Solar-absorbing metamaterial microencapsulation of phase change materials for thermo-regulating textiles

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This paper presents a novel concept for designing solar-absorbing metamaterial microcapsules of phase change materials (PCMs) integrated with thermo-regulating smart textiles intended for coats or garments, especially for wear in space or cold weather on earth. The metamaterial is a periodically nanostructured metal-dielectric-metal thin film and can acquire surface plasmons to trap or absorb solar energy at subwavelength scales. This kind of metamaterial microencapsulation is not only able to take advantage of latent heat that can be stored or released from the PCMs over a tunable temperature range, but also has other advantages over conventional polymer microencapsulation of PCMs, such as enhanced thermal conductivity, improved flame-retardant capabilities, and usage as an extra solar power resource. The thermal analysis for this kind of microencapsulation has been done and can be used as a guideline for designing integrated thermo-regulating smart textiles in the future. These metamaterial microcapsules may open up new routes to enhancing thermo-regulating textiles with novel properties and added value.

Keywords: metamaterial; microencapsulation; phase change material; thermo-regulating textile

The incorporation of phase change material (PCM) microcapsules into textile structures to improve their thermal performance has been studied since the early 1980s [1]. The formation of microcapsules is called microencapsulation, which, in this case, is usually carried out by coating individual PCM particles with a continuous film to produce capsules that are a micrometer to a millimeter in size [2]. Microencapsulation of PCMs is an effective technique for enhancing thermal transfer, resisting possible interaction with the surrounding environment, and preventing leakage during the melting process [3]. The thermo-regulated fibers and textiles can then be made through two different processes [1]: (a) PCM microcapsules are integrated inside the fiber itself by adding them to a polymer solution prior to fiber extrusion; (b) PCM microcapsules are attached onto the fiber surface or incorporated into the textile matrix through coating, laminating, finishing, melt spinning, bicomponent synthetic fiber extrusion, injection molding, the foam techniques, and so on. Conventionally, microencapsulated PCMs consist of two main parts [3]: a PCM that acts as a core and a polymer or inorganic shell that forms the PCM container. PCMs such as paraffins have largely been used in textile applications as either a solid or liquid that is then encapsulated into a polymer shell and integrated into a fabric to
improve the fabric’s thermo-regulating properties [4,5]. On the other hand, instead of using a polymer, specially designed nano-scaled thin film metamaterials can be used. These materials have been developed for solar absorption and have demonstrated being able to absorb more than 85% of infrared and visible light [6,7,8]. These kinds of metamaterials may provide novel opportunities for PCM microencapsulation. With potential applications in thermo-regulation that extends to textiles and even buildings, these microcapsules may improve the comfort and value of today’s clothing and buildings.

This paper will demonstrate an innovative concept for using a three-layer nanostructured metal-dielectric-metal metamaterial thin film as the shell of a PCM microcapsule with the metamaterial shell acting as a solar thermal resource for heating up the PCM. Compared to conventional polymer microencapsulation of PCMs, the metamaterial encapsulation can also provide largely enhanced thermal transfer, improved flame-retardant capabilities, and usage as an extra solar power resource for effective thermo-regulating fibers and related smart textiles.

By exciting plasmonic resonances at particular wavelengths inside the material structures [9], solar-absorbing metamaterials used for PCM microencapsulation can selectively absorb solar radiation in three different wavelength regions, including the visual region from 0.4 to 0.7 μm, the solar region from 0.3 to 3.0 μm, and the thermal region with wavelengths larger than 2 μm [10]. One of such metamaterials is shown in Figure 1 [6]. This material is composed of nanostructures with subwavelength tungsten planar stacks on a tungsten film with a silica dielectric spacer in between. Between a tungsten planar stack and the tungsten film, strong electromagnetic coupling may occur at selected wavelengths due to electric and magnetic responses of the metamaterial. The left inset of Figure 1 illustrates a unit cell of the metamaterial with double-sized tungsten patches of different widths \(w_1\) and \(w_2\). The patches with the same width are arranged diagonally such that the structure behaves exactly the same at normal incidence for either transverse electric or transverse magnetic waves. Each patch is centered in its quadrant with the

![Figure 1. Schematic of solar-absorbing metamaterials [6]: double-sized tungsten patches of different widths \(w_1\) and \(w_2\), and period \(\Lambda' = 2\Lambda\). The patches with the same width are arranged diagonally and each patch is centered in its quadrant. Spectral normal absorptance in the spectral region from 0.4 to 4 μm for solar-absorbing metamaterials with tungsten patch widths of \(w_1 = 250\) nm and \(w_2 = 300\) nm, in comparison with patches of single-sized width \(w_1\) or \(w_2\), \(\Lambda = 600\) nm, \(h = 150\) nm, and \(t = 60\) nm.](image-url)
The absorptance of the metamaterials with single-sized and double-sized tungsten patches is measured, using the same geometric parameters of $\Lambda = 600$ nm, $h = 150$ nm, and $t = 60$ nm but with different patch widths $w_1 = 250$ nm and $w_2 = 300$ nm, respectively [6]. Comparably, the double-sized metamaterial is preferable for PCM encapsulation because of its broader absorption band, as compared to the single-sized one with $w_1 = 250$ nm, and its higher absorbance, as compared to the single-sized one with $w_2 = 300$ nm. The calculated solar energy conversion efficiency is over 85% for these metamaterials [6] and will be used for thermal analysis of the PCM encapsulation in this paper.

The tungsten-silica-tungsten metamaterial can be coated on PCM using closed field magnetron sputtering, which can be carried out at room temperature, allowing different layered materials, like the tungsten and silica metamaterial, to be coated in the same batch [12]. Figure 2 illustrates the tungsten-silica-tungsten metamaterial microencapsulation of PCM (Figure 2a), and its potential applications [11]: coated on the surface of fibers or textiles (Figure 2b) and embedded in fibers or textiles (Figure 2c). Neglecting the temperature variation in the coated metamaterial shell and assuming that the temperature distribution in the base tungsten film around the PCM sphere surface is relatively uniform, since the thermal conductivity of tungsten is much higher than that of the PCM, a thermal equilibrium between the metamaterial solar thermal absorption, $Q_M$, and the latent heat storage capacity of the PCM, $Q_P$, can be expressed as (the heat loss from the metamaterial sphere is neglected as the microcapsule is assumed to be embedded in a thermally insulated medium)

$$Q_M = Q_P$$

$$Q_M = 4\pi r_p^2 J_\lambda t_s \eta \alpha$$

Figure 2. Illustration of metamaterial microencapsulation of PCM (a) and its potential applications [11]: coated on the surface of fibers or textiles (b) and embedded in fibers or textiles (c).
\[ Q_p = m[C_{sp}(T_m - T_i) + \alpha_m \Delta h_m + C_{lp}(T_f - T_m)] = \frac{4}{3} \pi r_p^3 [d_{sp}C_{sp}(T_m - T_i) + d_{lp}\alpha_m \Delta h_m + d_{lp}C_{lp}(T_f - T_m)] \quad (3) \]

When \( T_f \geq T_m \), the PCM final temperature \( (T_f) \) can be induced from Equations (1) to (3):

\[ T_f = T_m + \frac{3r_w^2 J_s t d \eta}{2r_p^2 d_{lp}C_{lp}} - \frac{d_{sp}C_{sp}(T_m - T_i)}{d_{lp}C_{lp}} - \frac{\alpha_m \Delta h_m}{C_{lp}} \quad (4) \]

where \( r_w \) is the radius of the outside surface of the base tungsten film in the metamaterial shell; \( r_p \) is the radius of the PCM particle; \( J_s \) is the standard solar radiation at the earth’s surface, 1000 W/m\(^2\) \([13]\); \( t_i \) is the working hours per day of the solar-absorbing metamaterial shell; \( \eta \) is the thermal efficiency of the solar-absorbing metamaterial shell, 85%; \( \alpha \) is the sunlight acceptance coefficient of the metamaterial shell, which is mainly influenced by the light acceptance angle and the light transparency of the medium around the metamaterial PCM microcapsules (here, it is taken as 0.5, assuming half of the metamaterial shell surface can accept sunlight and the medium around it is completely light-transparent); \( \alpha_m \) is the fraction of PCM that is melted, taken as 1; \( \Delta h_m \) is heat of fusion per unit mass PCM (J/kg); \( m \) is the mass of PCM (kg); \( d_{lp} \) is the density of liquid PCM; \( d_{sp} \) is the density of solid PCM; \( C_{sp} \) is the average specific heat of PCM between \( T_i \) and \( T_m \) (kJ/kg K); \( C_{lp} \) is the average specific heat of PCM between \( T_m \) and \( T_f \) (kJ/kg K); \( T_i \) is the initial temperature of PCM (°C); \( T_m \) is the melting temperature of PCM; \( T_f \) is the final temperature of the liquid PCM (°C). Table 1 shows physical properties of selected PCMs \([14,15]\). Paraffin C\(_{13–C_{24}}\) can typically be used as PCM encapsulation for thermo-regulating textiles; paraffin wax has over high melting point to use for textiles, here mainly for thermal modeling verification, and may be used for thermal-conforming buildings.

The calculated results according to Equation (4) are shown in Figures 3 and 4 for metamaterial microcapsules of Paraffin C\(_{13–C_{24}}\) and paraffin wax (Figures 3c and 4c). The PCM final temperature varies with solar absorbing time for different PCM particle sizes under different initial temperatures: (a) −10°C, (b) 0°C, and (c) 10°C. For example, for a typical PCM particle radius range of 15–45 µm, the metamaterial microcapsules need to be exposed under the sunlight for 2–9 hours to bring the PCM final temperature above the PCM melting point of 23°C (Figure 3). As shown in Figure 4, however, if the capsule radius can be shrunk from 5 µm down to 0.5 µm, the sunlight exposure time can be reduced to less than 0.7 hours or even under 0.05 hours to raise the PCM final temperature over its melting point, although such a small size may create fabrication challenges with present technology. These calculated results are in accordance with the

| PCM type       | Melting point (°C) | Density (kg/m\(^3\)) | Specific heat (J/kg K) | Latent heat (kJ/kg) |
|----------------|-------------------|-----------------------|------------------------|--------------------|
| Paraffin C\(_{13–C_{24}}\) | 22–24             | Solid 900 Liquid 760  | Solid 2900 Liquid 2100 | 189                |
| Paraffin wax   | 64                | Solid 916 Liquid 790  | Solid 2900 Liquid 2140 | 173.6              |
Figure 3. For metamaterial microcapsules of Paraffin C_{13}–C_{24} and paraffin wax (dashed lines) when the PCM particle radius is 5 µm and over, the PCM final temperature varies with solar absorbing time for different PCM particle sizes under different initial temperatures: (a) −10°C, (b) 0°C, and (c) 10°C.
Figure 4. For metamaterial microcapsules of Paraffin C_{13–C_{24}} and paraffin wax (dashed lines) when the PCM particle radius is less than 5 µm, the PCM final temperature varies with solar absorbing time for different PCM particle sizes under different initial temperatures: (a) \(-10^\circ\text{C}\), (b) \(0^\circ\text{C}\), and (c) \(10^\circ\text{C}\).
historical reported temperature measurements [16,17]. Previous research work also demonstrated the feasibility of integrating microencapsulated paraffin with textiles to obtain unique thermo-regulating properties, and showed that the microencapsulated paraffin still kept its geometrical profile and heat capacity after 1000 cycles [18,19].

As a starting point, this analysis provides a basic guideline for designing thermo-regulating smart textiles incorporated with these novel metamaterial microcapsules for coats or garments intended especially for space and outdoor wear in cold weather.

In addition, PCM metamaterial microencapsulation may have great potential in overcoming the problems or challenges facing conventional PCM smart textiles [1] with exceptional advantages, like:

(1) Significantly enhanced thermal conductivity of PCM because the thermal conductivity of tungsten film (173 W/m K) or silica spacer (1.1 W/m K [20]) is much higher than that of the polymers used in polymer microencapsulation of PCM (about 0.21 W/m K [14]). This may help promote the heat transfer of textiles and allow them to quickly reach a relatively uniform temperature distribution.

(2) Excellent flame-retardant capabilities over conventional polymer microencapsulation of PCM.

(3) Metamaterial microencapsulation can directly provide solar thermal power and can be incorporated with micro- or nano-scale thermoelectric modules to generate electrical power for smart textile structures.

Apart from use in thermo-regulating textiles, metamaterial microencapsulated PCMs such as Paraffin C_{13}–C_{24} and paraffin wax can be coated on the outer surface of buildings or integrated into convectional building materials to provide advantageous properties.

In summary, a novel concept for designing solar-absorbing metamaterial microcapsules of PCMs incorporated with thermo-regulating smart textiles for coats or garments has been presented and demonstrated through thermal analysis. The sunlight exposure time required to raise the PCM temperature is closely dependent on the radius of microencapsulates under certain weather environments. The metamaterial microcapsules can not only take advantage of latent heat that is stored or released from a PCM over a tunable temperature range, but also have the potential to overcome problems of conventional polymer microencapsulation by enhancing thermal conductivity, improving flame-retardant capabilities, and providing a solar power resource. These metamaterial microcapsules may open up a new way for providing thermo-regulating textiles and buildings with advanced properties and higher value. The potential applications of these microcapsules in textiles may include complex life support and health-care systems, specialized military uniforms, and performance sportswear.

Disclosure statement
No potential conflict of interest was reported by the authors.

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