



# Innovative method of metal coating of microcapsules containing phase change materials

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## Abstract

Microencapsulation of phase change materials (PCMs) is needed to prevent PCM leaking during melting. However, the low thermal conductivity of the microcapsules shell limits their applications. To enhance thermal conductivity of PCM microcapsules, a new method was developed for coating them with a metal using dopamine surface activation followed by electroless plating. The oxidative self-polymerization of dopamine (PDA) on the shell of the polymeric PCM microcapsules makes the surface active by providing chemisorption sites for metal deposition. Scanning electron microscope (SEM) images of the metal coated microcapsules without PDA pre-treatment did not show evidence of Ag metal on the surface of microcapsules. However, PCM microcapsules were completely covered with Ag metal when they were pre-treated with PDA as indicated by SEM and EDX tests. The enhancement in the thermal conductivity of silver coated PCM microcapsules of different size and for different silver coating coverage was investigated and discussed. This was confirmed by the enhancement in the performance of these silver-coated microcapsules using thermal cycling tests.

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## 1. Introduction

Desired characteristics of the latent heat thermal storage systems and their applications were reviewed in literature (Zalba et al., 2003; Farid et al., 2004). Phase change materials (PCMs) are among the most important heat storage materials, but they cannot be used practically in any application unless they are enclosed or encapsulated to prevent their leakage upon their melting or evaporation (Ma et al.,

2012; Giro-Paloma et al., 2015; Qiu et al., 2013), which leads to its loss and possible health hazards.

Organic or inorganic shells have been used for encapsulating PCMs (Zhao and Zhang, 2011; Tyagi et al., 2011; Jamekhorshid et al., 2014). Polymeric shells (such as poly methyl methacrylate, PMMA) are commonly used due to their good sealing characteristics and chemical and thermal stability (Yang et al., 2015; Sar± et al., 2009), while inorganic shells (such as silica) also have some desirable properties such as good thermal and chemical stability, compatibility with the building materials, and fire resistance (Cao et al., 2015b). Microencapsulation of PCMs has the advantages of providing a large heat transfer surface area; high thermal cycling stability; relatively constant

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bulk volume, and the ability to be dispersed and integrated into fluids or building materials (Salunkhe and Shembekar, 2012; Mehling and Cabeza, 2008).

PCM microcapsules are usually evaluated by their energy storage capacity, melting temperature, chemical stability, thermal stability, thermal conductivity, mechanical strength and their fire resistance (Su et al., 2015; Sittisart and Farid, 2011; Oró et al., 2012). Influence of shell materials and core-to-shell mass ratio on the characteristics of the PCM microcapsules were reviewed (Salunkhe and Shembekar, 2012). Overall, the applicability of PCM microcapsules is limited by their low density, high flammability and poor thermal conductivity (Su et al., 2015; Salunkhe and Shembekar, 2012; Jegadheeswaran and Pohekar, 2009). Therefore, enhancing the desired characteristics of PCM microcapsules is required to increase their performance and widen their applications as outlined in literature (Jegadheeswaran and Pohekar, 2009).

Organic PCMs have poor thermal conductivity ranging between 0.1 and 0.4 W/m K. For example, n-octadecane has a thermal conductivity of 0.35 W/m K in solid state and 0.149 W/m K in liquid state (Jegadheeswaran and Pohekar, 2009). Increasing the thermal conductivity can be achieved by (1) impregnating PCM into porous materials having a high thermal conductivity such as metal foam and porous graphite (Oró et al., 2012; Mills et al., 2006), (2) adding high thermal conductivity metal structure or particles of silver, aluminum or copper to the PCM (Song et al., 2007), or (3) encapsulating the PCM within high thermal conductivity shell materials such as silicon carbide and calcium carbonate (Zhang et al., 2010; Yu et al., 2014).

Although the low thermal conductivity of PCM microcapsules is not a limiting factor in large-scale applications (such as buildings), but it becomes a critical factor when used in dynamic applications (such as slurries for cooling electronics devices). To enhance their thermal conductivity, PCM microcapsules were embedded into epoxy matrix as reported elsewhere (Thiele et al., 2014; Su et al., 2011). The results show that the apparent thermal conductivity was between 0.409 and 0.565 W/m K, depending on the microcapsule size and PCM content. Coating PCM microcapsules with high thermal conductivity shell materials was also reported in literature. For example, the microencapsulation of organic PCM within a calcium carbonate shell led to enhancing the thermal conductivity (Yu et al., 2014). For a PCM/shell mass ratio of 50/50 and 30/70 the thermal conductivity was 1.246 W/m K ( $\Delta H_m = 84.37$  J/g) and 1.674 W/m K ( $\Delta H_m = 46.93$  J/g), respectively. Microencapsulating organic PCMs within a silica shell led to microcapsules having a thermal conductivity of up to 0.981 W/m K ( $\Delta H_m = 55.12$  J/g), compared to only of 0.2 W/m K using polymeric melamine resin (He et al., 2014). Increasing the ratio of silica to n-octadecane (as a PCM) led to increasing its thermal conductivity, but on the expense of reducing the thermal storage density (Zhang et al., 2010, 2011a; He et al., 2014). Further, grafting the silica microcapsules with graphene oxide led to

increase the thermal conductivity to 1.162 W/m K ( $\Delta H_m = 87.1$  J/g) (Yuan et al., 2015).

Recently, melamine–formaldehyde PCM microcapsules were coated with a silver layer and dispersed into Polyalphaolefins (PAOs) to produce a high thermal conductivity fluid (Cao et al., 2015a). Silver coating on PCM microcapsules was performed in an ammonia aqueous solution based on so-called silver mirror reaction (Xu et al., 2014). A rough silver layer was obtained when the surface of the PCM microcapsules was activated with a tin chloride solution before the electroless plating with silver. Moreover, this rough coating did not form a continuous silver layer but rather separate clusters of silver particles on the surfaces of PCM microcapsules. Surprisingly, smooth and very thin silver coating layer was obtained on PCM microcapsules without any surface activation of the PCM microcapsules. This is probably limited to the melamine–formaldehyde shell, since it has an amino functional group that can absorb the metal ions onto the surface. The thermal conductivity of PCM microcapsules was increased from 0.152 to only 0.251 W/m K. Moreover, the latent heat decreased from 42.6 to 32 J/g, respectively. It is clear that there is a need to enhance the thermal conductivity of PCM microcapsules further without sacrificing its latent heat. Also, it has been reported that silver coating cannot be achieved successfully without activation and sensitization (Gao and Zhan, 2009).

Fluid heating and cooling play important roles in many industries including power stations, production processes, transportation and electronics. A wide variety of nanofluids have been evaluated over the last decade, and their thermo-physical properties (such as thermal conductivity) were assessed (Chandrasekar and Suresh, 2009; Daungthongsuk and Wongwises, 2007; Yu et al., 2008). Chein and Chuang (2007) showed that copper oxide/water mixtures in a micro-channel heat sink have cooling capacities higher than pure water at low flow rates. Furthermore, several researchers showed experimentally a significant enhancement in convective heat transfer when metal nanoparticles were used with the working fluid (Chen et al., 2008; Heris et al., 2006, 2007). The use of PCM microcapsules in slurries enhances the fluid heat transfer through two mechanisms. The first is micro mixing caused by the particles agitation of the fluid. The second is caused by the improved temperature difference between the heating surface and the slurry, caused by the increased fluid thermal capacity by PCM latent heat (Dammel and Stephan, 2011; Rao et al., 2007; Sabbah et al., 2009). As a result, they are expected to have promising potentials in such applications.

Electroless plating of metal onto a wide range of polymer shells can be achieved by using one of two approaches as reported in literature: (a) covering the particles with mercaptosilane-based coating followed by metal electroless coating as was applied on silica and alumina nanoparticles (Mondin et al., 2013a), and (b) formation of thin layer polydopamine (PDA) coating before metal electroless

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