as the base fluid and paraffin as the core material was prepared and it was tested for thermophysical properties and rheological properties. The main factors affecting the viscosity of suspension were pointed out, and a correction factors were introduced to modify the Tomas viscosity formula to get higher precision viscosity formula for micro-capsulated phase change suspension.

2. Stability and particle size distributions of MPCM

2.1. Preparation of MPCM samples
Paraffin and MPCM28 of melamine formaldehyde were selected as wall material and core material respectively for the phase change micro-capsulated particles in the present investigation. The outlook of the particles are white dry powders, with phase change temperature of 28 °C, relative density of 0.9, phase change latent heat of 180 ~ 195 J/g. The materials property data are obtained from the manufacturer, American Microtek. The base fluid is mixed solution of isopropanol (with density of 0.785 g/ml) and deionized water. The boiling temperature of isopropanol is as high as 82.5°C. It is also easily solved in water and presents good fluidity and low viscosity (2.4 Mpaꞏs at 20 °C). All these properties make isopropanol suitable for preparation of micro-capsulated phase change suspension.

In the first round of experiments, 5 types of isopropanol/water mixed base fluids with densities of 0.916, 0.938, 0.947, 0.949, 0.954 and 0.974 g/ml was formulated. The purpose is to compare the properties of slurries with different base fluid composition. Then, the phase change micro-capsulated particles of different masses were weighed and added to the base fluid respectively, and stirred for 10 minutes at a rate of 2000 rpm using a high-speed shear emulsifier. Then the emulsion was stirred at a rate of 600 rpm for 3 hours within a constant temperature magnetic stirrer. Finally, the mixtures were oscillated at a frequency of 16 kHz for 10 minutes using an ultrasonic oscillator. In this way, the micro-capsulated phase change suspensions with 15 wt% were obtained. The suspensions were put into test tubes, attached with labels, and remained on the test tube rack for observation every 0.5 hours until up to 48 hours. The results show that the phase change micro-capsulated particles float up when the density of the isopropanol/water mixed base fluid is larger than 0.938 g/mL. On the other hand, the particles settle with isopropanol/water mixed base fluid density lower than 0.916 g/mL. Accordingly, the isopropanol/water mixed base fluid density should be controlled within the range of 0.916-0.938 g/mL, in order to obtain good stability.

In the second round of experiments, the densities of the isopropanol/water mixed base fluids were precisely controlled within the range of 0.916-0.938 g/mL. The isopropanol/water ratio of the samples are presented in Table 1. The experiment steps in the first round of experiment were repeated. After 48 hours deposition, it was observed the micro-capsulated phase change suspension with the mixed base fluid of 0.936 g/ml did not appear stratification. Moreover, its dynamic stability was the best of all six samples. As shown in figure 1, the rest of the suspensions appeared stratification on different levels. The better performance of the specific base fluid (with density of 0.936 g/ml) is because of the similar density with the micro-encapsulated particles when no stabilizer was added.

| Density of mixed solution (g/mL) | Quality of deionized water (g) | Isopropanol (g) |
|---------------------------------|--------------------------------|-----------------|
| 0.938                           | 41.64                          | 18.36           |
| 0.936                           | 41.42                          | 18.58           |
| 0.932                           | 41.05                          | 18.95           |
2.2. Testing of particle size distributions
Particle size distributions of the MPCM28 were tested with scanning electronic microscope (model SEM, Hitachi, S4800). The results were presented in figure 2. The phase change micro-capsulated particles show uniform spherical structure. Uniform particle sizes distribution was observed. Particle size distribution of the phase change micro-capsulated particles were analyzed with Wet measurement system of Laser particle size analyzer (model Bettersize2000LD), and the results were shown in figure 3. From the curve of different particle sizes distribution in figure 3, the particles are mostly distributed in the range of 17-26μm.

3. Rheological properties

3.1. Rheological curve of MPCM
The rheological property of fluid refers to the relationship between shear stress and shear rate in the process of fluid flow under external shear stress. The expression formula is:

\[
\tau = K \left( \frac{du}{dy} \right)^n = Ky^n
\]

Where \(\tau\) is the shear stress, \(\gamma\) is the shear rate, \(K\) is the consistency coefficient, \(n\) is the parameter of the material. When \(n = 1\), the fluid is Newtonian fluid, and \(K\) is the viscosity value of the fluid; when \(n < 1\), the fluid is pseudo-plastic or shear thinning fluid; when \(n > 1\), the fluid is expanding fluid or a shear thickening fluid.

In this study, the rheological properties of micro-encapsulated phase change suspension with 5 wt%, 10 wt% and 15 wt% were tested by the test system of Antonpa MCR102 Rotational Rheometer, as shown in figure 4. The temperature is controlled at 20.0 °C.
From figure 4, the shear stress increases linearly with the increase of shear rate from 0 to 100s⁻¹ with temperature of 20.0 ℃. Therefore, the 3 micro-encapsulated phase change suspension samples are all Newtonian fluids.

Figure 2. The SEM photograph of the MPCM (micro-capsulated phase change suspension)

Figure 3. The particle size distribution of the MPCM (micro-capsulated phase change suspension)

Figure 4. Relationship of shear stress with shear rate of MPCM
3.2. Influence of mass concentration and temperature on viscosity of MPCM

| Temperature (℃) | Base liquid viscosity (mPa·s) | 5 wt.% Test value (mPa·s) |
|-----------------|-----------------------------|--------------------------|
| 10℃             | 5.013                       | 7.085                    |
| 20℃             | 3.516                       | 4.406                    |
| 30℃             | 2.344                       | 2.808                    |
| 40℃             | 1.676                       | 2.050                    |
| 50℃             | 1.261                       | 1.621                    |

| Temperature (℃) | Base liquid viscosity (mPa·s) | 10 wt.% Test value (mPa·s) |
|-----------------|-----------------------------|--------------------------|
| 10℃             | 5.013                       | 9.200                    |
| 20℃             | 3.516                       | 5.941                    |
| 30℃             | 2.344                       | 3.751                    |
| 40℃             | 1.676                       | 2.669                    |
| 50℃             | 1.261                       | 2.152                    |

| Temperature (℃) | Base liquid viscosity (mPa·s) | 15 wt.% Test value (mPa·s) |
|-----------------|-----------------------------|--------------------------|
| 10℃             | 5.013                       | 15.760                   |
| 20℃             | 3.516                       | 9.122                    |
| 30℃             | 2.344                       | 5.501                    |
| 40℃             | 1.676                       | 3.923                    |
| 50℃             | 1.261                       | 2.914                    |

The viscosity values of micro-encapsulated phase change suspensions with 5 wt% (volume fraction \( \alpha = 5.19\% \)), 10 wt% (\( \alpha = 10.39\% \)) and 15 wt% (\( \alpha = 15.58\% \)) were measured with a rheometer at 10 ℃, 20 ℃, 30 ℃, 40 ℃ and 50 ℃. The results are listed in Table 2. With the increase of mass concentration, the viscosity of the micro-encapsulated phase change suspension also increased. With test temperature of 10-30 ℃, the viscosity differences between the suspension samples are larger, and the increase of temperature reduced the viscosity of suspension significantly. On the contrary, the viscosity differences between the suspension samples are smaller with test temperature of 30-50 ℃, whereas the viscosity of suspension increased slightly with the increase of temperature. This phenomenon was similar to the study of Inaba [1] and Yang [4]. The viscosity of the micro-encapsulated phase change suspension prepared in this study is much lower than the traditional phase change emulsion. The viscosity of micro-capsulated phase change suspension was fabricated with 15 wt%, which is ten times smaller than the viscosity data of phase change emulsion with 15 wt% fabricated by Inaba [1] and several times smaller than the viscosity data of phase change emulsion with 16.25 wt% fabricated by Zhao Zhennan [2].

4. Rheological properties

From the aspect of engineering application, it is important to calculate the MPCM viscosity under different conditions with high precision. There are 4 classical methods to calculate the viscosity when MPCM is concerned, namely Einstein [7], bachelor [8], van [9] and Tomas [10]. However, the accuracy of
these methods need to be evaluated through comparison with experimental measurement. For this purpose, the viscosity values from measurement and these 4 classical methods are compared in figure 5.

Einstein formula: \( \mu = \mu_f (1 + 2.5\varphi) \)

Batchelor formula: \( \mu = \mu_f (1 + 2.5\varphi + 6.25\varphi^2) \)

Vand formula: \( \mu = \mu_f \exp \left( \frac{2.5\varphi + 2.7\varphi^2}{1 - 0.609\varphi} \right) \)

Tomas formula: \( \mu = \mu_f \left[ 1 + 2.5\varphi + 10.05\varphi^2 + 0.00273\exp(16.6\varphi) \right] \)

It should be noted that the unit of mass fraction had been converted to volume fraction \( \varphi \), since volume fraction is used in all the 4 empirical models. From figure 5(a), the calculated viscosity values with the 4 classical models fit well with the experimental data for the 5wt% MPCM. Whereas the prediction is deviated from the measurement data for the 10 wt% and 15 wt% MPCM, as demonstrated in figure 5(b) and (c). The deviation between the measured value and the theoretical calculated value increased with the weight percentage of MPCM. Meanwhile, the difference between theoretical calculated values and experimental measurement is larger under lower temperature. For example, when the temperature is 20 ℃, the calculated values is smaller compared with the experimental measurement for 10 wt% MPCM, and % for 15 wt%.

The large discrepancy between theoretical calculation and real condition are caused by two reasons: (1) There are certain hypothesis within classical viscosity formulas\(^{[10]}\), which makes the formulas not suitable for the MPCM samples under investigation; and (2) the effects of particle size on viscosity is totally ignored in classical viscosity formulas whereas the distribution of micro particle sizes would cause the variation of macro MPCM viscosity. The calculation error will cause trouble for engineering application of the MPCM under investigation and the accurate prediction of viscosity is of great importance. Hitherto, the modified Tomas formula is porposed in the present investigation. The factor of \( a\varphi/d \) representing the influence of particle size on MPCM viscosity is introduced and the modified formula is as following:

\[
\mu = \mu_f \left[ 1 + 2.5\varphi + 10.05\varphi^2 + 0.00273\exp(16.6\varphi) \right] \frac{1 + 51.89\varphi}{d}
\]

Where \( \mu_f \) is the viscosity of base fluid, \( a \) is 51.89, \( \varphi \) is the volume fraction (%), \( d \) is the average particle diameter (\( \mu m \)).

In order to evaluate the accuracy of modified formula, the viscosity values of MPCM from theoretical calculation and experiment measurement are compared and presented in figure 6. It is obvious that the discrepancies between calculation and testing are much smaller with the modified formula. The calculation error is controlled within 5.7% when the volume concentration is less than 15.58%. This proves the reliable and high accuracy of the modified formula.
Figure 6. The comparison of MPCM viscosity from measurement and theoretical calculation based on the modified formula

5. Conclusions

(1) The base fluid was prepared by reducing the density difference between solid and liquid, and it was found that the micro-capsulated phase change suspension prepared with a volume ratio of 1:1.75 of isopropanol/water mixed solution as the continuous phase, suspension stability is up to 48h.

(2) When testing the rheological properties of micro-capsulated phase change suspension with 5 wt%, 10 wt% and 15 wt%, it was found that when the shear rate changed from 0 to 100 s⁻¹, the shear stress on the suspension changed linearly with the shear rate. Therefore, it can be considered that the micro-capsulated phase change suspension with a concentration of less than 15% can be regarded as Newtonian fluid.

(3) It was found that the viscosity of phase change suspension increases with the increase of mass concentration (volume concentration) of particles. The theoretical analysis shows that the effects of particle size on the micro-capsulated phase change suspension was ignored in the derivation process of the classical viscosity formula. In this study, the influence factor of particle size was introduced, and the Tomas viscosity formula was modified to get the fitted viscosity formula, as below:

$$\mu = \mu_i \left[ 1 + 2.5\varphi + 10.05\varphi^2 + 0.00273 \exp(16.6\varphi) \left( 1 + 51.89 \frac{\varphi}{d} \right) \right]$$

This viscosity formula can be used to calculate the viscosity value of the micro-capsulated phase change suspension prepared in this study, and the error is less than 5.7%.

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