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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

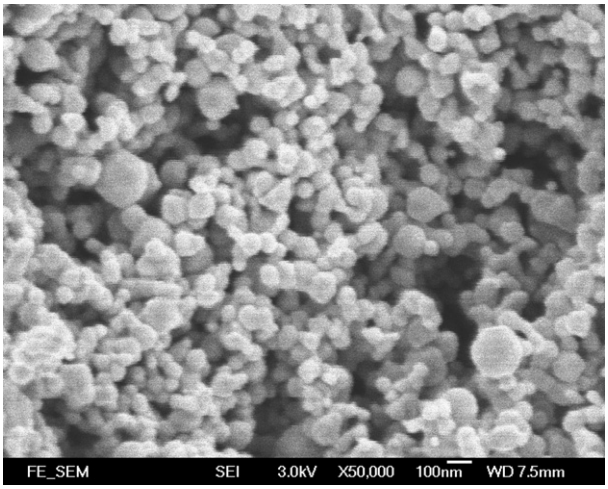

Fig. 1. SEM image of silver nano-particles.

slides and dried them with hot air. The slides were cured in an oven with a temperature setting of 130 °C for 50 min, and then these samples, including samples without the curing treatment were plated with a layer of gold in a vacuum circumstance. For SEM observation of silver nano-particles, silver powders were fixed on a clean glass slide by double-side adhesives tape. The scanning electronic microscope observations were carried out by JSM6335F (Japan) (see Figs. 1–3).

2.2.2. Surface elemental analysis

Energy dispersive X-ray fluorescence (EDX) is the instrument that performs a qualitative and quantitative analyses of element composition by measuring re-emitted characteristic X-ray from atoms of certain elements. The basic principal of EDX may be defined as a micro-analytical technique that uses the characteristic spectrum of X-rays emitted by the specimen after excitation by high-energy electrons in order to obtain information about the elemental composition [27]. Sample preparations were the same as that of SEM, except that the gold plating procedure was omitted for the EDX samples. The washed and dried samples were tested by a scanning electron microscope (Leica Stereoscan 440). The energy dispersive X-ray spectroscopy (EDX) provides information about elemental compositions of the sample to a depth of 2 μm on the sample surface [25,26].

2.2.3. Thermal gravimetry (TG) and DSC analyses

Thermogravimetric analyzer/differential scanning calorimeter (Netzch TGA/DSC, 25 °C–1500 °C) was used to test the NCPCMM and PCMM samples in the temperature range from room temperature to 450 °C in a programmed procedure. During the testing process, about 10 mg of clean and dried NCPCMM and PCMM powder samples were heated at temperature raising rate of 10 K/min in argon atmosphere. The property of thermal stability of the samples was characterized by measuring the weight (mass) loses with temperature increase. DSC analysis for the tested samples was carried out simultaneously.

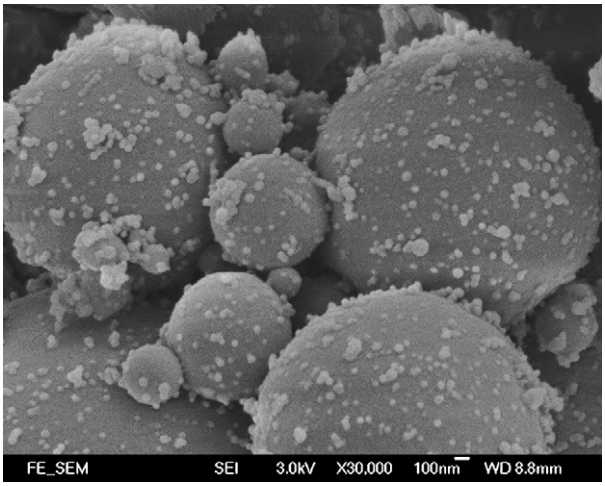

Fig. 2. SEM observation of NCPCMMs.

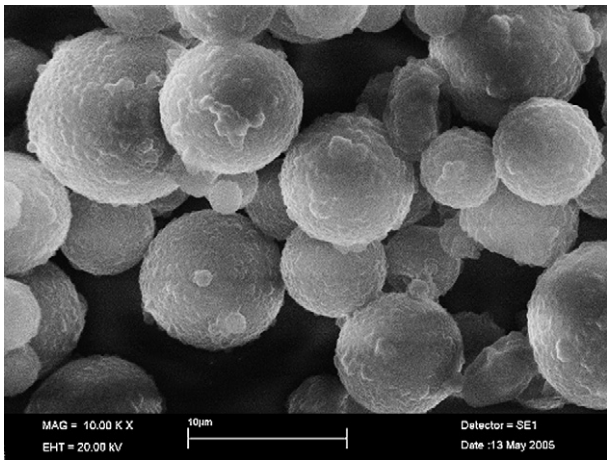

Fig. 3. Conventional PCMMs.

To further study the thermal stability of the PCMM and NCPCMM under the conditions of the industrial manufacturing processes, 5–6 g of washed and dried microcapsules were put into a bottle with known dry bottle weight. The samples were dried at 80 °C until the weight of sample was stable. Then, the lid was opened and put the bottle swiftly into an oven with a temperature setting of 130 °C. Cure the samples for the first 10 min. Take the bottle out and cover the bottle with a lid, weigh it and record as W_1 when it cools down. Put the bottle without lid into the oven again, 10 min later, take the bottle out and weigh it and record as W_2. Repeat this procedure several times until W_5 was obtained. The weight measured by this process represents the property of high temperature resistance of the microcapsules under a constant temperature commonly applied in practical textile manufacturing processes. Three parallel experiments were conducted for one specimen in the experiment. The weight losing percentage (WLP) was calculated as:

$$\mathrm{WLP}(\%) = (-1)\frac{W_n - W_0}{W_0} \times 100$$

where, W_n (g) is the dry weight of microcapsule powder after been cured for n time ($n \times 10$ min) and W_0 (g) is the original dry weight of microcapsule powder.

3. Results and discussion

3.1. Surface morphology

As shown in the SEM image in Fig. 3, many nano-particles were distributed on the surface of the capsules. Nano-particles were dispersed in different locations of capsules: on the shell and/or wrapped by shell materials. Paraffin (PCM) core materials were wrapped into the capsules and no broken capsules were observed. Comparing with the conventional PCM microcapsules shown in Fig. 3, NCPCMMs had a rougher surface due to the nano-composite shell structure. There were no obvious differences between the NCPCMMs and PCMMs in the shape and size distributions of microcapsules, indicating

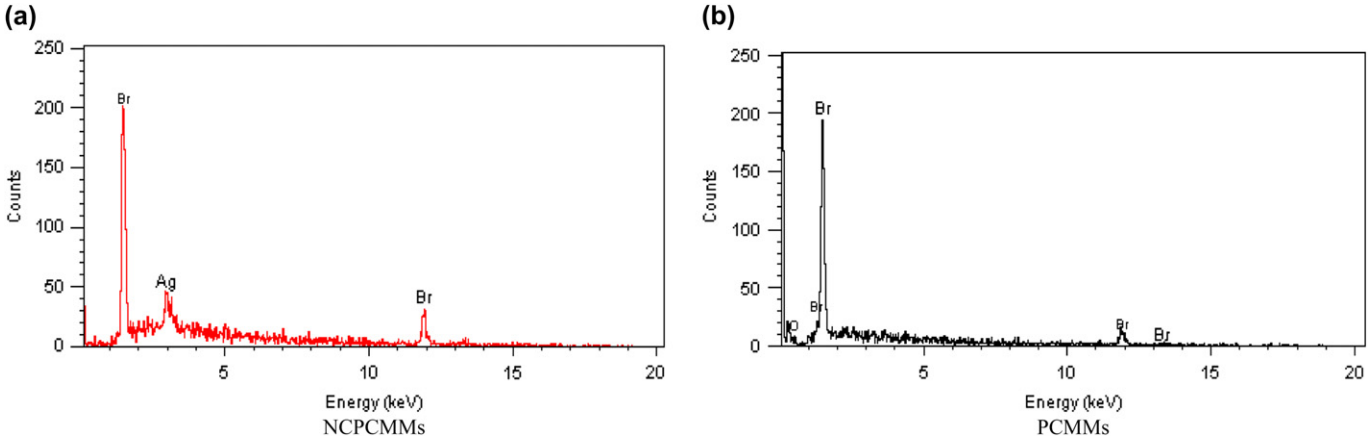

Fig. 4. The surface analysis EDX: (a) NCPCMMs and (b) PCMMs.

that the addition of metal silver nano-particles and the formation of nano-composite structure had no adverse effect on the formation of PCM microcapsules.

3.2. Surface elemental analysis

Comparing the EDX test result shown in Fig. 4, the NCPCMMs have more species of surface elements than the conventional PCMMs. The metal element Ag appears in the spectrum, while conventional PCMMs do not have any metal elements. Meanwhile, some elements appear in both the specimens, such as nonmetal element of nitrogen, bromine, and oxygen, which represent shell composition of aminoplast and core material of bromo-octadecane, as high-energy electron beams can penetrate up to 2 μm of depth on the sample surface. Bromine as one part of composition in the core material was detected. The two peaks for bromine element at different characteristic energy bands represent the K_α and K_β X-rays, the radiations caused by the outer electron filling the inner vacancy of an element shell [27]. Carbon element, which surely existed in the composition of microcapsules in the shell and core, was not detected by EDX spectrum due to the small weight of the carbon atom.

These analysis results show that the two kinds of microcapsule were different in shell composition, as metal Ag elements appeared on the NCPCMM surface. Combining with the observation of SEM, silver nano-particles obviously existed on the surface of NCPCMMs to form composite structures.

3.3. Thermal stability

Fig. 5 shows the results of thermal stability tests from Netzch TGA/DSC, which is expressed as sample mass loss (%) and temperature (150–400 °C). Both NCPCMM and PCMM samples loose weight as temperature increases. PCMM loss continuously and significantly from 150 °C and about 80%–90% of their total mass was vaporized when the temperature increased to 300 °C. On the other hand, NCPCMM was able to keep more than 80% of weight when temperature increased to 300 °C. These results indicate that the shell material of NCPCMMs provides a significantly better protection for core PCM in the range between 150 °C and 300 °C.

The corresponding DSC thermalgram curves are shown in Fig. 6. There are two sharp endothermic peaks in the temperature range of 240–300 °C for conventional PCM microcapsules, while there is only one sharp endothermic peak at the temperature of 304 °C for the NCPCMMs. The two peaks indicate that large amount of core PCM vaporized and

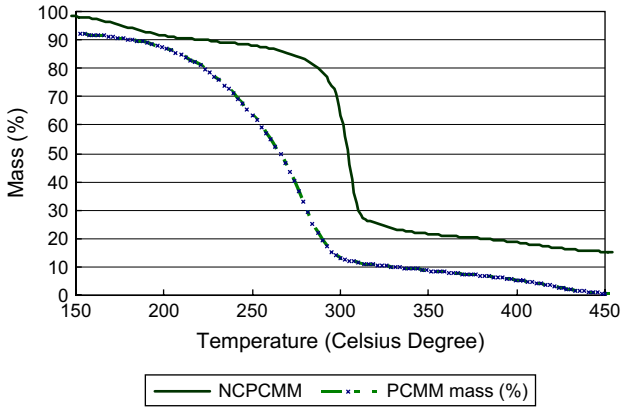

Fig. 5. Thermal gravimetry analysis of NCPCMMs and conventional PCMMs.

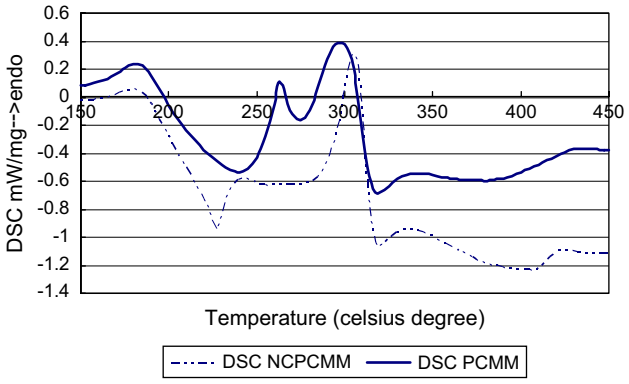

Fig. 6. DSC thermalgram curves of NCPCMMs and conventional PCMMs.

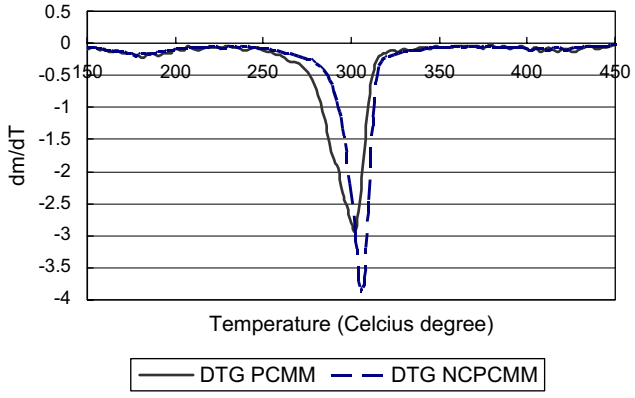

Fig. 7. Differential derivative thermal gravimetry for NCPCMMs and PCMMs.

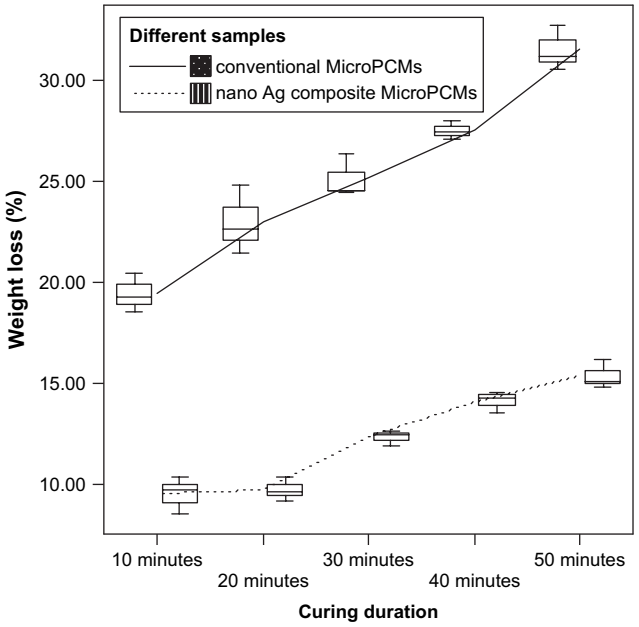

Fig. 8. Comparison of the weight losing percentage under 130 °C at different time interval for NCPCMMs and PCMMs.

absorbed significant amount of heat at 260 °C and 297 °C for conventional PCMMs; while the endothermic peak appears at temperature of 304 °C for NCPCMMs, showing higher thermal stability and better protection of the composite shell structure than that of conventional PCMM. These results confirm the observations in Fig. 5.

To obtain a more precise analysis of thermal stability, differential derivative thermal gravimetry (DTG) was calculated. The weight losing rate (dm/dT) with temperature was compared between the two samples, as shown in Fig. 7. Both curves have a large inflexion at the temperature of 307 °C and 302 °C for NCPCMMs and PCMMs, respectively. The dm/dT curve for NCPCMMs is significantly deeper and sharper than that of PCMMs. The weight remains at each temperature inflexion were about 30% and 20%, as shown in Fig. 5. The weight losing rates for both samples accelerated at 250 °C until they reached their inflexion, accompanied by a dramatically weight drop. The weight losing rate of PCMM's was higher than that of NCPCMM's, indicating that the shell structure of NCPCMMs provided a better protection and prevented core materials licking from the capsules. The weight lose of the samples seems to stop further at the high temperature of 350–450 °C. About only 10–20% of the total mass of microcapsules remained. The remaining masses would probably be some carbonized substances in the capsules, which are not easily decomposed at this temperature range.

Fig. 8 shows the percentages of weight loss of NCPCMM and PCMM samples under the condition of temperature of 130 °C for about 10–50 min. This is a simulation of the curing process in textile manufacturing. The maximal weight loss percentage for 50 min curing was about 15% for NCPCMMs and 32% for PCMMs. Fig. 9 reveals the images of the two kinds of microcapsules which have been cured under the temperature of 130 °C for 50 min. As shown in Fig. 9(a), NCPCMMs still maintained undamaged structure for each microcapsule with a total weight loss of about 10–15%, except a few deformed microcapsules. Meanwhile, most of

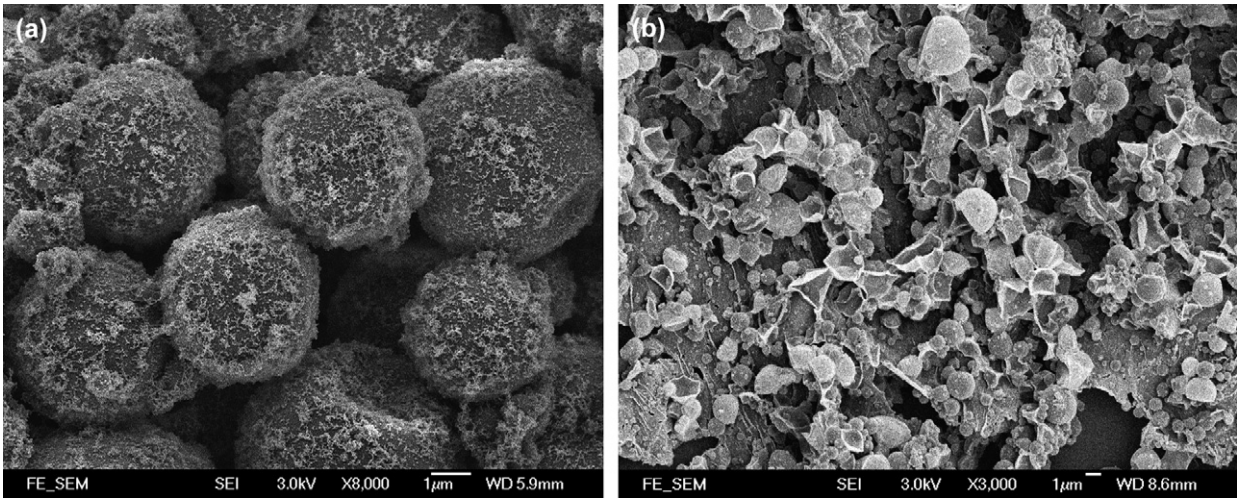

Fig. 9. SEM images of PCM microcapsules after being cured at 130 °C for 50 min: (a) NCPCMMs and (b) PCMMs.

the conventional PCMM microcapsules were destroyed and collapsed at 130 °C as shown in Fig. 9(b).

In summary, all the test results of TG, DSC, DTG and SEM images have shown that NCPCMMs have significantly better thermal stability in the temperature range of 250 °C–300 °C than PCMMs. These results are consistent with the results from previous studies that the mechanical property of high polymer materials can be improved by the addition of nano-particles to increase their toughness [17,28,29]. The potential explanation is that the huge surface areas of nano-silver particles enable them to be closely combined with polymer matrix to create composite structured wall that has higher strength to resist crack and failure of wall polymer in the curing process. This effect can be explained by the energy absorption of the nano-composite mechanism reported by several authors [30–33].

In the composite material, the existence of rigid particles in the nanometer scale gives rise to a stress concentration and can easily stimulate micro-cracks among the surrounding polymer, which can absorb the distortion works. On the other side, crack propagation among base polymers is blocked and passivated due to the nano-particles dispersed in the matrix. Therefore, the cracks cannot be developed into large destroyed cracks. The finer the rigid particles are, the more the contact areas of the particles with polymer matrix. Furthermore, the micro-cracks could be generated due to the difference of the Poisson ratio between rigid nano-particles and base polymer, whenever materials are treated by heat. The more the energy be absorbed, the base material collapse in larger scale can be prevented. Therefore, PCM microcapsules doped with rigid silver nano-particles in the shell have a better thermal stability compared with conventional PCM microcapsules due to the increase of toughness and strength by the addition of silver nano-particles.

4. Conclusion

In this paper, thermal stability of PCM microcapsules incorporated with silver nano-particles (NCPCMMs) are evaluated in comparison with conventional PCM microcapsules (PCMMs). Test results show that in addition to intrinsic temperature regulating functions of PCMMs, NCPCMMs have significantly increased strength due to the formation of a more compact nano-composite core/shell structure.

Comparing with conventional PCMMs, the surface appearance of NCPCMMs is coarser with nano-particles dispersed onto the shell. This nano-composite structure solves the common problem of particle agglomeration, which is difficult to overcome in practical applications of nano-materials. This makes it a great advantage for the silver nano-particles to be utilized fully for their functionalities. The observations of surface SEM and analysis of EDX reveal that nano-silver particles were distributed mainly on the surface of the shell and within shell structure, and formed compact composite structures with capsule shell. Thermal gravimetry analysis (TGA) results prove that the addition of silver nano-particles can significantly reinforce the strength of the high polymer wall material due to the nano-scale particle size, high activity and huge surface areas. The NCPCMMs demonstrated higher thermal stability performance and capable of enduring higher temperature during textile manufacturing processes.

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