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Thermal stability of composite phase change material microcapsules incorporated with silver nano-particles

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Abstract

This paper reports a study on the thermal stability of phase change material microcapsules that are incorporated with silver nano-particles (Ag-NPs). The novel microcapsules were fabricated by the technique of in situ polymerization, with aminoplast as the wall and phase change material bromo-hexadecane (PCM BrC16) as the core. Thermal gravimetry (TG) analysis was applied to measure the thermal stability of these microcapsules and surface morphology of the microcapsules was observed by means of scanning electron microscopy (SEM) after an application of curing treatment at 130 °C. Comparing with conventional phase change material microcapsules (PCMMs), nano-composite phase change material microcapsules (NCPCMMs) have higher thermal stability. This can be attributed to nano-composite structure of the microcapsules, in which metal Ag-NPs distributed on the surface to increase wall toughness and strength. The possible reinforcement mechanisms of the nano-composite structure are explored.

Keywords: Microcapsules; Phase change material; Thermal stability

1. Introduction

Phase change material microcapsules (PCMMs) are granular substance with a core and shell structure, where phase change materials (PCMs) are the core enwrapped by shell material. The encapsulated PCMs are not easily affected by the surrounding environment due to the protection of the shell. PCMMs can absorb and release heat from surroundings in dynamic heat exchange processes, when they take place at the melting point (MP) and/or crystallization temperature resulting in a temperature regulating function for the PCMMs. Thus, a relatively comfortable microclimate can be provided to wearers if these PCMMs are applied in garments [1,2].

In recent years, a range of techniques has been developed to make temperature regulating textiles and smart garment products [3–6]. In these applications, the PCMMs are required to have good thermal stability and mechanical strength for ensuring intact structure during manufacturing processes. However, the thermal stability properties and physical strength of these PCMMs at present are not capable of making high quality thermal regulated textile products, and studies are needed to address such problems [7].

Bryant summarized that there are three possible mechanisms for the damage of microcapsules during the heating process [8]: (i) increased internal pressure leading to wall rupture, (ii) diffusion of core materials through the microcapsule shell; and (iii) thermal degradation of wall, followed by a release of the core material.

Many studies have been carried out to increase the thermal and mechanical stabilities of PCMMs in order to meet the requirements of thermal stability in manufacturing process. Traditional techniques to improve the thermal and mechanical stabilities of PCMMs are as follows:

(i) Selecting suitable wall material. It has been found that amino-aldehyde cross-linking structure copolymer

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(e.g., melamine-formaldehydes condensate) as shell materials for PCMMs has a better thermal and mechanical stability than other shell materials, such as gelatin–Arab gum complex and polyurethane wall materials, and could provide better protective functions to the encapsulated PCM core material in dry air as the temperature is higher than 120 °C [9,10];

(ii) Decreasing the ratio of weight percentage of core material and;
(iii) Encapsulating the core by multi-layers of shell materials [11], or;
(iv) Trying to find the optimal molecule ratio of melamine–formaldehyde to modify the property of M–F wall polymer in order to have the best compact texture for wall polymers [12],
(v) Increasing microcapsule size [13], and;
(vi) Putting volatile materials into the core, and microencapsulating them together with PCMs into the microcapsule. Then heat them to allow the materials to vaporize and obtain a certain reserved volume in the inner capsule. Thus, the thermal stability of the microcapsules is enhanced [14].

Although these techniques have certain effects in increasing thermal stability, limitations are obvious. For example, increasing the shell ratio and multi-wall encapsulation will surely decrease the thermal regulating performance of the PCMMs and thermal regulated textiles.

Wall properties of PCMMs play an important role in the thermal stability of PCMMs, and how to strengthen the wall's toughness is the key to improve the performance of PCMMs. Novel techniques using the nano-scale particles have showed promising potential in changing the characteristics of the wall polymer matrices. It was reported that the rigid nano-scale particles incorporating with polymer matrices can create nano-composite structures which demonstrated superior properties in mechanic, optics, magnetism, etc. [15–17].

To enhance the wall strength of these PCM microcapsules, novel nano-composite PCMMs were prepared by using phase change materials (bromo-hexadecane with purity 99%) with the melting point of 16–18 °C as core thermal regulating material and silver nano-particles as functional additives. This type of composite PCM microcapsules incorporated with functional nano-materials were fabricated by employing an in situ polymerization technique [22].

Properties of metal nano-particles are different from those of bulk materials because of dielectric and quantum confinement effects, which arise due to the reduction in particle size down to nanometer range [18,19], which can lead to better thermal stability of the PCM microcapsules. Moreover, the silver nano-particle may make the microcapsules with other novel functional properties, such as antibacterial, anti-fugal and IR radiations [20,21]. Therefore, it can be expected that silver nano-particles are good potential candidates to be used to increase wall strength of the microcapsules.

Experiments were conducted to characterize the properties of NCPCMMs. This paper focuses on the thermal stability of the new PCM microcapsules with silver nano-particles (Ag-NPs). The thermal stability and anti-deformation properties of the NCPCMMs are compared with conventional PCMMs with same core materials and shell materials. Their performances during the drying and curing processes are investigated to see whether the toughness and strength of the wall material can be enhanced by the addition of functional nano-particles.

2. Experimental

2.1. Nano-composite PCM microcapsules

In the experiments, silver nano-composite PCM microcapsules were supplied by the Nano Sports Technologies Ltd. The PCM microcapsules with core/shell ratio of 5:1 were prepared by an in situ polymerization technique, which was described in detail in Refs. [12,23,24]. Bromo-hexadecane (PCM BrC16) was used as core PCM material with the melting point of around 17–18 °C and purity of 99% (Sigma-Aldrich Trading Co. Ltd). The loading rate of Silver nano-particles (Ag-NPs) as nano-functional additives was 3% of the mass of core materials. The size of the silver nano-particles was in the range of 40–60 nm with surface area of 30–50 m^2/g (BET); most of these silver nano-particles were in spherical shape, as shown in Fig. 1.

2.2. Material characterization

The microcapsules were characterized in terms of surface morphology observation (SEM), surface elemental analysis (EDX), thermal gravimetry (TG) and differential scanning calorimeter (DSC).

2.2.1. Surface morphology

The de-ionized water was added to both of the emulsions of NCPCMMs and PCMMs, rinsed the samples 3 times by centrifugal machine, applied the rinsed samples to clean glass

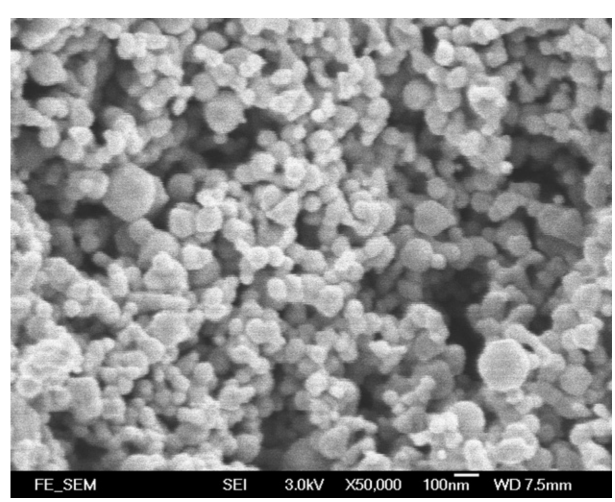

Fig. 1. SEM image of silver nano-particles.