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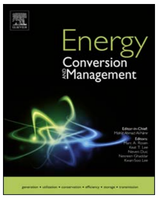

Nanoencapsulated phase change materials with polymer-SiO_2 hybrid shell materials: Compositions, morphologies, and properties

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ABSTRACT

Organic-inorganic hybrid materials are promising for encapsulation of phase change materials (PCMs) to achieve exceptional capsule properties. In this work, novel polymer-SiO_2 hybrid shelled nanoencapsulated PCMs (NanoPCMs) were fabricated in one-pot, through sequentially executed interfacial hydrolysis-polycondensation of alkoxy silanes and radical polymerization of vinyl monomers. The morphologies, chemical compositions, and crystal structures of the NanoPCMs were characterized by SEM, TEM, FT-IR, and XRD methods. The thermal energy storage capability, thermal reliability, and thermal conductivity were tested by DSC, accelerated thermal cycling test, and heat flux method, respectively. The leakage proof property and mechanical property were evaluated by seepage test and nanoindentation test, respectively. Compared with NanoPCMs with SiO_2 shell, the NanoPCMs with polystyrene (PS)-SiO_2 shell possess smaller size and bowl like shape, while NanoPCMs with poly (hydroxylethyl methacrylate) (PHEMA)-SiO_2 shell possess larger size and perfect spherical shape. The polymer types have great impact on the supercooling behavior of the NanoPCMs. The polymer-SiO_2 hybrid shell materials endow the NanoPCMs with improved thermal reliability, thermal conductivity, and leakage proof property. More importantly, the compressive load at yield increases remarkably from 14.7 μN for nanocapsules with SiO_2 shell, to > 34.6 μN for that with PS-SiO_2 shell, and 65 μN for that with PHEMA-SiO_2 shell.

1. Introduction

Phase change materials (PCMs) are substances that can undergo phase transitions at defined temperature range, and store/release large quantity of latent heats during the process [1]. Due to their high heat storage capacity, PCMs are good choice to overcome the uneven energy distribution in space and time, and the mismatch between energy supply and demand [2]. Moreover, based on their near isothermal characteristics during the thermal energy storage/release process, PCMs can also provide thermal comfort for buildings in an energy efficient and environmentally friendly way [3]. Therefore, PCMs can greatly contribute to development of renewable and sustainable energy sources, less consumption of fossil fuels, and less emission of green house gas.

Most practically valuable PCMs, including paraffin, fatty acids, alcohols, and salt hydrates, perform thermal energy storage through solid–liquid phase transition, and suffer from leakage in liquid state and low thermal conductivity. In last decades, micro (1 μm < size < 1000 μm)/nano (size < 1 μm) encapsulation of PCMs with protective shell materials have been widely explored. Those capsules can effectively prevent the leakage of PCMs, improve the thermal conductivity and heat storage/release efficiency, and control the volume change during phase change process [4,5]. Through encapsulation, the application fields of PCMs have been greatly extended, such as latent functionally thermal fluids [6,7] and smart textiles [8]. Encapsulated PCMs with various organic and inorganic shell materials were prepared by using different methods, such as in-situ polymerization, suspension polymerization, interfacial polymerization, sol-gel method, and self-assembly method, etc [4]. Generally, the well developed organic shell materials, such as melamine-formaldehyde (M − F) resin, polyurea [9], polystyrene (PS) [10,11], polymethylmethacrylate (PMMA), can withstand the volume change during phase change process efficiently, but possess low thermal conductivity. Inorganic shell materials, mainly including SiO_2 [12,13], TiO_2 [14,15], and $CaCO_3$ [16], have attracted intensive research interests during the latest ten years, due to their higher thermal conductivity and thermal stability than the organic counterparts. However, inorganic shell materials like SiO_2 and TiO_2 are generally obtained through sol-gel or interfacial

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hydrolysis-polycondensation processes. They often exhibit mesoporous structure [17] and are mechanically weak. In recent few years, many research efforts have been devoted to organic-inorganic hybrid shell materials, which can combine the advantages of organic and inorganic materials, to achieve outstandingly high performances [18]. Consequently, several novel types of micro/nano encapsulated PCMs with organic-inorganic hybrid shell materials have been invented.

Some inorganic materials like SiO_2, TiO_2, Al_2O_3, Si_3N_4, graphene oxide (GO), and graphene, were introduced into organic shell materials of microencapsulated PCMs (MicroPCMs) as fillers during the preparation process. These highly thermal conductive fillers were dispersed either by direct mixing or serving as Pickering stabilizers. Yin et al. [19] prepared MicroPCMs with PS-SiO_2 hybrid shell material via Pickering emulsion polymerization method, in which organically-modified SiO_2 particles were used as stabilizer. The prepared MicroPCMs present good durability and thermal reliability. Zhao et al. [20] fabricated MicroPCMs with PMMA-TiO_2 hybrid shell for thermal energy storage and UV-shielding. Sun et al. [21] synthesized a novel kind of MicroPCMs with PMMA/BN/TiO_2 ternary hybrid shell material by Pickering emulsion method, in which nano-BN/TiO_2 particles were used as stabilizer. Jiang et al. [22] synthesized new MicroPCMs based on paraffin wax core and poly(methyl methacrylate-co-methyl acrylate)-Al_2O_3 hybrid shell material. Yang et al. [23] reported MicroPCMs with PMMA-Si_3N_4 hybrid shell material. Chen et al. [24] prepared novel MicroPCMs with M − F resin-GO hybrid shell material by in situ polymerization, and the products possessed high latent heat and improved thermal conductivity. Zhang et al. [25] prepared MicroPCMs with PS-GO hybrid shell material by Pickering emulsion method, and achieved high encapsulation ratio and good thermal stability. Su et al. [26] synthesized MicroPCMs with methanol-modified M − F resin-graphene hybrid shell material through in situ polymerization, to improve the mechanical properties and thermal conductivities. In addition to the above mentioned method, a different method for preparation of MicroPCMs with hybrid shell material was reported by Li et al. [27]. Specifically, vinyl functionalized alkoxy silanes were employed as raw materials, which were subjected to simultaneous sol-gel reaction and free radical polymerization and resulted in polymer-SiO_2 hybrid shell material to encapsulate the PCMs. The products possess high encapsulation ratios and low leakage rate. In summary, through these approaches, the obtained hybrid shell materials brought lots of merits for micro/nano encapsulated PCMs: enhanced encapsulation ratio [28], improved thermal conductivity [24,26], and better leakage proof properties [29].

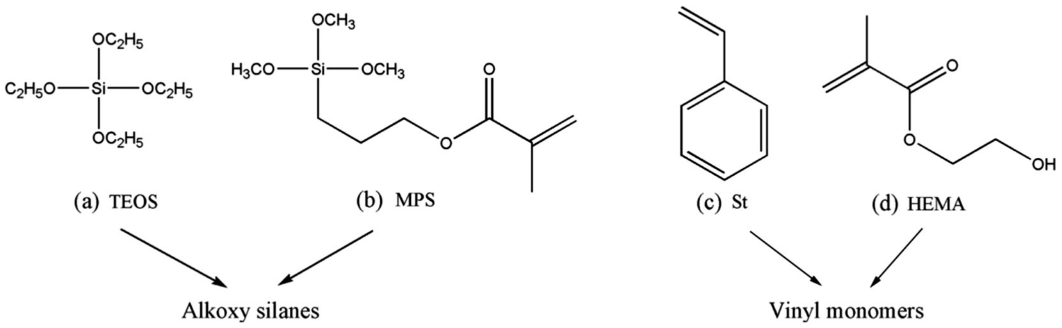
It is observed that most of the previous works were focused on modification of organic shell materials with some inorganic substances, but the modification of inorganic shell materials with organic polymers was rare. In addition, from the view point of capsule size, most previously reported encapsulated PCMs with organic-inorganic hybrid shell materials were limited to MicroPCMs, while nanoencapsulated PCMs (NanoPCMs) were almost ignored. Compared with MicroPCMs, NanoPCMs have much larger specific surface area, which can result in much faster thermal energy storage/release [30]. When applied in latent functionally thermal fluid, NanoPCMs do not fracture easily in the course of flow [5]. However, it is obvious that the shell of NanoPCMs is generally much thinner than that of MicroPCMs, so its compactness and toughness are especially important to achieve desirable sealing performance and durability. Therefore, it is very valuable for practical application to develop novel NanoPCMs with organic-inorganic hybrid shell materials.

In this work, we conduct modification of SiO_2 shell material with PS and poly(hydroxylethyl methacrylate) (PHEMA), to obtain novel NanoPCMs with organic-inorganic hybrid shell materials. SiO_2 is a classic type of inorganic shell material for micro/nano encapsulated PCMs, because it can be facilely and controllably synthesized through sol-gel (i.e. interfacial hydrolysis-polycondensation) process with inexpensive raw materials like tetraethyl orthosilicate (TEOS) [31,32] and sodium silicate [33]. PS and PHEMA [34] were selected as representatives of hydrophobic and hydrophilic polymers, respectively. The prices of the monomers for both polymers are also very cheap. The polymer-SiO_2 hybrid shelled NanoPCMs were fabricated in one-pot, through sequentially executed interfacial hydrolysis-polycondensation of alkoxy silanes and free radical polymerization of vinyl monomers. The low costs of raw materials and simplicity of preparation can endow the target NanoPCMs with good potential for mass production and practical use. Through this preparation strategy, excellent morphologies can be obtained, and the polymer content can be facilely tuned. The influences of the two polymers with different contents on the morphologies, thermal energy storage properties, thermal conductivities, leakage proof properties, and mechanical properties of the NanoPCMs were comprehensively investigated. On the basis of the results of this research, the overall properties of the NanoPCMs can be optimized with respect to their compositions.

2. Experimental

2.1. Materials

n-Octadecane (n-OD, 90 wt%), γ-methacryloxypropyl trimethoxy silane (MPS), and polyvinylpyrrolidone (PVP, M.W. 58,000 g/mol) were purchased from Alfa Aesar. Tetraethyl orthosilicate (TEOS), anhydrous ethanol, $NH_3{\cdot}H_2O$ (25 wt%), styrene (St), and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagents. Hydroxyethyl methacrylate (HEMA) was purchased from Aladdin. St and HEMA were purified by passing through a neutral alumina column, to remove retardants. AIBN was recrystallized from 95% ethanol before use. Cetyltrimethylammonium bromide (CTAB) was commercially supplied by Tianjin Kermal Chemical Reagents. All chemicals were of reagent quality and used without further purification, unless stated otherwise.



Scheme 1. Raw materials used for fabrication of polymer-SiO_2 hybrid shell materials.