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Enhancement in thermal property of phase change microcapsules with modified silicon nitride for solar energy

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ABSTRACT

Thermal behavior is one of the most important properties for phase change microcapsules in solar energy storage. Here, a new type of phase change microcapsules was synthesized based on n-octadecane core and polymethylmethacrylate shell supplemented with modified silicon nitride powders, aiming to achieve improvement of thermal property in the phase change materials. SEM micrographs showed that the as-prepared microcapsules have a regular spherical shape with a well-defined core-shell structure. FTIR curves and EDS spectrogram demonstrated that silicon nitride can be well cross-linked with microcapsules after surface modification. In addition, TGA, forward looking infra-red system and DSC (before and after 500 heating and cooling cycles) analyses were performed to investigate the thermal property of the as-prepared microcapsules. The results indicated that the microcapsules have high thermal storage capability, enhanced thermal reliability and stability, and increased thermal conductivity. Especially, the thermal conductivity of microcapsules is enhanced by 56.8% compared with that of the microcapsules without the addition of silicon nitride.

1. Introduction

With the rapidly increasing energy consumption and excessive exploitation of fossil fuels in the past several decades, energy crisis has become one of the most crucial problems worldwide. Therefore, great efforts have been made to develop new and sustainable energy. Solar energy is considered as one of the most promising green energy for large-scale application; however, the uneven distribution in space and time has severely restricted its practical application. One solution to the problem is the development of phase change materials (PCMs), which are capable of absorbing/releasing a large amount of energy at a defined range of temperatures [1–5]. To prevent erosion and leakage of PCMs, many researches have been focused on the development and use of phase change microcapsules (micro-PCMs), which are composed of a shell of macromolecules and a core of phase change materials [6–10]. Micro-PCMs can prevent interior phase change materials from leaking as well as increase the heat transfer area and promote crystallization [11,12].

Polymer is one of the most popular materials for preparing micro-PCMs. Due to its appropriate plasticity, the polymeric shell is able to tolerate the volume changes caused by the phase transformation and thus can safely isolate the PCMs from the environment [13–15]. Excellent thermal properties have been achieved by different researchers using various shell materials. For instance, Ma et al. [16] prepared polyuria/polyurethane microcapsules with butyl stearate and paraffin as binary core via interfacial polymerization method, and the content of binary core in the micro-PCMs reached 45–60%. Zhang et al. [17] successfully prepared stearic acid/polycarbonate(SA/PC) microcapsules. The melting temperature, freezing temperature and latent heat of the microcapsule were reported to be 60 °C, 51.2 °C and 91.4 J g^{-1}, respectively. Chen et al. [18] synthesized polyurea microcapsules using the method of interfacial polycondensation. The latent heat of fusion was about 80 J g^{-1}, and the phase change temperature and enthalpy of encapsulated butyl stearate kept nearly constant over 400 heating and cooling cycles. The above researches undoubtedly mark the great progress in the field of PCMs. However, although excellent thermal properties have been achieved, the poisonous formaldehyde released by the shell materials, which is hazardous to environment and health, greatly hinders the further application of the technique. In an attempt to overcome such drawbacks, Qiu et al. [19], Sari et al. [20] and Huang et al. [21] attempted to employ a non-toxic and commercially available

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acrylic resin (polymethylmethacrylate, PMMA) as the shell material, which is proved to be an effective material.

Thermal conductivity is another important property of micro-PCMs [22–25]. Many researches have been focused on the preparation of microcapsules with high thermal conductivity. Zhang et al. [26] prepared microcapsules based on n-eicosane core and ZrO_2 shell with the dual-functional characteristics of thermal energy and photoluminescence. Li et al. [27] used carbon nanotubes grafted with stearyl alcohol (CNTs-SA) in synthesizing phase change microcapsules to enhance the thermal conductivities of the microcapsules. The thermal conductivity of microPCMs/CNTs-SA with 4% of CNTs was increased by 79.2% compared with that of the original micro-PCMs. Jiang et al. [28] synthesized phase change microcapsules based on paraffin wax core and poly(methyl methacrylate-co-methyl acrylate) shell with nanotubes alumina (nano-Al_2O_3) inlay. The optimized percentage of nano-Al_2O_3 introduced into the microcapsules is 16% of the monomer mass, which results in a phase change temperature of 23.75 °C, an enthalpy of 93.41 Jg^{-1} and a thermal conductivity of 0.3104 $W\,m^{-1}K^{-1}$.

In our previous work, we successfully developed the phase change microcapsules supplemented with modified silicon nitride, which showed high thermal performance [29]. As an important ceramic powder [30–32], silicon nitride has various advantages such as economy, stable abradability, non-oxidizability, thermal vibration resistance and high thermal conductivity. It has been demonstrated to be an efficient supplementary material for thermal performance improvement of phase change microcapsules. However, nano-silicon nitride is easily attached to each other and forms a large cluster. In order to separate these nano-particles, a new desiccation method was proposed in this study. The thermal behavior of the microcapsules prepared with such silicon nitride nano-particles was systematically evaluated using DSC, TGA, forward looking infra-red system and heating-cooling cyclic oven.

2. Materials and experimental

2.1. Materials

Silicon nitride was provided by Tianjin Nitride Advanced Materials co., Ltd, China. Methacryloxy propyl trimethoxyl silane (Silane coupling agent KH-570) was purchased from Sinopharm Chemical Reagent Co., Ltd. Methylmathacrylate (MMA, A.R.,) was supplied by Tianjin Damao Chemistry Regent Co., Ltd. as a monomer of shell material. N-Octadecane(99 wt%, Alfalfa) was used as the core material. Pentaerythritol triacrylate (PETRA, 80 wt%) was provided by Nanjing Shoulashou Co., Ltd. and was used as crosslinking agents. Sodium salt of styrene-maleic anhydride polymer (Shanghai Leather Chemical Works) was used as dispersant. 2, 2-azobisisobutyronitrile (AIBN, 98 wt%, Shanghai Jingchun Chemical Co., Ltd.) was employed as initiator. All chemicals were used as received without further purification.

2.2. Synthesis

2.2.1. Surface modification of silicon nitride

In order to eliminate the negative interfacial effect between inorganic and organic matters, pretreatment was conducted for silicon nitride prior to polymerization. The surface modification process is as follows: 10 g silicon nitride was dissolved in 10 g KH570 with ultrasonic vibration for 15 min. Meanwhile, 3 g deionized water was first dissolved in 50 g C_2H_5OH and then oxalic acid was added to adjust the pH value to a range between 4.5 and 5.5. The mixture was then poured into a flask bathed in 80 °C water and stirred at 1000 r min^{-1} for 2 h. Finally, the modified silicon nitride was obtained by freeze drying after filtering and washing with deionized water for several times.

2.2.2. Synthesis of micro-PCMs/silicon nitride

Fig. 1 is the schematic illustration of synthetic strategy for the microcapsule with modified silicon nitride. The method of preparing phase change microcapsule with modified silicon nitride was as same as that described in the previous research [29]. Recipes for various types of polymerization monomers are given in Table 1. 7 g sodium salt of styrene-maleic anhydride copolymer was dissolved in 100 g distilled water for 15 min under vigorous agitation of 1000 rpm. Meanwhile, 3 g modified silicon nitride and 7 g Methylmethacrylate, 3 g Pentaerythritol tetraacrylate and 10 g n-octadecane were ultrasonically dispersed separately for 15 min. Afterwards, all the materials prepared were mixed into a 250 mL three-neck round bottomed flask and kept in a 35 °C water bath for 15 min under vigorous agitation of 1000 rpm to form a stable oil-in-water emulsion. After the addition of 2, 2-azobisisobutyronitrile, the flask was placed in 80 °C water bath and subjected to a moderate agitation of 540 rpm for 5 h. Finally, the obtained microcapsules were purified by centrifugation and dried in an oven at 45 °C for 24 h.

2.3. Characterization

Field emission scanning electron microscope (FESEM, S4800, HITACHI) was used to observe the surface morphology of the samples. The chemical structures of the modified silicon nitride and the phase change microcapsules were identified using fourier transformed infrared spectrophotometer (FTIR, VERTEX 70, BRUKER). Differential scanning calorimeter (DSC, 823E METTLER TOLEDO) was used to measure the thermal properties of the materials at the temperatures

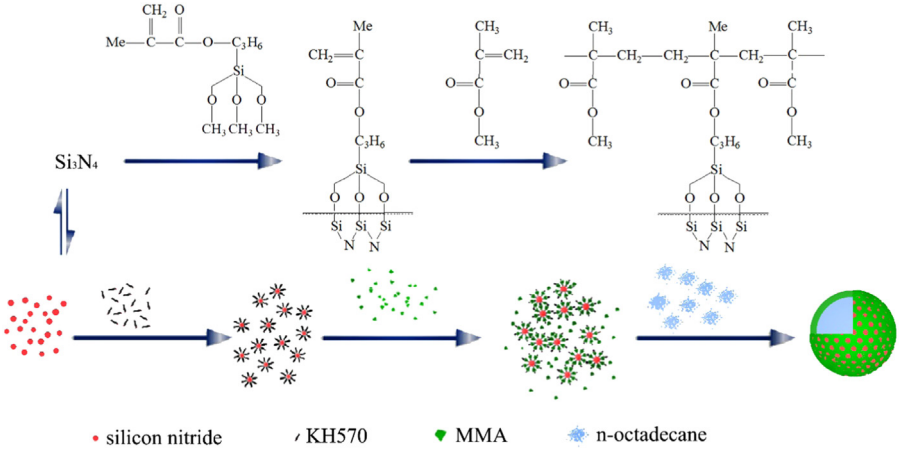

Fig. 1. Schematic of synthetic strategy for microcapsules with modified silicon nitride.