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Preparation and Rheological Properties of Amide-based Multiwalled Carbon Nanotube Mirabilite Phase Change Materials

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Abstract: The multi-walled carbon nanotubes (MWCNTs) are modified by redox methods, and the surface groups of the MWCNTs are analyzed by infrared spectroscopy. And the modified MWCNTs were added to the mirabilite-based phase change materials (PCMs) at 40℃ to prepare the mirabilite-based phase change composite material. The results show that when the volume fraction is 0.05% and 0.25%, when the temperature rises from 30℃ to 50℃, the viscosity drop of the phase change composite material is 35.86% and 37.50%, respectively. That is, the larger the volume of the fraction of nanoparticles, the higher the viscosity, thus the greater the ability to perceive temperature fluctuations. In addition, the amide multiwalled carbon nanotube mirabilite PCMs was placed for 30 days, and the dispersion stability was good, and no phase delamination occurred.

Keywords: MWCNTs; Glauber's salt-based PCMs; Preparation; Rheological properties

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1. Introduction

The phase change energy storage material is a new type of multiphase medium, which can integrate heat transfer and heat storage. The fundamentals of the phase change energy storage materials are the PCMs. PCMs have both a sensible heat process and a latent heat process [1]. Glauber's salt (GS, $Na_2SO_4 \cdot 10H_2O$), GS-based PCMs, as an inorganic hydrated salt PCMs, is non-toxic, absorbs and releases heat at a constant temperature, has a wide phase change temperature range, and has a large energy storage density [2]. However, this material has limitations such as low heat transfer efficiency and phase stratification [3], Which will affect its further promotion and application. Liu et al. found that the nano-carbon powder composite PCMs has no obvious phase delamination [4]. Li et al. found that adding sodium carboxymethyl cellulose to the PCMs of GS can inhibit the phase delamination and supercooling of GS [5].

MWCNTs are formed by curling multiple layers of graphite [6], where it has good thermal conductivity [7]. However, MWCNTs are non-polar substances and have poor dispersibility in water [8]. This article uses redox and other methods to modify MWCNTs [9]. Structure and morphology analysis of the MWCNTs before and after the modification were studied, and the dispersion stability was discussed.

2. Materials and Methods

2.1. Experiment material

2.1.1. Test raw materials

MWCNTs (Shanghai Aladdin Bio-Chem Technology Co., LTD. Inner diameter: 3-5 nm, outer diameter:

8-15 nm, length: ~50 μm)

2.1.2. Test reagents

Sodium sulfate decahydrate, sodium carbonate decahydrate, borax, concentrated sulfuric acid, concentrated nitric acid, DMSO, ammonia water is all analytically pure.

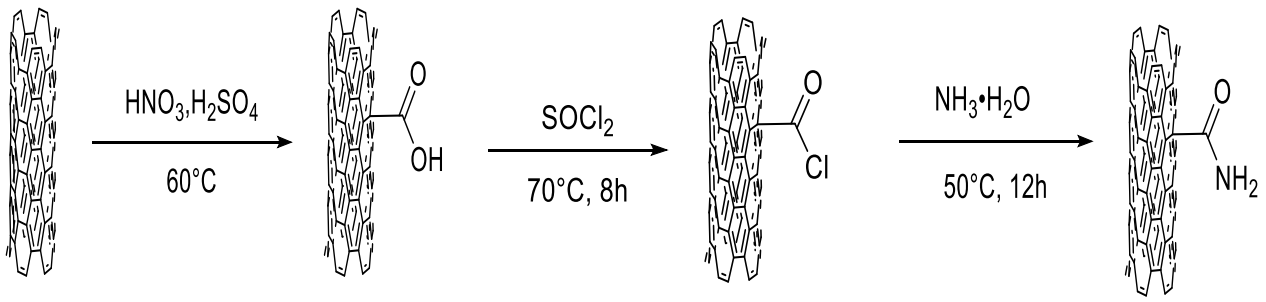
2.1.3. Test instruments

Tap density meter (PF-100B, Litian Magnetoelectric Technology Co., Ltd.), Field emission scanning electron microscope (JSM-7900F, Japan (JEOL)), infrared spectrometer (Nicolet 6700, Thermo Fisher Scientific), and rotational rheometer (Kinexus lab, Malvern Instruments Co., Ltd., UK).

2.2. Experiment method

2.2.1. Preparation of modified MWCNTs

Weighed 2g of MWCNTs, put them in a reagent with a ratio of 60mL concentrated sulfuric acid and 20mL concentrated nitric acid, heated to 60℃ and stirred for 20 minutes to cause oxidation-reduction reaction [9] to obtain carboxylated MWCNTs. Then 1.5g of carboxylated MWCNT was weighed, DMSO was added, and the reaction was carried out at 70℃ for 8 hours. After the temperature of the reaction solution was lowered to room temperature, an acid chloride Chemical MWCNTs filter cake was obtained. Finally, 0.5g of acid chloride MWCNT was weighed, and 50mL of ammonia water was added to react at 50℃ for 12 hours to obtain amide MWCNT. The reaction equation is as follows:



2.2.2. Preparation of Glauber's nitro PCMs

Weighed the reagent in the ratio of 70g sodium sulfate decahydrate, 30g sodium carbonate decahydrate and 2g borax [10]. The weighed mixed sample was heated and stirred at 40℃, mixed and dissolved, and then an appropriate amount of distilled water was added to make the material a uniform and stable fluid at 40℃. Then added the MWCNTs according to the volume ratio. Due to the MWCNTs were relatively fluffy, first converted them into a mass ratio according to the volume ratio. In actual weighing, weighed the MWCNTs according to the mass ratio. The density of MWCNTs is measured by a tap density meter.

The relationship between the nanoparticles vol.% (φ_p) and the mass fraction wt% (ω_p) is as follows: [11]

$$\varphi_p = \frac{\rho_f \omega_p}{\rho_p + \rho_f \omega_p - \rho_p \omega_p}$$

Where ρ_f is the density of the base fluid, and ρ_p is the density of the nanoparticles. The mirabilite-based liquid and nanoparticles were sonicated at 40℃ for 60 min to obtain mirabilite-based PCMs with the volume fraction of MWCNTs of 0.05%, 0.1%, and 0.25%, respectively. The choice of nanoparticles was amide MWCNTs. When the base fluid density was 1.230 g/mL, the nanoparticle density was 1.300 g/mL,

and the vol.% are 0.05%, 0.10%, and 0.25%, the mass fractions are 0.0525%, 0.105%, and 0.261%.

2.2.3. Performance testing

The functional groups of MWCNTs were measured by infrared spectrometer. The microscopic morphology of MWCNTs was measured by scanning electron microscope. The rheological properties of nanofluids were measured by Malvern rotational rheometer.

3. Results and Discussion

3.1. Surface structure and morphology of MWCNTs before and after modification

Figure 1. shows the infrared spectra of MWCNTs before and after modification. In **Figure 1.**, 3434cm^{-1} is the -OH stretching vibration peak of moisture in the air [12]. In **Figure 1b.,** the N-H stretching vibration peaks (primary amide characteristic peaks) are at 3430.65cm^{-1}, 3128.08cm^{-1}, 1630.29cm^{-1} is the N-H deformation vibration peak, and 1402.30cm^{-1} is the C-N stretching vibration. The peak, 1153.0cm^{-1} is the N-H in-plane deformation vibration peak, and 611.90cm^{-1} is the N-H out-of-plane deformation vibration peak, indicating that the amide group is contained in **Figure 1b.** That is, through the modification treatment, hydrophilic groups are obtained on the surface of the MWCNTs.

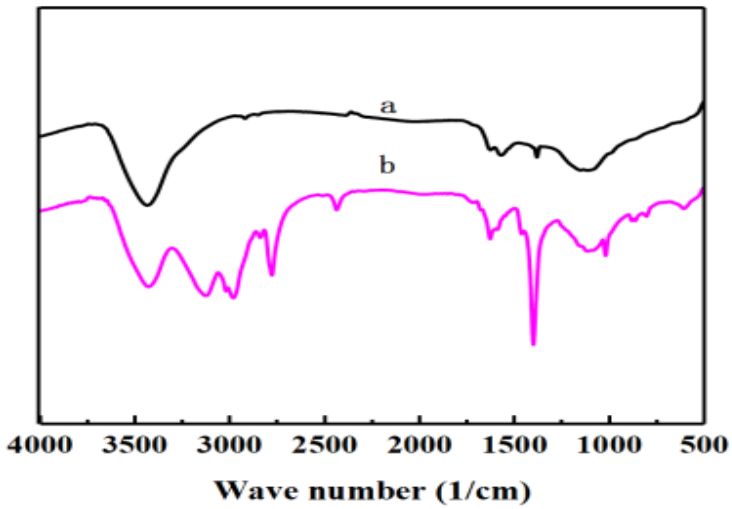


Figure 1. Infrared spectra of MWCNTs before and after modification, where “a” is unmodified MWCNTs and “b” is Amido-MWCNTs

Figure 2. shows the SEM images of MWCNTs before and after modification. **Figure 2a.** is an SEM image of unmodified MWCNTs. The average outer diameter is about 8-15nm, and the tube surface is arranged in disorder. **Figure 2b.** is the SEM image of amide MWCNTs. Compared with the SEM image of unmodified MWCNTs, the arrangement is more regular. This is due to the amide inserted on the surface of the modified MWCNTs. The group makes the arrangement of the material more regular.

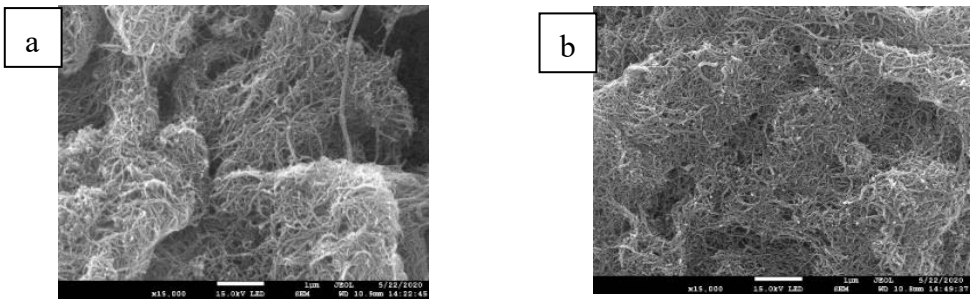


Figure 2. SEM images of MWCNTs before and after modification, where “a” is Unmodified MWCNTs and “b” is Amido-MWCNTs

3.2. Rheological properties of GS-based PCMs

The nano particles with vol.% of 0.05%, 0.1%, and 0.25% were selected to prepare GS-based PCMs. **Figure 3.** shows that as the vol.% increases, the viscosity of the GS-based PCMs nanofluid also increases. This is because van der Waals forces exist between the molecules of the liquid phase. When nanoparticles are added to the base fluid, there is also van der Waals force between the nanoparticles and water molecules, which will increase the van der Waals force between the molecules of the base fluid, and the nanofluid will flow at the same time. At this time, there is also friction between the nanoparticles. The greater the proportion of nanoparticles in the mirabilite PCMs nanofluid, the greater the friction between the nanoparticles, the larger the proportion of the nanoparticles is the mirabilite PCMs nano The greater the viscosity of the fluid system. Under the same measurement system conditions, as the temperature increases, the viscosity of the nanofluid will decrease. This is because the increase in temperature will increase the between the molecules of the mirabilite PCMs nanofluid, and the energy possessed by the molecules will increase.

Figure 3. shows the change of the viscosity of the GS-based PCMs with temperature at different vol.%. It can be seen from **Figure 3.** that when the vol.% is 0.05%, when the temperature rises from 30℃ to 50℃, the viscosity of the nanofluid decreases from 2.674 mPa·s to 1.715 mPa·s, a decrease of 35.86%, and the vol.% is 0.25% When the temperature rises from 30℃ to 50℃, the viscosity of nanofluid decreases from 4.667 mPa·s to 2.917 mPa·s, a decrease of 37.50%. The results show that the larger the vol.% of the nanoparticles, the greater the van der Waals force between the nanoparticles and water molecules, and the greater the sensitivity of viscosity to temperature fluctuations.

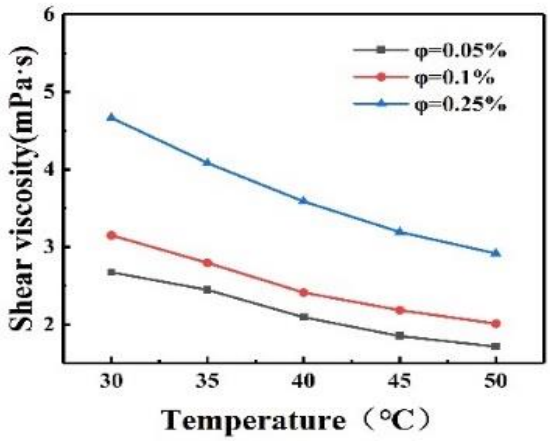


Figure 3. Viscosity of GS PCMs with Temperature in different vol.% of MWCNTs

3.3. Stability analysis of GS-based PCMs

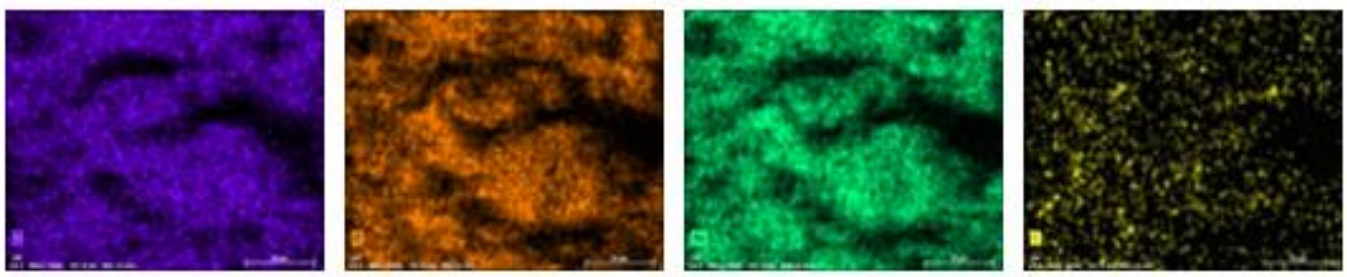


Figure 4. Element distribution on the surface of GS PCMs nanofluid

Figure 4. shows a mirabilite PCMs with a 0.25% vol.% of amidated MWCNTs for EDS testing to observe the distribution of nanoparticles. It can be seen from the figure that the distribution of Na, S, and O is basically the same, and the distribution of nanoparticles is relatively uniform.

4. Conclusions

This paper studied the structure and morphology analysis of modified MWCNTs, as well as the rheological properties of mirabilite-based PCMs. Additionally, the dispersion stability was analyzed and the following has been concluded from each study:

(1) Amido-based MWCNTs are obtained by modifying MWCNTs with ammonia water, and the amido-based MWCNTs are hydrophilic.

(2) When the amide-based MWCNTs-GS PCMs has a nanoparticle vol.% of 0.05% and 0.25%, the temperature rises from 30℃ to 50℃, and PCMs decreases by 35.86% respectively. And 37.50%. The larger the vol.% of nanoparticles, the greater the sensitivity of viscosity to temperature fluctuations.

Unmodified MWCNTs are insoluble in water, resulting in unstable system and sinking of particles. After surface treatment of MWCNTs, hydrophilic groups of amide-based MWCNTs are obtained, which makes the modified MWCNTs. The dispersion stability of carbon nanotubes in GS is significantly improved.

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Disclosure statement

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