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Phase-Change Materials

Emerging Applications of Phase-Change Materials (PCMs): Teaching an Old Dog New Tricks

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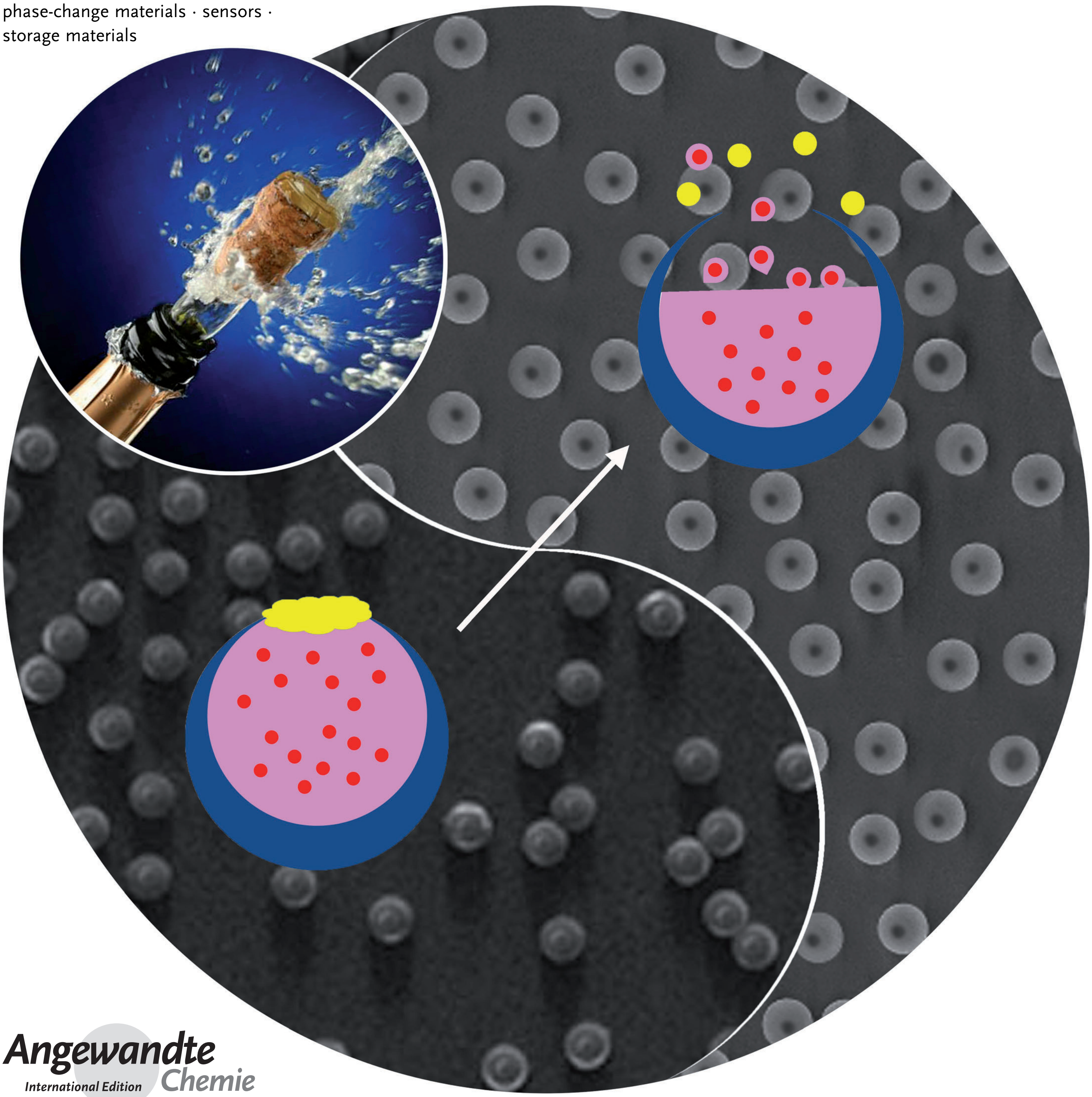

The nebulous term phase-change material (PCM) simply refers to any substance that has a large heat of fusion and a sharp melting point. PCMs have been used for many years in commercial applications, mainly for heat management purposes. However, these fascinating materials have recently been rediscovered and applied to a broad range of technologies, such as smart drug delivery, information storage, barcoding, and detection. With the hope of kindling interest in this incredibly versatile range of materials, this Review presents an array of aspects related to the compositions, preparations, and emerging applications of PCMs.

From the Contents

1. Introduction

The ancient Greeks were the first to identify three classes (what we now call states or phases) of matter on the basis of their observations of water. However, as posited by the philosopher Thales (624–545 BC),[1] it was incorrectly suggested as a single principal element in the universe, from which all other substances were made. Of course, anyone who has taken high-school chemistry knows this is not the case. In matter, atoms and molecules of a substance are attracted to each other as a result of various intermolecular interactions such as electrostatic forces, hydrogen bonding, and van der Waals forces. These interactions determine the states of matter and the amount of energy released/absorbed during the phase transition of matter from one state into another. The released/absorbed energy is known as latent heat.

The term phase-change materials (PCMs) generally refers to materials having large latent heats of fusion with regards to melting and solidifying at a nearly constant temperature. PCMs release or gain isothermal energy during their phase transitions and have a heat storage capacity about 5 to 14 times higher than the conventional thermal storage materials such as masonry and rock.[2] The ability of PCMs to store and release large amounts of heat energy in response to a small temperature change has attracted a great deal of attention in recent years.[3–7] To this end, PCMs have been explored for use in direct thermal energy storage, solar energy applications, and, more recently in response to growing international concern on climate change, regulation of building temperatures. As a consequence of their excellence in direct thermal energy storage, PCMs have been widely used in commercial applications, such as, for example, general containers for temperature sensitive food,[8–11] isothermal water bottles for cycling,[12] catering products,[13,14] and medical devices.[14]

Most recently, PCMs have been recognized as being applicable to the sector of "high technology". This has been achieved by focusing on the change in state as well as the fixed temperature/heat involved in a phase transition, rather than the latent heat associated with the transition. To our knowledge, there has been no literature review on the use of PCMs in such new applications. Most available reviews have focused on PCMs and their applications as thermal storage materials.[2,15–21] This Review presents a much broader coverage of recent developments related to PCMs, detailing some potential materials that can be used in various emerging applications such as drug delivery, information storage, detection, and barcoding, in addition to heat management.

2. Classification of PCMs

PCMs can undergo three types of phase transitions: solid–solid, solid–liquid, and liquid–gas. Solid–solid PCMs generally have high transition temperatures which are beyond the scope of practical use. Liquid–gas PCMs are not considered useful for most applications because of the large volume change associated with their phase transition. Solid–liquid PCMs, however, have seen substantial use in research and applications as they have high latent heat capacities and good thermal conductivity, thus making them viable for a wide range of products.

A large number of solid–liquid PCMs have been reported in the literature. In general, these PCMs can be broadly classified into two types: organic and inorganic. Organic PCMs can be further divided into two categories: paraffins and non-paraffins. Inorganic PCMs can be subdivided into salt hydrates and metals. Table 1 lists a variety of PCMs with melting points in the range of 0 to 100 °C, which are the focus of this Review because of their convenience and utility. The advantage and disadvantages of the four main groups of

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PCMs are presented in Table 2. More comprehensive lists of materials can be found in earlier publications.[2,15,16,19,22–24]

2.1. Organic PCMs

Organic PCMs cover a range of melting points between 0 and 200 °C. Most of them are not stable at high temperatures because of their high levels of carbon and hydrogen. In most cases, the densities of organic PCMs are lower than 1 $g\,cm^{-3}$, which is lower than those of most inorganic PCMs.[25] As a result, organic PCMs usually have smaller heats of fusion per volume than inorganic PCMs.

2.1.1. Paraffins

The term paraffins usually refers to paraffin waxes with the chemical formula C_nH_{2n+2}, where $20 \leq n \leq 40$.[23] Crystallization of the long, straight chain releases a large amount of latent heat, and the melting point increases with the number of carbon atoms in the chain.[26] As a consequence of this, as well as to their availability over a broad temperature range, paraffins make excellent thermal storage materials. However, because pure paraffin waxes are very expensive, technical grade paraffins are generally used.[27] Technical grade paraffins are a mixture of hydrocarbons with different chain lengths, and thus show a broader phase-transition temperature than pure paraffins.

In addition to having large heats of fusion, paraffin waxes are chemically inert and stable, and as such are reliable and predictable.[28–31] Despite these advantages, paraffin waxes display several undesirable properties that offset their utility, including low thermal conductivity, noncompatibility with plastic containers, relatively high cost in the case of pure paraffins, and moderate flammability.[23,29]

2.1.2. Non-Paraffins

Previous publications have extensively surveyed organic non-paraffin PCMs, including a number of esters, fatty acids, fatty alcohols, and glycols.[2,19] Although there is a wide variety of non-paraffin PCMs with diverse characteristics, they share several defining features, both advantageous (such as large heats of fusion, and no or limited supercooling for fatty acids) and disadvantageous (such as inflammability, low thermal conductivity, and instability at high temperatures).[2]

Fat and oil derivatives are a quickly growing area in PCM research. Advances in the processing of these derivatives support them as a biomaterial alternative to paraffins and salt hydrates. Bio-based PCMs can be derived from these fats and oils, in the form of fatty acids or fatty alcohols. Fatty acids, characterized by the chemical formula $CH_3(CH_2)_{2n}COOH$, have useful properties, such as melting congruency and low toxicity. In a liquid phase, they have a surface tension of 2×10^{-4} to $3\times10^{-4}\,N\,cm^{-1}$, which is high enough to allow impregnation in a host material.[32] They have large latent

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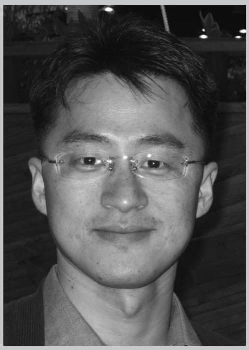

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Table 1: A list of some commonly used PCMs.[2]

		Materials	Melting point [°C]	Heat of fusion [$kJ\,kg^{-1}$]
organic	paraffins	paraffin C15	10	205
		paraffin C17	21.7	213
		paraffin C19	32	222
		paraffin C23	47.5	232
		paraffin C26	56.3	256
		paraffin C30	65.4	251
		paraffin C34	73.9	268
	non-paraffins	oleic acid	13.5–16.3	n.d.[a]
		acetic acid	16.7	184
		1-dodecanol	24	215
		capric acid	36	152
		1-tetradecanol	38	205
		lauric acid	49	178
		9-heptadecanone	51	213
		phenylacetic acid	76.7	102
		acetamide	81	241
inorganic	salt hydrates	$LiNO_3\cdot 3\,H_2O$	30	189
		$Na_2(SO_4)_2\cdot 10\,H_2O$	32	251
		$LiBr_2\cdot 2\,H_2O$	34	124
		$FeCl_3\cdot 6\,H_2O$	37	223
		$CoSO_4\cdot 7\,H_2O$	40.7	170
		$Ca(NO_3)\cdot 4\,H_2O$	47	153
		$NaAl(SO_4)_2\cdot 10\,H_2O$	61	181
		$Mg(NO_3)_2\cdot 6\,H_2O$	89.9	167
	metals	Ga	30	80.3
		Bi-Cd-In alloy	61	25
		Bi-Pb-In alloy	70	29
		Bi-In alloy	72	25

[a] n.d. = not determined.

heats of transition and high specific heats (1.9–2.1 $J\,g^{-1}\,°C^{-1}$), and exhibit only small volume changes during melting or freezing.[33] In addition, little or no supercooling occurs during the phase transition.[2] Fatty alcohols are usually high-molecular-weight, straight-chain primary alcohols, which range in length from as few as 4–6 carbon atoms to as many as 22–26. They usually have an even number of carbon atoms, and fatty alcohols with a chain length of up to C_{18} are known to be biodegradable.[34] In fact, 100% biodegradation was observed within 10 days for chain lengths of up to C_{16}. Chain lengths of C_{16}–C_{18} were found to biodegrade by 62–76% in 10 days, while carbon chain lengths greater than C_{18} only showed a degradation of 37% during the same period.

These bio-based PCMs can be considered "food grade", that is, they have no effect when ingested, unlike paraffins. The low toxicity and biocompatibility led to the successful use of bio-based PCMs in the cosmetic and food industries.[35–37] Recently they have shown potential in building and construction applications as well as in biological applications such as smart drug delivery and formulation of green solvents.[38,39]

2.2. Inorganic PCMs

Inorganic PCMs usually have melting enthalpies per mass similar to those of organic PCMs, but larger enthalpies per volume because of their high densities. They have high thermal conductivity and sharp melting points, and cover a wide temperature range. Inorganic PCMs can be further classified as either salt hydrates or metals.

2.2.1. Salt Hydrates

The term salt hydrates refers to inorganic salts containing n moles of water molecules that form a typical crystalline solid of general formula $AB\cdot n\,H_2O$. The bonds are usually ion–dipole bonds or hydrogen bonds. The water molecules are located and oriented in the structure in a well-defined manner, although in some structures the water is more closely oriented to the anion, and in others to the cation of the salt.[25] The solid–liquid transformation of salt hydrates is actually dehydration/hydration of a salt, a process very similar to melting/freezing in thermodynamics. At the melting point,

Table 2: Advantages and disadvantages of PCMs.[2]

		Advantage	Disadvantage
organic	paraffins	- availability in a broad range of temperatures - chemically stable and inert - high heat of fusion - no or minor supercooling - noncorrosive	- low thermal conductivity - moderately flammable - relatively high costs of pure paraffins - noncompatible with plastic containers
	non-paraffins	- high heat of fusion - no or minor supercooling (depending on form of application)	- low thermal conductivity - flammable - instability at high temperatures
inorganic	salt hydrates	- sharp melting point - high thermal conductivity - high heat of fusion per unit volume - small volume change - low cost	- phase separation - cycling stability - supercooling - corrosive
	metals	- sharp melting points - high thermal conductivity - small volume change	- corrosive - toxicity, environmental concerns

a hydrated crystal breaks up into a lower hydrate with m moles of water [Eq. (1)] or anhydrous salt and water [Eq. (2)].

$$\mathrm{AB}\cdot n\,\mathrm{H_2O} \rightarrow \mathrm{AB}\cdot m\,\mathrm{H_2O} + (n-m)\mathrm{H_2O} \tag{1}$$

$$\mathrm{AB}\cdot n\,\mathrm{H_2O} \rightarrow \mathrm{AB} + n\,\mathrm{H_2O} \tag{2}$$

Salt hydrates are currently the most notable group of PCMs, having been extensively studied, especially for their use in latent-heat thermal-energy storage systems.[40,41] The most attractive properties of salt hydrates include high latent heats of fusion per unit volume, relatively high thermal conductivity (almost double that of a paraffin wax), and small volume changes upon melting. Additionally, they are not very corrosive, are compatible with plastics, and are only slightly toxic. The most readily available salt hydrates are $\mathrm{CaCl_2{\cdot}6\,H_2O}$ and $\mathrm{Na_2SO_4{\cdot}10\,H_2O}$.[19,23]

The major problem with salt hydrates is their incongruent melting. As n or $n-m$ moles of hydration water are not sufficient to dissolve anhydrous or lower hydrate salts, the solution becomes supersaturated at the melting point. As a result of their relatively high densities, the anhydrous or lower hydrate salt settles at the bottom of the container, thereby making it unavailable for recombination with water during the reverse process of freezing. This problem can generally be circumvented by mechanical stirring, encapsulating the PCM, use of excess water to prevent supersaturation, or modification of the compound.[2,42,43]

Another problem is the poor nucleation of salt hydrates, which results in supercooling of the liquid. This leads to freezing at lower temperatures and a loss of energy. One solution to this problem is to use an additive to provide nucleation sites for the salt.[2]

2.2.2. *Metals*

The other broad category of inorganic PCMs is metals. The characteristics of these materials include[2] small heats of fusion per unit weight, large heats of fusion per unit volume, high thermal conductivity, small specific heats, and relatively low vapor pressures. Previously, these materials had not been considered practical as PCMs because of their high densities and relatively high melting points. Recently, however, the advancement of technology for the fabrication of nanomaterials has made metal PCMs substantially more viable.[44,45] Their high thermal conductivity and sharp, well-defined melting behaviors are attractive for a number of applications, especially as absorptive heat sinks in electronic components.[46] In addition, the rich metallurgic knowledge that has been accumulated over the past hundred years enables easy design of metal PCM alloys with controlled melting points and latent heats. Among them, metals with low melting points (Bi, Pb, In, Sn, Cd, and their alloys) are of particular interest.

3. *Preparation of PCMs as Colloidal Particles*

The size of the PCM structure plays an important role in determining its melting behavior. When a PCM experiences a phase transition from solid to liquid and vice versa, the heat transfer flowing to and from the PCM is defined as $Q = hA\Delta T$ (Q in $\mathrm{J\,s^{-1}=W}$),[47] where h is the heat transfer coefficient ($\mathrm{W\,m^{-2}K^{-1}}$), A is the heat transfer surface area ($\mathrm{m^2}$), and ΔT is the difference in temperature between the PCM surface and its surroundings. It can be deduced from this formula that if the size of a PCM structure is reduced by a factor of 10, the time required for complete melting will be reduced by a factor of 100.[48] To fully use the latent heat of fusion, it is best to have the PCM structures as small as possible so that they can completely melt almost instantaneously. Additionally, encapsulating PCMs into separate, small enclosures can solve the problem of incongruent melting.[49]

The easiest way to fabricate small PCM structures is to process them as particles. PCM particles can be conveniently prepared either from preformed PCMs (top-down), or by decomposition of a precursor or crystallization of molecular building blocks (bottom-up). In the following sections, we will discuss several representative techniques for the preparation of PCM particles by these two distinct approaches.

3.1. *Top-Down Approach*

3.1.1. *Fabrication with a Microfluidic Device*

Microfluidic devices consisting of networks of small channels have recently emerged as a powerful route for the synthesis of microparticles.[50–53] The major advantage of a microfluidic synthesis is the ability to independently vary the size, structure, and composition of the particles. Figure 1 a shows a schematic diagram of the fabrication of uniform spherical particles of n-octadecane in a tubular microfluidic device and an image of the produced PCM droplets. As shown in the left panel of Figure 1 a, the inner capillary is positioned in the center of the outer capillary. When the flow rates of both fluids are sufficiently low, individual droplets are periodically formed at the tip of the capillary orifice, in a process called dripping.[54–56] At this point, the droplet at the end of the capillary tube feels two competing forces: viscous drag pulling it downstream and surface tension holding it to the capillary. Initially, surface tension is dominant, but as the droplet grows, the drag force becomes comparable to the surface tension and the droplet eventually breaks off,[56] and is carried along with the flow of the continuous phase, as shown in the right panel of Figure 1 a.[57]

If the flow rate of either fluid is beyond a certain critical limit, the inner fluid becomes a jet with a long stream, which eventually will break up into droplets. This transition is due to a different balance of forces on the jetting fluid, which changes the size of the droplet and the corresponding particle. Figure 1 b,c, shows the variation in particle size as a result of the transition driven by the flow rate of fluid. As the flow rate of the outer liquid increases, the droplets formed at the tip become smaller and thus smaller particles are formed (Figure 1 b). In contrast, the size of the particles increases linearly with the flow rate of the inner liquid, as shown in Figure 1 c.

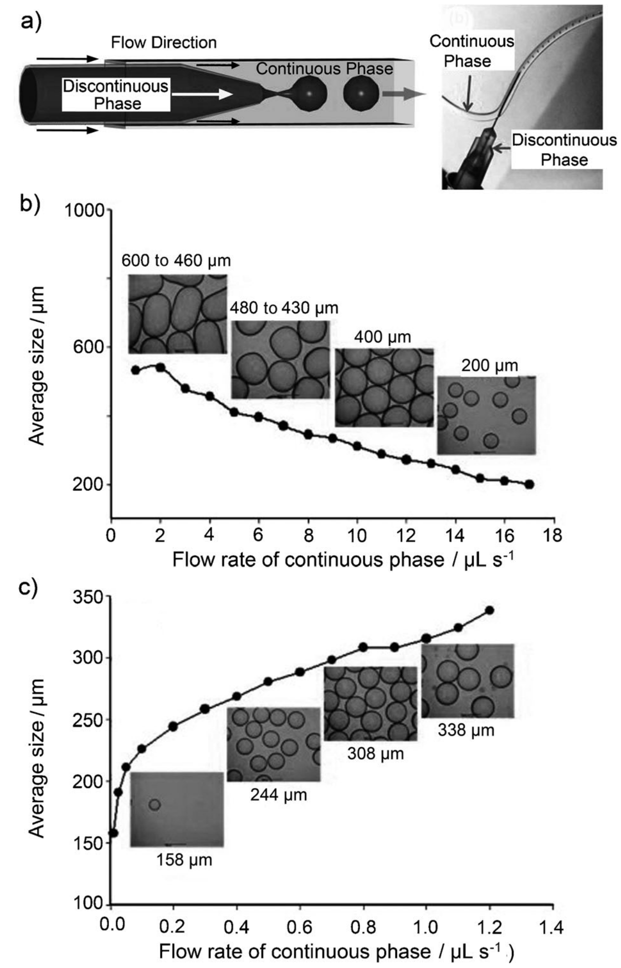

Figure 1. a) Microfluidic device used for the fabrication of uniform *n*-octadecane particles encapsulated by polyurea and a photograph of oil/water (o/w) PCM droplets produced at the tubular junction. Both the shape and size of the particles can be controlled by varying the flow rates of the b) continuous and c) discontinuous phase. The insets are bright-field optical micrographs. Reproduced from Ref. [57] with permission.

*3.1.2. **Fabrication by Replication in Non-Wetting Templates***

Cross-linked poly(ethylene glycol) (PEG) is an interesting organic PCM as its phase transition provides clear advantages: no liquid or gas generation, a small volume change, no seal, and no encapsulation prior to use.[58–60] In addition, the thermal properties of PEG can be easily tuned through control of the degree of cross-linking.[61] These particles can be fabricated using the "particle replication in non-wetting templates" (PRINT) technique.[62–66]

Figure 2a illustrates the major steps involved in the PRINT technique. Patterned molds with size- and shape-specific cavities are replicated from a master. After a PEG liquid precursor is drop-cast onto the mold, a polyethylene terephthalate (PET) sheet is laminated to the top of the mold, thereby leaving the wells of the mold filled while simultaneously removing excess solution. Solidification of the liquid yields particles, which are then transferred from the mold onto an adhesive layer that can be dissolved with a solvent. This results in the production of free-flowing PEG particles. An important requirement of this technique is to produce isolated structures without a residual layer. This can be accomplished using a perfluorinated polyether (PFPE) mold with a low surface energy, which leads to non-wetting of the liquid precursor.[63,67]

Figure 2b,c shows wormlike cross-linked PEG particles on the adhesive layer and free-flowing cross-linked PEG microparticles with a hexagonal shape, respectively. The particle shape was determined by the cavity in the mold. Independent controls over the particle size and composition can be readily achieved with this technique.[62–66]

*3.1.3. **Fabrication Using a Mechanical Shear Force***

A liquid filament dispersed in another liquid may go through Rayleigh instability and undulate with a finite wavelength.[68] As the instability is augmented, the magnitude of the wavelength increases, and the filament finally breaks up into many small droplets of the same size. Big liquid droplets can be stretched and broken by this mechanism into small droplets until the droplets are too small to be elongated by the shear force. This phenomenon can be harnessed to create colloidal PCM's.

For example, organic PCMs have been prepared as colloidal particles by directly emulsifying the materials under a shear force through mechanical agitation, as shown in Figure 3.[69,70] Typically, a PCM melt or solution in an oil solvent is prepared. An emulsion is then formed by dropping the PCM melt or solution into an aqueous solution, followed by shearing by means of high-speed homogenization, sonication, or mechanical stirring. Surfactant molecules are dissolved in the water to form a monolayer at the interface between the PCM phase and water, thereby stabilizing the emulsion. Small particles with narrow size distributions and good stability can be achieved when a high concentration of surfactant is used.[71] Upon solidifying through evaporation of the oil solvent or cooling of the melt, the emulsion is converted into a suspension of PCM particles.[72,73] Conventionally, two main strategies have been used for the formation of emulsions: single emulsion (oil-in-water, o/w) or double emulsion ((water-in-oil)-in-water, (w/o)/w).[74]

The use of shear force is also applicable to the fabrication of metal PCM particles. Figure 4a illustrates the fabrication procedure for uniform colloids of metal PCMs with melting points below 400 °C (e.g., Bi, Pb, In, Sn, Cd, and their alloys).[75] In this case, commercial metal powders were added into a solvent heated to a temperature slightly above the melting point of the metal to obtain large drops of the metal. A mechanical shear was then applied to break the drops into smaller pieces and transform them into uniform droplets. The solvent should have a high melting point and be viscous enough to transfer the shear force and prevent vortex formation in the solution.[44] Figure 4c shows SEM and TEM images of Bi colloids that were prepared using this emulsification process. Large droplets were generated by adding Bi powders directly into boiling di(ethylene glycol) and melted. Uniform colloidal particles were obtained when

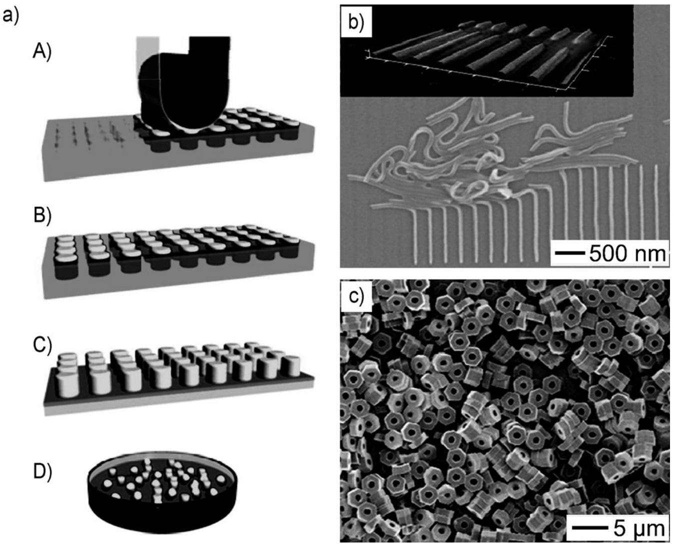

Figure 2. a) The PRINT technique used for the fabrication of poly(ethylene glycol) (PEG) colloidal particles: A) an even distribution of a pre-particle solution on an elastomeric mold by using a roller with a high-surface-energy polymer sheet, B) solidification of the particle solution in the mold, C) release of the particles from the mold with a harvesting film, and D) release of the particles into a solution. b) 80 nm × 2 μm wormlike nanoparticles of cross-linked PEG on a harvesting layer. The inset shows an AFM image of the harvested layer. c) Hexagonal-shaped, cross-linked PEG microparticles. Reproduced from Ref. [67] with permission.

the hot, emulsified mixture was poured into a cold ethanol bath.

Mechanical shearing is an important factor in the preparation of the particles because it can strongly affect the particle size. It has been reported that the sonication intensity had to reach a certain threshold to generate particles with controllable sizes and narrow distributions.[76] Altering the stirring rate can also tune the particle size, as the size is inversely proportional to the shear stress ($\eta_e\gamma$) or the stirring rate (γ), which corresponds well to Taylor's equation ($d \approx \sigma/\eta_e\gamma$), where d is the diameter of the particle, σ is the Laplace pressure, η_e is the effective viscosity, and γ is the stirring rate.[77]

3.2. Bottom-Up Approach

The bottom-up approach is a simple and powerful method for the fabrication of colloidal particles from inorganic PCMs.[78–80] The key component is a precursor that can be converted into the desired material through a specific reaction, such as reduction, decomposition, or hydrolysis.[44] Once supersaturation is reached, nucleation of the building blocks (atoms, ions, or molecules) creates seeds, which grow into colloidal particles.

Figure 4b illustrates the synthesis of metal PCM particles by using the bottom-up approach.[77] In a typical process, a precursor is decomposed in a solvent with a relatively high boiling point to generate metal atoms that coalesce into colloidal particles through nucleation and growth. In this example, poly(vinylpyrrolidone) (PVP) was added to stabilize the colloidal suspension. By maintaining the system at a temperature above the melting point of the metal, the particles stay in a liquid state during the entire growth process. As a result, the growing particles adopt a spherical shape to minimize the surface energy. When the reaction is quenched by pouring the hot mixture into a cold bath of ethanol, the spherical shape is retained. Figure 4d shows the SEM image of Bi colloidal particles prepared by

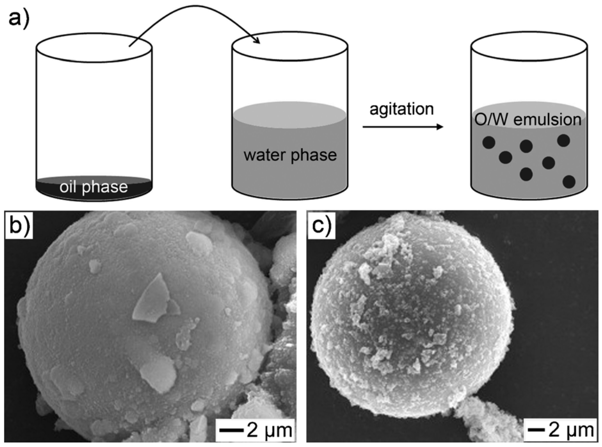

Figure 3. a) Fabrication of PCM particles using an o/w emulsion. A PCM melt or solution (oil phase) is added to an aqueous solution containing a proper surfactant. Mechanical agitation results in phase separation between the two immiscible phases (oil and water). The surfactant molecules may form a monolayer at the interface between the oil and water, thereby producing an emulsion. Upon solidifying through cooling of the melt or evaporation of the oil solvent, the emulsion will be converted into a suspension of PCM particles. b,c) *n*-Octadecane encapsulated in (b) silica and (c) resorcinol-modified melamine-formaldehyde. Reproduced from Refs. [70] and [74] with permission.

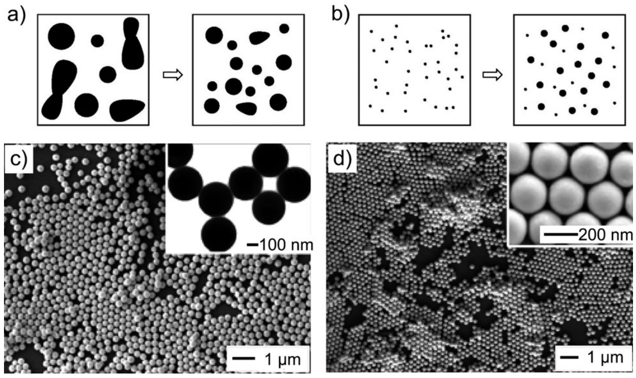

Figure 4. Fabrication of uniform spherical colloids of metals with relatively low melting points (e.g. Bi, Pb, In, Sn, Cd, and their alloys). a,b) Schematic illustrations of two different approaches: a) top-down, where large droplets of a metal are broken into smaller pieces and then transformed into uniform droplets by shear forces and b) bottom-up, where a molecular precursor is decomposed to generate metal atoms that nucleate and grow into uniform spheres. c,d) Electron micrographs of Bi colloidal spheres synthesized by using c) top-down and d) bottom-up methods. Reproduced from Ref. [75] with permission.

using this method, and demonstrates the uniformity in size and shape. The diameter has a relationship of $C \approx d^3$ with respect to the concentration. This result implies that the total number of colloidal particles (or the density of nuclei formed in the nucleation stage) was approximately the same in each round of synthesis, even though the exact amount of bismuth acetate varied. This bottom-up approach has also been extended to other metal PCMs such as Pb, In, and a Cd/Pb alloy with low melting points.[75,81]

4. Microencapsulation

Microencapsulation is the covering of a core material with a coating or shell material. When applied to PCMs, this can take the form of a surfactant, a stabilizing matrix, or some other useful casing. The primary purpose of microencapsulation is to hold the liquid and/or solid phase of the PCMs and keep it isolated from the surrounding, thereby preventing the PCMs from interacting adversely with the surrounding environment. Advantages that stem from this include retardation of the possible reaction of PCMs with the environment, flexibility in frequent phase-change processes, increase in heat transfer rate, and enhancement in the thermal and mechanical stability of the PCM. It can also improve the compatibility of hazardous PCMs that cannot be directly used or immersed in sensitive applications such as blood transport and food storage. Figure 5 shows an example of microencapsulation with switching between the liquid and solid states of *n*-octadecane encapsulated in polyurea microcapsules.[57] It demonstrates that the encapsulated PCM can be reversibly switched between solid and liquid states without a loss of material. There are a multitude of microencapsulation techniques, and the following list is by no means comprehensive.

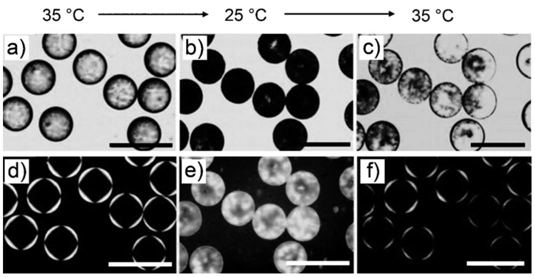

Figure 5. Reversible switching between the crystalline and amorphous states of *n*-octadecane encapsulated in polyurea. a–c) Bright-field optical micrographs of the microcapsules under normal illumination: a) at 35 °C, b) at 25 °C, and c) again at 35 °C. d–f) The corresponding polarized optical micrographs of the encapsulated PCMs shown in (a–c). Scale bars: 310 μm. Reproduced from Ref. [57] with permission.

Air suspension is a technique in which a coating material, usually a polymer solution, is sprayed onto PCM particles. This cyclical process can be repeated until the desired coating thickness is obtained. This technique has the advantage of being applicable to a wide variety of materials; however, it is hampered by a tendency towards particle aggregation, thus limiting the smallest size that can be produced.[81]

Coacervation, a phase-separation technique, relies on the forced precipitation of nanoparticles through some changes in the solution.[82] This process involves three steps that are carried out under continuous agitation: 1) dispersion of core material in a solution of coating polymer, 2) deposition of the coating by controlled, physical mixing of the coating material and the core material in aqueous phase, and 3) solidification of the coating by thermal, cross-linking or desolvation techniques. Coacervation can be either simple (with one colloid) or complex (with more than one colloid), and has the advantage of not necessarily involving any organic solvents.[83] It is especially useful for solid lipid nanoparticles, as alkaline salts of fatty acids are readily available.[84]

Solvent evaporation is a simplistic technique in which an organic solution of a polymer is added as a coating material to an aqueous solution of the core material, followed by vigorous stirring or sonication, until the organic solvent is evaporated.[85] The mixture of core particles and coating material can be used in suspension form, coated onto substrates, or isolated as powders.

Spray drying is a technique in which an emulsion is forcefully expulsed through an atomizer in a hot jet of air, thereby creating microparticles and removing the solvent simultaneously. This process can lead to a powder of microcapsules with encapsulation efficiencies up to 58 %.[86] Spray congealing functions similarly to spray drying in that the particles are formed by atomization and collected as a powder, but unlike spray drying, spray congealing utilizes molten forms of the coating material and the core material, which are sprayed into a cooling chamber.[87] Waxes, fatty acids, fatty alcohols, polymers, and sugars, which are solids at room temperature but melt at elevated temperatures, are applicable to this method.

Interfacial polymerization involves polycondensation at the interface of a two-phase system. This leads to a possibility of two different types of microcapsules, depending on the solubility of the polymer within the droplet. If the polymer is soluble in the droplet, a matrix will be formed in the particle. If the polymer is insoluble in the droplet, a single-core microcapsule will be formed.[88] Interfacial polymerization and microfluidics have been combined to provide a fabrication route to highly uniform microcapsules.[57] The microfluidic technique has also been utilized in conjunction with coaxial electrospinning (Figure 6) to fabricate soy wax core/polyurethane shell PCM microfibers[89] as well as TiO_2 microfibers embedded with hydrocarbon PCM segments.[90]

Dip coating is a technique in which an aqueous solution of shell polymer is formed by directly pipetting onto the core particles.[91]

Each of these techniques has its own advantages and disadvantages in terms of size, size dispersion, usable material, as well as other factors, but given the great number of techniques available, as well as the versatility of each technique, microencapsulated PCMs are virtually unlimited in both composition and application.

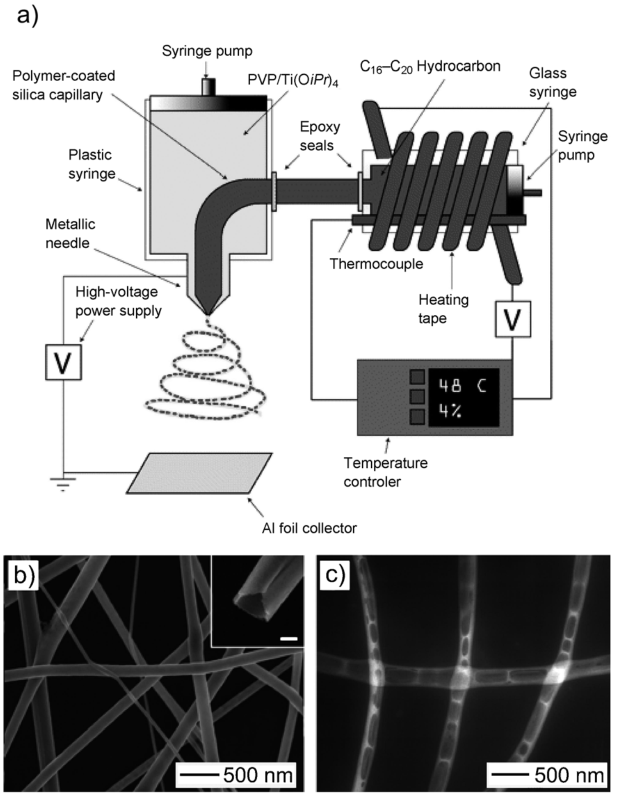

Figure 6. a) The coaxial electrospinning setup used for fabricating nanofibers containing segments of *n*-octadecane. An insulated heating mantle was used to control the temperature of a glass syringe to keep the PCM in a molten state. With this spinneret, a PCM can be injected concentrically into a spinning jet together with a carrier phase. During the spinning process, quick cooling of the jet as a result of solvent evaporation causes the inner liquid to solidify, thereby leading to its encapsulation in the nanofibers. b) SEM image of octadecane@TiO_2-PVP nanofibers with 45% *n*-octadecane. The scale bar in the inset is 100 nm. c) TEM image of the nanofibers after the PCM had been removed by soaking in hexane for 24 h. Reproduced from Ref. [90] with permission.

5. Commercial Successes

The global PCM market is estimated to grow from \$460 million in 2013 to \$1.15 billion by 2018, at a compound annual growth rate (CAGR) of 20.1% for the same period.[92] The highest growth is observed in Europe, where the majority of PCM producers are established, but large markets also exist in North America. Many international companies such as BASF, Climator, Cristopia, EPS Ltd., Mitsubishi Chemical Corporation, Rubitherm GmbH, TEAP, and Witco market PCMs and PCM-based products.[46] Currently, there are more than 50 different PCMs commercially available, most of which are based on modified compositions of salt hydrates, paraffins, or eutectic salt water solutions. Apart from encapsulated PCMs, these companies are also marketing products such as PCM wallboards, PCM-polymer or PCM-silica dry composite powders for use in a wide range of applications including building and construction, HVAC (heating, ventilation, and air conditioning), textiles, fixed refrigeration, and thermal energy storage.

Of these various applications, construction and building applications hold the majority of the market share. The low thermal mass of light-weight building materials causes large fluctuations in temperature, thus demanding high heating and cooling processes. Using the thermal energy storage capability of PCMs with melting points from 15 to 35 °C is one of the most effective ways to mitigate this. PCM-containing wallboards were developed as a creative method to minimize the temperature variation in a building. The large surface area of a wall supports maximal heat transfer between the wall and the surrounding. Wallboards are cheap and widely used in a variety of applications, thus making them very suitable for incorporation with PCMs. Recently, Dupont Energain began distributing wall panels containing a copolymer and paraffin compound, and similar panels have already been utilized in numerous buildings, including the Badenova building in Offenburg and the Haus der Gegenwart (Contemporary House) in Munich.[46]

In addition to large-scale building applications, PCMs are also being incorporated into personalized items. Garmisch Partenkirchen, in Germany, has introduced pocket heaters for mountain-rescue teams. M/S Climator AB is marketing the “cool” vest to provide a stable temperature of 28 °C to the wearer for up to 3 h. An American company, Outlast Thermocules, is marketing fibers and fabrics containing microencapsulated PCMs. PCMs have been incorporated in gloves, shoes, jackets, kidney belts, sleeping bags, and even underwear. In a twist on this fashionable use of PCMs, Outlast has also produced ballistic vests containing PCMs. Lavatherm GmbH are marketing PCM products for heat therapy, and a PCM jacket to protect batteries from extreme climatic conditions is being marketed by TEAP together with Power Conversion Products and MJM Engineering.

Various types of transportation containers for carrying medicines and food items to field conditions are also being marketed by various companies. These containers must be kept in a refrigerator or freezer before use to solidify the embedded PCM. An example of such a device is the container commercialized by SOFRIGAM with PCMs that melt at 0 °C, −15 °C, and −20 °C. PCM pads which can be used in any container have been commercialized by companies such as TCP Reliable, Inc., PCM Thermal Solutions, and PCM Products, Inc.

6. Emerging Applications

As previously mentioned, PCMs have two unique characteristics: a phase transition at a specific temperature and the involvement of thermal energy transfer in the phase transition. These two characteristics make PCMs useful in a variety of applications, which can be divided into three major categories: a) use of the latent heat associated with phase transition, b) use of the state change involved in phase transition, and c) use of the fixed temperature/heat intrinsic to a phase-transition process.

6.1. *Use of the Latent Heat Associated with Phase Transition*

6.1.1. *Latent Heat Storage*

The intermittent and dynamic nature of solar irradiance contrasts with the necessity to use solar energy in a continuous and static way, which makes the use of energy storage systems essential for solar energy applications. The most common method of thermal energy storage is the sensible heat method, which utilizes the heat capacity and the change in temperature of a given material during the process of charging and discharging. In contrast, solid–liquid PCMs absorb a lot of heat energy during phase changes without any change in temperature. This latent heat of fusion, which is large compared to the heat capacity, is promising for thermal energy storage and heat transfer[58,65,67] because, unlike the sensible heat storage method, the PCM storage method provides much higher storage density, with a smaller temperature difference when storing and releasing heat.[59,60] Many different PCMs have been studied in this application, including paraffin waxes, salt hydrates, fatty acids, and eutectic compounds.[61,68] Depending on the applications, PCMs are selected on the basis of their melting points. For example, PCMs below 15 °C have been used for air conditioning applications, while PCMs that melt above 90 °C are available for absorption refrigeration. All other materials that melt between these two temperatures can be applied in solar energy storage applications.[93–95]

Extensive efforts have been made to apply the latent heat storage method to solar energy systems. For example, a new method for satellite power testing using PCMs has been put forward by Revankar,[96] in which a series of metal PCM cells that are liquid under high temperatures are utilized. The heat released during the relatively cold dark periods can be used to generate electricity through a thermoelectric device. This system can generate at least three times more power than batteries of comparable size, and can therefore be seen as a possible alternative to the conventional satellite solar power system that relies on batteries.

Similar to addressing the solar cycle issues, several projects have been devoted to the development of PCM systems to utilize off-peak electricity,[97–100] as PCMs can melt or freeze to store electrical energy in the form of latent heat, and the energy is then available when needed. These systems, coupled with conventional active systems, can reduce the peak load. The shift of the peak load to the off-peak load will provide economic benefits, because the electricity tariff is much cheaper at night than during the day in many countries.[2] An active floor system is effective for the off-peak storage of thermal energy. For example, a layer of paraffin wax (m.p. 40 °C) placed between the heating surface and the floor tiles significantly increased the heat output of the floor from 30 $\mathrm{W\,m^{-2}}$ to 75 $\mathrm{W\,m^{-2}}$.[101]

6.1.2. *Heat Sink*

A high flux of heat is generated in high-power lasers, electronic devices, and engines, as well as in industrial chemical reactors. The ability to remove heat efficiently from these devices determines their performance, lifetime, and safety. A heat-transfer fluid (HTF) is generally used as a coolant to transfer thermal energy from a hot source to a cold source.[102,103] Although many coolants have been designed for different operating ranges, the heat transfer of liquid coolants is too low to remove the large amount of thermal energy, because most liquids cannot support phonons or do not have free electrons to remove thermal energy.[104] Nanoparticles with high thermal conductivity, such as those made of copper and alumina, have been added to fluid coolants to enhance their heat-transfer properties,[105,106] but the results did not meet expectations.

The heat-transfer efficiency of a liquid depends on its heat capacity, thus providing an alternative for enhancing its heat-transfer ability.[107] Unfortunately, the heat capacity of a pure liquid is very small, because the specific heat of a liquid is not a sensitive function of temperature, and the temperature difference between the hot and cold sources is small.

To address these issues, nanoparticles made of PCMs have been added to liquids to enhance their heat capacity.[108–111] When a suspension of the particles is pumped continuously between a hot source and a cold source, the latent heat of fusion in the PCM greatly enhances the heat-transfer capability of the fluid, thereby leading to a better performance in the mixture than that of a pure liquid. A theoretical calculation demonstrated that the phase-change characteristics of the PCMs would have a great impact on the effective specific heat, as outlined in the equation $C_{\mathrm{eff}} = C_0 + \Phi H_{\mathrm{particle}}/\Delta T$, where H_{particle} is the latent heat of the nanoparticles per unit volume, and ΔT is the temperature difference between the melting and freezing points of the nanoparticles.[108] To illustrate this, if the volume fraction of a suspension of In particles is 8 %, the enhancement of the specific heat in the working temperature will be 20 %. In practice, though, the use of PCMs in heat transfer is still limited by several barriers, such as a) supercooling caused by many factors, such as size factors and nucleation, b) high viscosity because of added particles that will increase the power needed for rotation, and c) aggregation of PCMs out of the fluid during multiple melting/crystallizing cycles.

Encapsulation of PCM particles in structurally robust and chemically inert shells seems to have overcome these hurdles; for example, the supercooling of bare In nanoparticles was dramatically reduced when the particles were encapsulated in silica shells formed from tetraethylorthosilicate (TEOS).[112] This is because both the surface roughness and the semicrystalline structure of silica lowered the threshold of nucleation, thereby inducing heterogeneous nucleation. The reduced supercooling was found to enhance the effective heat-transfer coefficient of the fluid by 5–6 times. The higher viscosities arising from the clustering of nanoparticles and poor dispersions in the fluids could also be lowered by surface modification of the silica shells to increase the repulsive force between the particles.

6.2. Use of the State Change Involved in a Phase Transition

6.2.1. Control of Diffusivity and Drug Release

Stimuli-sensitive drug delivery is a promising strategy for on-demand release of medicine in a target area. Temperature has commonly been used as a stimulus to trigger drug release, since local body temperature can vary in response to ambient conditions and even to diseases in some cases. PCMs present a new class of thermosensitive material that can be utilized as a temperature-regulated drug-delivery system, because the solid–liquid transition of a PCM in response to temperature variation can control the diffusivity of a drug or its carrier.[113–115] Below their melting points, solid PCMs block the passing of drug molecules or their carriers and the drug will be released when the temperature rises above the melting point. Fatty alcohols and fatty acids are good PCM candidates for such an application because of their biocompatibility/degradability.

Figure 7 shows uniform PCM (1-tetradecanol, m.p. 38–39 °C) beads containing gelatin particles loaded with an organic dye, and their temperature-regulated release.[113] Above the melting point of the PCMs (ca. 60 °C), the particles containing the drugs leached out from the melted PCM matrix and the drugs could be subsequently released from the colloidal particles, as shown in Figure 7c. This temperature regulation was even also possible at 40 °C, which is close to the temperature of the human body. The use of a binary mixture of PCMs (1-tetradecanol and lauric acid) with different melting points to tailor the melting behaviors of the PCMs even made it possible to release the organic dye in a controlled manner from hollow polymer particles at 39 °C (Figure 8).[114] The PCMs used, 1-tetradecanol and lauric acid, are generally known to have very low toxicity in small doses. The administration of doses up to 10.0 g kg^{-1} of lauric acid by gavage to rats resulted in no deaths and no significant gross lesions at necropsy. Although the minimal lethal or toxic dose of 1-tertadecanol has not been established, the estimated acute fatal dose based on rat data is 80–200 g in an adult human case.[114] These results suggest that PCMs have great potential in a thermally regulated drug-delivery system.

The integration of inorganic components, such as gold nanocages (AuNCs), may offer multifunctionality, a feature required for theranostic applications.[115–117] Figure 9a shows AuNCs encapsulated with a dye and a PCM mixture.[115] The dye can be released in a controlled manner from the AuNCs by direct heating to 40 °C (Figure 9b–d).[115] Irradiation with near-infrared (NIR) laser or high-intensity focused ultrasound (HIFU) can cause a rapid increase in the temperature for the AuNCs, thereby leading to a fast switching of phases and consequently instantaneous release of the dye. The release behavior displayed a strong dependence on the power of the HIFU, thus making it possible to control the release dosage (Figure 9e). This new hybrid system shows the feasibility of drug delivery by using PCMs, and can be further developed into a theranostic system with an array of functions, including the capability for in vivo molecular imaging, as well as combined chemo- and photothermal therapy.

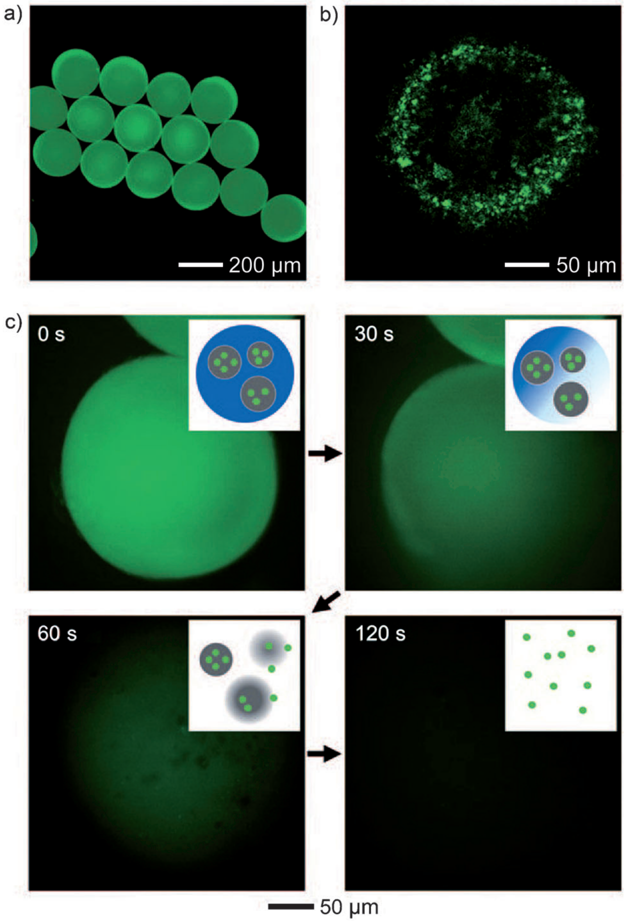

Figure 7. a) Fluorescence and b) confocal micrographs of uniform PCM spheres containing gelatin particles loaded with a dye. c) Time-lapse fluorescence micrographs showing the melting of the PCM sphere and release of the dye from the gelatin particles as the temperature was increased beyond the melting point of the PCM. The insets show the three major steps for dye release: melting of a PCM sphere, leaching out of gelatin particles, and release of dye as gelatin is dissolved. Reproduced from Ref. [113] with permission.

6.2.2. Optical Information Storage and Readout

A swiftly developing application for PCMs is in information storage and memory devices. Research in this area is aimed at overcoming the limitations of the current Flash-based technology, such as writing speed, endurance, and scaling.[118] The use of PCMs is being explored, as the differentials between the amorphous and crystalline states (differences in electrical conductance and reflectivity, among other properties) lend themselves to solid-state memory and optical-storage applications. These materials function as memory by switching between amorphous and crystalline states either through laser switching in optical memory or through electrical current in solid-state memory (SSM). Figure 10 shows the working mechanism of a PCM-based optical memory storage system. The difference in reflectivity (for optical storage) or resistance (in SSM) between the crystalline and amorphous states corresponds to 0 and 1, "on" and "off". Additionally, the entire PCM layer may be

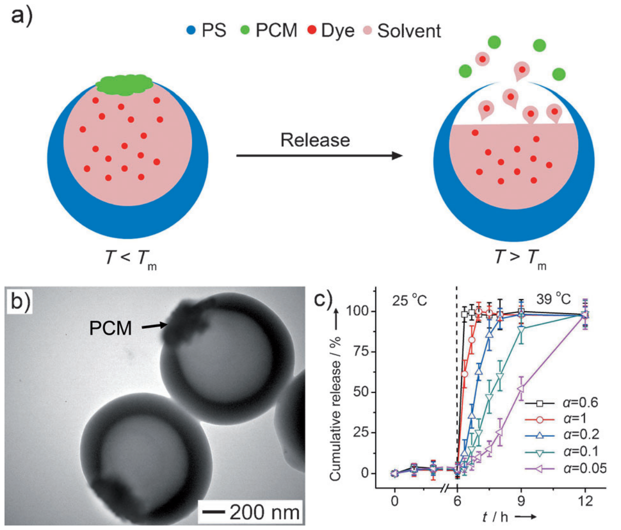

Figure 8. a) Release of dye from a polymeric hollow particle whose surface opening was corked by a PCM. PS = polystyrene, T_m = melting temperature. b) TEM images showing the particles corked with 1-tetradecanol. c) Release profiles of rhodamine B from the particles capped by a binary mixture of PCMs consisting of 1-tetradecanol and lauric acid in a buffer solution at pH 7.4. The volumetric ratio (α) of 1-tetradecanol to lauric acid was varied from 0.05:1 to 1:1 to adjust the melting point of the PCM. Reproduced from Ref. [114] with permission.

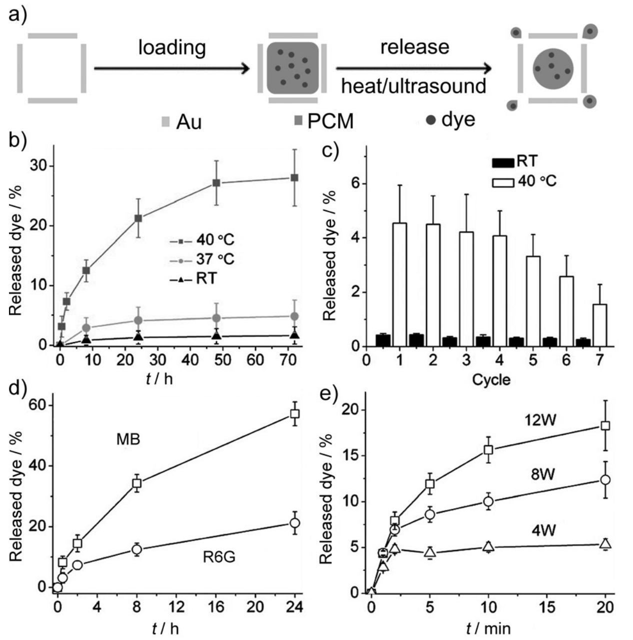

Figure 9. a) Loading the hollow interior of an Au nanocage with a dye-doped PCM and then releasing the dye from the nanocage by direct or ultrasonic heating. Release profiles of b) R6G under direct heating to various temperatures for different periods of time, c) R6G through different cycles of heating (40 °C, for 2 h) and cooling (to room temperature), d) R6G and MB by direct heating to 40 °C for different periods of time, and e) R6G by high-intensity focused ultrasound (HIFU) at different applied powers. R6G = rhodamine 6G, MB = methyl blue. Reproduced from Ref. [115] with permission.

recrystallized at a certain temperature, thus functioning as a memory wipe and allowing the storage to be rewritable.[119] In particular, chalcogenide materials, specifically Ge, Sb, and Te alloys, are currently being utilized because of their rapid recrystallization and high optical contrast, as well as the stability of their amorphous phases, which makes them ideal for optical-storage applications such as DVD and Blu-Ray.[120–124] $Ge_2Sb_2Te_5$ (GST) is the hallmark of these materials, and "still considered as a reference for phase-change electronic storage".[125] It was recently shown by Takata and co-workers to derive its rapid crystallization from a unique ring structure.[126] Although these materials present a promising new avenue of data storage, they bring new challenges along with novel properties. A key challenge lies in the reliability and endurance of the materials, as a criterion for reliable data storage is retention after 10 years, with longer retention times clearly being desirable.[118] This can potentially be alleviated through

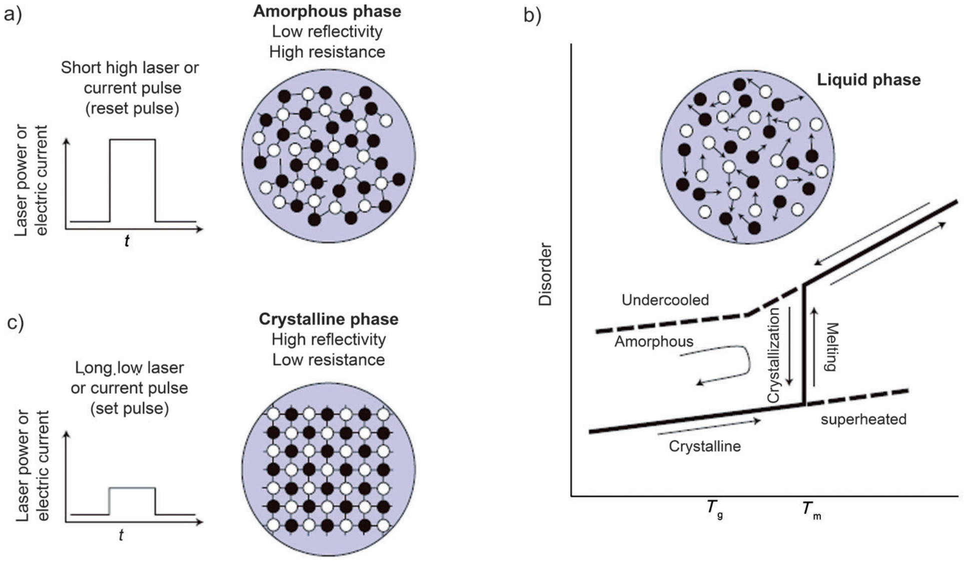

Figure 10. Optical data storage using PCMs. a) A short pulse of a focused, high-intensity laser beam locally heats the PCM to a temperature above its melting point. b) Rapidly cooling the alloy quenches the liquid-like state into a disordered, amorphous phase. This amorphous state has different optical properties from the surrounding crystalline state. c) To erase the stored information, a laser pulse with an intermediate power has to be used. Above the glass transition temperature (T_g), the atoms become mobile, reverting to the energetically favorable crystalline state and thereby erasing the recorded information. Reproduced from Ref. [119] with permission.

doping, as demonstrated by Ielmini and Lacaita.[125] Another issue is the energy consumption, as chalcogenides require fairly large amounts of energy to induce a phase change. This is being addressed through various engineering solutions, such as decreasing the electrode area and reducing the dimensionality of chalcogenide-PCMs.[125,127] As the physical ramifications of chalcogenide-PCM properties are being discovered, better predictions into alloy construction can be made, and this field promises to remain important in the evolution of data storage.

6.3. Use of the Fixed Temperature/Heat Involved in Phase Transition

6.3.1. Sensing or Detection

The use of biomarkers in cancer detection is plagued by a number of problems, including the range of biomarker concentrations, the fact that single biomarkers cannot be reliably used to differentiate lethal and indolent cancers, and the lack of multiplicity (i.e. simultaneous detection of different types of signals) in the currently used techniques.[128] Su and co-workers have utilized the sharp melting peaks afforded by PCMs on differential scanning calorimetry (DSC) as thermal signatures to fabricate a PCM-based system for the simultaneous detection of multiple biomarkers.[129] PCMs of different compositions have different melting points, but are all responsive to a very small change in temperature.[45] Standard equipment for thermal analysis has a range of 100–700 °C, and many PCM particles can be tuned to a peak width of 0.6 °C for a particular ramp rate, which means that there could be 1000 potential particle melting peaks.[45] By modifying particles with ligands particular to a certain biomarker, multiple biomarkers can be detected simultaneously by using a cocktail of particles with different DSC peaks and biomarker specificity (Figure 11). This technique has the advantage of relying only on the melting point, and therefore is not affected by solution turbidity or by the presence of colored molecules, salts, or conductive materials.[45] This technique has shown multiplicity over a concentration range of 11 orders of magnitude, and has been used by Su and co-workers to accurately detect two different DNA biomarkers with a concentration difference of three orders of magnitude (100 nM and 100 pM).[128] This method of thermally sensing multiple biomarkers could become a crucial tool in cancer detection in the future.

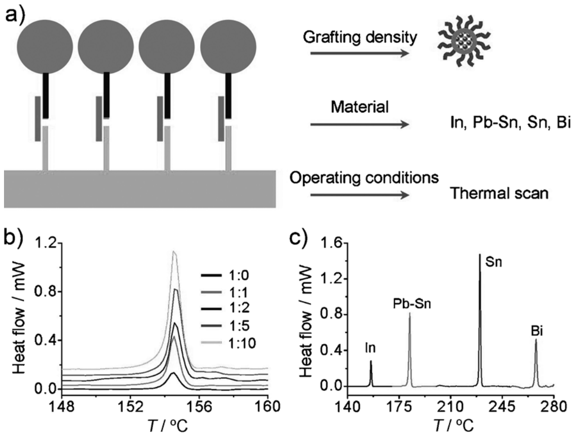

Figure 11. Biosensing using PCM nanoparticles. a) Each type of nanoparticles is conjugated with a ligand for the corresponding protein or DNA biomarker and then immobilized on the ligand-modified substrate. The type and concentration of biomarkers are reflected in the melting points and fusion enthalpies of the nanoparticles by DSC. b) DSC curves showing the effect of ligand grafting density on the range and sensitivity of detection. c) DSC curve demonstrating the ability to simultaneously detect multiple materials. Reproduced from Ref. [128] with permission.

6.3.2. Barcoding

An ultrahigh capacity coding system with small dimensions to identify each object in a large group of objects is desired. Optical barcodes, RFID chips, and microfibers are currently utilized to code and identify various objects, but as of yet no current technology can inexpensively barcode a large number of small objects. The discrete sharp melting peaks associated with metal PCM nanoparticles during a linear thermal scan are useful for barcoding.[130–132] Mixtures with unique DSC fingerprints can be created by utilizing the melting properties of various metal PCMs (Figure 12). Assuming that each melting peak is sufficiently sharp and does not overlap each other, the encoding capacity is dependent on the number of melting peaks or nanoparticle compositions. The number of different barcodes can be derived from Yang Hui's triangle (1238–1298) or Pascal's triangle (1653), and will be 2^n-1, where n is the total number

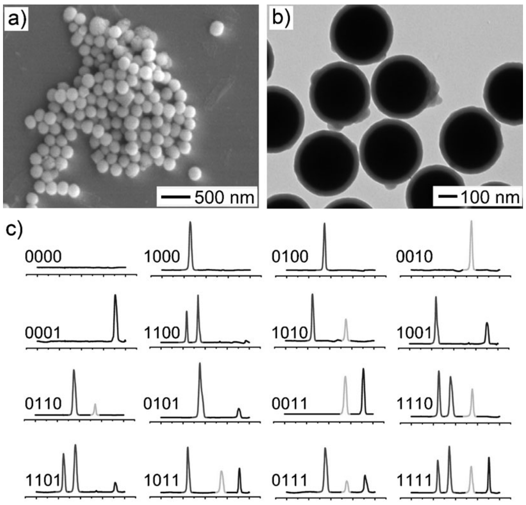

Figure 12. Barcoding with PCM nanoparticles. a,b) SEM and TEM images of Bi particles encapsulated in silica shells designed for a barcoding application. Reproduced from Ref. [45] with permission. c) Thermal barcodes using four types of nanoparticles at different ratios: In, Pb-Sn alloy, Sn, and Bi. The DSC curves were recorded in the range of 100 to 300 °C. Each number corresponds to a unique tag created from a mixture of four PCMs with different melting points (a total of 16 possible combinations). Reproduced from Ref. [132] with permission.

of melting peaks.[132] As demonstrated by Su and co-workers, the utilization of 10 different PCM particles would afford more than 1000 possible barcodes, while using 50 different particles would afford 10^{15} possible barcodes, which is sufficiently large for most of the identification requirements.[132] Of course, the necessity for a large number of PCM particles with discrete melting peaks raises an inherent challenge, that is, creating 50 different PCM particles with unique melting peaks that will not interfere with each other or with the matrix in which they are embedded. However, it has been shown that a mixture of four PCM particles could be embedded in aluminum and accurately identified on the basis of the particle ratio.[132] In the four-element system, each melting peak can be denoted as one or zero depending on whether the heat flux is higher or lower than a threshold value (Figure 11). There are 16 combinations of four elements: 0000, 1000, 0100, 0010, 0001, 1100, 1010, 1001, 0110, 0101, 0011, 0111, 1001, 1101, 1011, and 1111. This application carries the potential to change the nature of identification systems as they are currently known, and could be of great assistance to law enforcemen. For example, it will be more straightforward to identify objects previously difficult to trace through ubiquitous tagging.

7. Concluding Remarks

We have in this Review introduced PCMs and discussed their characteristics, the most notable of which is their high latent heat during phase transition. We have discussed just a few of the thousands of materials that have been investigated for their use as PCMs in the past several decades. Broadly divided into the categories of inorganic and organic, each PCM composition carries its own advantages and disadvantages. For example, in most cases, organic PCMs have lower densities than most inorganic PCMs such as water and salt hydrates, thus usually resulting in organic PCMs with smaller melting enthalpies per volume than the inorganic counterparts.

Beyond the source material, the processing of PCMs adds yet another layer of multiplicity, with different techniques creating vastly different forms of PCMs. The PCM particles enable full use of latent heats of fusion, which leads to their instantaneous melting. The encapsulation of the PCM particles can hold the liquid phase, especially during solid–liquid phase changes, and prevents contact of the PCM with the environment, which might harm the environment or change the composition of the PCM. Furthermore, the encapsulation material can serve as a construction element, thus adding mechanical stability.

Recently, the utilization of PCMs has expanded beyond their commercial successes to incorporate high technologies. For example, biocompatible and degradable PCMs such as fatty acids and fatty alcohols may enable a new class of temperature-regulated drug-delivery system. Different diffusivity of the drug/carrier in solid and liquid PCMs allows the system to perfectly contain a drug at a temperature below the melting point, and beyond which rapid release of the drug is achieved. PCM-based drug-release systems may be useful in situations involving the elevation of body temperature as a result of fever and inflammation. It may also be feasible to release an anticancer drug to target the cancer cells with a higher temperature than the normal cells.

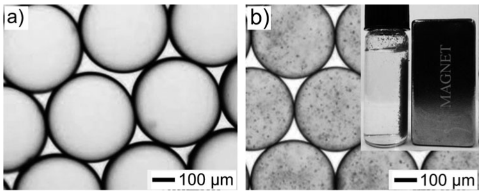

Figure 13. Optical micrographs of *n*-octadecane@polyurea microparticles: a) without and b) with the encapsulation of Fe_3O_4 nanoparticles. The inset shows the microparticles in (b) under the action of an external magnetic field. Reproduced from Ref. [57] with permission.

The integration of functional materials into PCMs may provide new features. Figure 13 shows PCM particles containing Fe_3O_4 nanoparticles, as reported by Cheong and co-workers.[57] The encapsulation of such magnetic or metal nanoparticles enables the fast switching of the phase transition by the heat generated through irradiation of external electromagnetic waves, thereby achieving the on-demand release of drugs. Incorporating quantum dots of various semiconductors can also provide interesting luminescent properties for PCMs, thus making them potentially useful as probes for biological imaging. In addition, encapsulation in a PCM may offer a new strategy for tuning the emission energy of a quantum dot, in which the energy can be precisely controlled through the local strain associated with the volume change of the PCM, a phenomenon being exploited in quantum communication and quantum information processing.[133,134]

In summary, PCMs offer a host of formulations, can be fabricated through a plethora of techniques, and can be utilized in a diverse array of applications, which provides for virtually infinite combinatorial possibilities. We hope this Review will stimulate interest in an area that seems to have limitless potential. PCMs are certainly going to be a source of continual scientific and technological progress for years to come.

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