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Study on performance of colloidal mixtures consisted of stearic acid and $Na_2HPO_4 \cdot 12H_2O$ for use as phase change materials of thermal energy storage

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ABSTRACT

The thermal energy storage performance and phase change stability of mix phase change materials consisted of stearic acid and $Na_2PO_4 \cdot 12H_2O$ are studied by means of Fourier transformation infrared spectrum analyses (FTIR) and Differential Scanning Calorimetry (DSC). The specific heat capacity of mix materials is also determined experimentally. The results show that all absorption peaks of functional groups and chemical bonds of stearic acid still exist, which suggests that these crystal materials composed of stearic acid and $Na_2PO_4 \cdot 12H_2O$ have good phase change stability and chemical compatibility. Thus, disadvantages caused by the subcooling of $Na_2PO_4 \cdot H_2O$ and the low specific heat capacity of stearic acid can be solved, it is speculated that complement each other on the basis of organic/inorganic characteristics in itself is carried out for these two component materials of the mixture.

1. Introduction

Thermal energy storage (TES) technology using latent heat in phase change is an effective means of improving energy utilization ratio as it can be used to solve the mismatch between energy supply and demand both in time and space. It also has broad application prospects, such as the utilization of solar energy, "peak-load shifting" of power supply, residue heat recovery and utilization, industrial and civil buildings, etc. [1–5]. According to the phase change behavior, latent TES can generally be divided into four kinds: solid–solid phase changes, solid–liquid phase changes, solid–gas phase changes, and liquid–gas phase changes. Solid–gas and liquid–gas phase changes are rarely adopted as there are very large volume variations with occurrence of the vapor phase. While solid–solid phase change materials have usually the higher phase change temperature, it is difficult to obtain the solid–solid phase change material suitable for buildings. Solid–liquid phase change materials are most widely used because of its appropriate phase change temperature, large latent heat, and relatively small volume change. In the process of the phase change, the solid–liquid phase change material produces the liquid-phase which makes this material certain flowability. Therefore, it must be filled with some corrosion-resistant containers which must be sealed to prevent leakage resulted in other component corrosion or environment pollution. As these shortcomings, practical engineering applications of the solid–liquid phase change material are hampered to a great extent. It is interested that certain colloidal mixtures made from some organic and inorganic phase change materials (which are compatible and miscible) are better phase change materials. This method facilitates the phase change material to fit mobility in liquid phase, on the other hand, the phase change material is flexible in solid phase, so that it is easily fabricated with the available, simple and cheap molding process. Stearic acid and $Na_2PO_4 \cdot 12H_2O$ are selected to prepare the mixtures of phase change materials in our study. Experimental results are reported in the paper. It is shown that this method has the advantage of complement each other, namely, fully utilizing the intrinsic characteristics of these organic and inorganic materials. This compromise idea may be a better development direction in producing phase change materials.

2. Experimental set-up and procedure of colloidal mixture preparation

The sol–gel method is mainly used in preparation of organic–inorganic mixture phase change materials. In resulted products, contributions of the organic and inorganic phase to them are as follows: the inorganic phase gives high strength, high thermal conductivity, high modulus, high scratch resistance, corrosion resistance and other properties, and on the other hand, the organic phase gives low density, good flexibility, and excellent heat storage characteristics, etc. Thus, it is easy to change the organic and inorganic components participated in mixing so as to control the material properties satisfied requirements. Besides, these colloidal

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mixtures have also advantages of simple and easy control processes and the low synthesis temperature.

Put stearic acid (analytically pure) into a flask with three opens. Turn on power supply of the magnetic heating stirrer with constant temperature control, stir stearic acid and maintain it at the constant temperature of 75 °C until it is completely dissolved. Make-up dry $Na_2PO_4 \cdot 12H_2O$ (analytically pure) into the powder, add it slowly and uniformly to the melting stearic acid on the basis of the suitable ratio while adding 1% polyacrylamide. Stir continuously for 10 min to obtain the white colloidal mixture which is thixotropic. The colloidal mixture can be more flexible when being crushed. After repeated heating and cooling, the state of the colloidal mixture remains unchanged in an air-tight case.

3. IR analyses of colloidal mixtures

The chemical nature of fatty acids ($CH_3(CH_2)_nCOOH$) depends on the type, number and location of the functional group. Fatty acids contain carboxyl (–COOH). Chemical characteristics of the carboxyl are important for the fatty acid. Formally, carboxyl is composed of carbonyl (C=O) and hydroxyl (–OH), however, this does not simply mean that the characteristics of the carboxyl are equivalent to the superimposed characteristics of the carbonyl and the hydroxyl. Carboxyl has its own characteristics, which depend on the mutual effect between the carbonyl and the hydroxyl. No sharing electron pairs in oxygen atoms of the hydroxyl can form a ρ, π conjugated system with π bonds of the carbonyl. In this conjugated system, the electron cloud density for oxygen atoms of the hydroxyl has reduced while the electron cloud density of the carbonyl has increased owing to electron cloud density averaging. Thus, hydrogen atoms can easily transform into hydrogen ions and the carboxyl appears acidic. After fatty acid absorbs water, its molecular is dissociated and hydrogen ions are generated.

$$RCOOH \rightarrow RCOO^- + H^+ \tag{1}$$

Fatty acid can produce salt with metal oxides, metal hydroxides, for example:

$$2RCOOH + MO \rightarrow (RCOO)_2M + H_2O \tag{2}$$

$$2RCOOH + M(OH)_2 \rightarrow (RCOO)_2M + 2H_2O \tag{3}$$

Therefore, when the phase change material is in a moist environment, it is likely to absorb water and become acidic and then reactions of (2) and (3) may occur in it. While fatty acids in phase change materials become fatty acid salts, heat storage performance of these materials loses. In order to test the colloidal mixture prepared according to the above procedure whether it becomes salts and has any heat storage effect, infrared analyses of some samples were carried out.

The infrared spectra of stearic acid and the colloidal mixture are shown in Figs. 1 and 2.

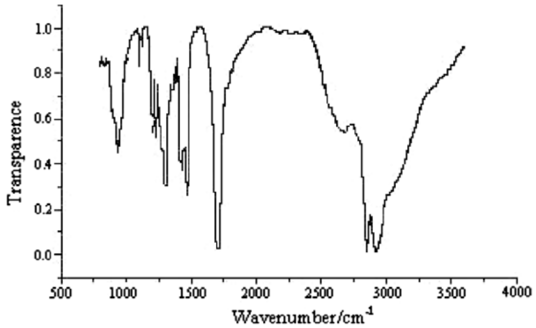

Fig. 1. IR spectra of stearic acid.

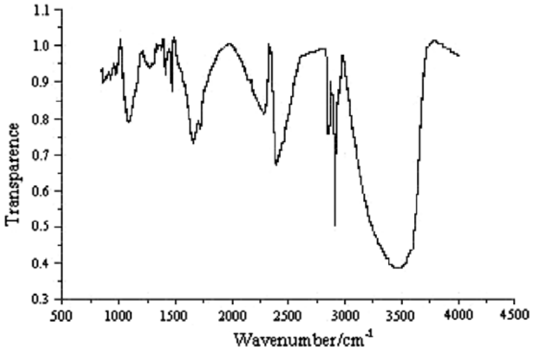

Fig. 2. IR spectra of the colloidal mixture consisted of stearic acid and $Na_2PO_4 \cdot 12H_2O$.

From the IR spectrum of pure stearic acid shown in Fig. 1, it is seen that main characteristic peaks are as follows: (1) There is a broad and unfocused absorption band when the wave number is on the interval for 2500–3000 cm^{-1}, which is the O–H absorption band of stretching–contracting vibration (v_{OH}). The location, band width and shape of the absorption band depend on the dimer formed of molecular hydrogen association. Normally, it overlaps with the C–H absorption peak of stretching–contracting vibration of the aliphatic group, which is the typical characteristic of carboxylic acid. This interval has four peaks, their wave numbers are as follows: 2955.36 cm^{-1}, 2917.14 cm^{-1}, 2873.23 cm^{-1}, and 2848.91 cm^{-1}. They are respectively corresponding to four C–H absorption peaks of the stretching–contracting vibration: $v_{as}CH_3$ (asymmetric stretching–contracting vibration), v_sCH_3 (symmetric stretching–contracting vibration), $v_{as}CH_2$ (asymmetric stretching–contracting vibration) and v_sCH_2 (symmetric stretching–contracting vibration). (2) There is a very strong peak at 1702.27 cm^{-1}, which is the $v_{C=O}$ absorption peak of carbonyl (C=O) of carboxylic acid dimer. This is a very typical characteristic peak of carboxylic acid. (3) There is a strong peak at 1432.46 cm^{-1}, which is the absorption band of deforming vibration (the absorption peak of the face-inside bending vibration). It is mixed with the CH_2 absorption band of deforming vibration and difficult to distinguish from the latter. (4) There is a medium strong absorption peak at 933.95 cm^{-1}, which is the absorption peak of the face-outside bending vibration of carboxylic acid dimer. It is the characteristic peak of carboxylic acid with wider band. In addition, the shoulder–absorption band can also be seen at the 2500–2700 cm^{-1} in the spectrum figure. This is resulted from the C–O stretching–contracting vibration, the O–H deforming vibration and the frequency doubling of the C–O stretching–contracting vibration frequency. Fig. 2 is the IR spectra of the colloidal mixture consisted of stearic acid and $Na_2PO_4 \cdot 12H_2O$, which is prepared by the authors.

If stearic acid can react chemically with $Na_2HPO_4 \cdot 12H_2O$, sodium stearate will be produced. Then all carboxyl peaks will be disappeared, replaced by the two equivalent C=O bond absorption

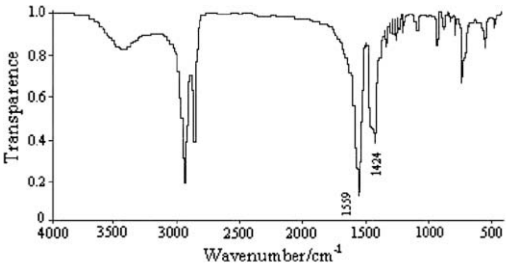

Fig. 3. IR spectra of sodium stearate.