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Encapsulation of phase change materials using rice-husk-char

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HIGHLIGHTS

- Rice-husk-char particles are successfully used in the encapsulation of phase change materials.
- Carbon-based phase change microcapsules aim at using the high thermal conductivity of carbon materials.
- Carbon from biomass can be used in low and intermediate heat harvest and storage.
- Carbon in biomass is captured and to be used in improving energy efficiency.

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ABSTRACT

This paper explored a new approach to prepare phase change microcapsules using carbon-based particles via Pickering emulsions for energy storage applications. Rice-husk-char, a by-product in biofuel production, containing 53.58 wt% of carbon was used as a model carbon-based material to encapsulate hexadecane. As a model phase change material, hexadecane was emulsified in aqueous suspensions of rice-husk-char nanoparticles. Water soluble polymers poly(diallyldimethyl-ammonium chloride) and poly(sodium styrene sulfonate) were used to fix the rice-husk-char nanoparticles on the emulsion droplets through layer-by-layer assembly to enhance the structural stability of the microcapsules. The microcapsules formed are composed of a thin shell encompassing a large core consisting of hexadecane. Thermal gravimetrical and differential scanning calorimeter analyses showed the phase change enthalpy of 80.9 kJ kg^{-1} or 120.0 MJ m^{-3}. Design criteria of phase change microcapsules and preparation considerations were discussed in terms of desired applications. This work demonstrated possible utilisations of biomass-originated carbon-based material for thermal energy recovery and storage applications, which can be a new route of carbon capture and utilisation.

1. Introduction

Energy consumed for low and intermediate rank heat accounts for ~90% of energy consumption in industrial and household applications [1]. A large proportion of the heat is discharged into the environment through undesired heat loss in maintaining temperatures. In order to reduce the overall energy consumption and CO_2 emission worldwide, cost-effective thermal systems have been under development to reduce the heat loss and to harvest solar energy and store it as heat for reuse [2,3]. Thermal media are keys to effective thermal systems. In general, the desired thermal media should have (a) a high dynamic thermal energy density; (b) long term stability, (c) low cost for economic sustainability and (d) excellent flow and heat transportation properties (if in the form of working fluids). Phase change material slurries have been developed to serve as thermal fluids for both heat transfer and energy storage [2,3], where the phase change materials encapsulated are dispersed in an immiscible liquid carrier in order to maintain the fluidity of the media during phase changes. In this way, the phase change material slurries have higher heat density at points around the phase change temperature and also the desired fluidity.

Active research into phase change microcapsules by experiments and simulations in different thermal systems are reviewed in Refs. [3,4]. Different results were observed in relation to application scenarios. The well-known Micronal® phase change microcapsules were commercialised, which can be incorporated in interior

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walls of buildings for intelligent temperature management. Its enhancement in energy efficiency has been well approved in the stagnant environment for a low frequency heat charge and discharge [5,6], but its economic efficiency has been questioned. In laminar or transient flow regions, heat transfer enhancements can be spotted clearly in heat pumps [7]. While enhancements are less significant in more intense processing environments such as solar heat harvest and release due to slow heat transfer rates [8,9].

Critical analysis has shown that polymers such as poly(methyl methacrylate) [10,11], poly(melamiformaldehyde), poly urea and (urea formaldehyde) [4,12], polystyrene [13] and polyethylene [14] are commonly studied encapsulates for phase change microcapsules. These polymers inherently have low thermal conductivities (~0.25 W m^{-1} K^{-1}) and low densities, hence slow heat capture and release rates and limited volumetric heat densities. In recent years, inorganic materials including metal, metal oxides, insoluble salts and carbon-based materials (graphene and carbon nanotube) have been used in the modification of the microcapsule shell by coating or as additives for enhancing their thermal conductivity. Microcapsules with silver coating as the second layer [15,16], hybrid magnetic Fe_3O_4/SiO_2 [17], silicon nitride powder-modified polymethylmethacrylate [18] and calcium carbonate shells [19] have all displayed significant improvements in thermal conductivity.

Carbon-based materials varying from diamond, graphite (carbon fibre), carbon nanotubes and graphene to amorphous carbons are well known for their wide range of thermal conductivities (~21–5000 W m^{-1} K^{-1}). The addition of 20 wt% expanded graphite in paraffin results in a 7.5 fold thermal conductivity increase for the formation of a carbon network structure [20]. As an example composite panels consisting of phase change materials and expanded graphite (ECOPHIT®) installed as radiant ceilings at the Deutsche Bank headquarters demonstrated a 67% reduction in energy use for heating and cooling [21,22]. Both the heat storage capacity of the phase change materials and the high thermal conductivity of graphite sheets contributed to the result. Phase change microcapsules of urea–formaldehyde resin with 4% of carbon nanotubes showed an increase in thermal conductivity by 79.2% compared with that without carbon nanotubes [23]. These results inspire researchers to develop carbon-based phase change microcapsules aiming at achieving large heat capacities and high heat transfer rates as desired properties.

Using carbon-based materials as microcapsule shells their absolute thermal conductivity is expected to be higher than that of polymer nanocomposites containing a small fraction of carbon nanotubes [23–25]. However, high thermal conductive carbon materials can form only at high temperatures, typically above 600 °C, which is much higher than the decomposition temperature of organic carbon-carbon bonds. As a result, it is very difficult to grow thermally conductive carbon on the surface of phase change "droplets". Fortunately, solid particles can be directly used to manufacture microcapsules through a Pickering emulsion, which is the emulsion using solid particle as emulsifier [26]. All the carbon materials mentioned above are available as solid micro- or nanoparticles.

Pickering emulsion droplets are formed by the adsorption of one monolayer of solid particles on the droplet surface, thus generating core-shell structures [27,28]. Many different types of inorganic nanoparticles such as silica [26–28], metal organic framework nanoparticles [29,30] and carbon nanotubes [31] have been successfully incorporated in stabilising Pickering emulsions either as a single emulsifier or co-emulsifier [32], among which silica nanoparticles have been more extensively studied. For example, Ding et al. prepared structured microcapsules using silica nanoparticles that are formed in-situ by the hydrolysis of methyl trimethoxysilane and 3-aminopropyl trimethoxysilane [28]. The prepared microcapsules contained a significant core of *n*-octodecane, a phase change material, with a monolayer of silica nanoparticles as shell giving a high volumetric encapsulation ratio of 65 wt%. The nanoparticles can be manipulated for the desired arrangement on the droplet surface through tailoring size, shape, surface chemistry and adsorption kinetics [32]. Pickering emulsions, in particular those stabilised by latex nanoparticles, have been successfully encapsulated by polymer melting [33,34], cross-linking from the inside [27] or outside of microcapsules. The microcapsule wall formed has been tailored to have a different permeability from vapour-proof to highly porous with desired pore sizes [27,28,34]. This knowledge stimulated our study of using carbon-based particles to produce phase change microcapsules.

The model carbon-based material used in this study is rice-husk-char, which is rich in carbon and silica [35,36]. It is an abundant by-product in countries which produce and consume rice. Up to now, there are insufficient applications of rice-husk-char (ash) to support a sustainable consumption chain. This study proposes its use in the development of new applications of carbon-based materials for thermal energy storage in civil engineering.

Rice husk char used in this study was obtained from slow pyrolysis for bio-oil production. After milling down to desired sizes the rice husk char particles were dispersed in water to be used as a solid emulsifier in the stabilisation of phase change material emulsion. The emulsion droplets were then subjected to a layer by layer assembly of polyelectrolyte chains in an aqueous solution for encapsulation. Following this, thermogravimetric and differential scanning calorimetric analyses were carried out on the microcapsules produced in order to assess their thermal stability and heat storage capacity.

2. Experimental

2.1. Materials

n-Hexadecane (99%, Acros Organics) was used as a model phase change material to be encapsulated for a phase change at around 20 °C to be used in a living environment. The rice husk char was used as a Pickering emulsion stabiliser and also as the wall construction material of the *n*-hexadecane microcapsule. The char was made from the slow pyrolysis of Brunei rice husk at 450 °C for 30 min in the presence of nitrogen gas [37], which generated 42 wt% of char based on dry rice husk.

Poly(diallyldimethyl-ammonium chloride) (PDADMAC 20 wt% aq., 400,000—500,000 g mol^{-1}, Sigma Aldrich) and poly(sodium styrene sulfonate) (PSS 30 wt% aq., 200,000 g mol^{-1}, Sigma Aldrich) were used as negatively and positively charged polymers, respectively, for layer-by-layer adsorption to fix the rice husk char particles on the emulsion droplets. Sunflower oil (Tesco UK) was used as an osmosis additive to the oil phase for better size and stability control in emulsification. Deionised water was used in all the sample preparation.

2.2. Sizing of the rice husk char

The rice husk char received from the pyrolysis was ground dry in air using a planetary ball mill (Fritsch Pulverisette 6). The milling used a 250 mL zirconia grinding bowl and zirconia milling balls (1 mm in diameter) of 200 g, and was carried out at 6000 rpm for 5 min to size down the rice husk char down to a nanometer range. The rice husk char (RHC) nanoparticles were analysed using laser scattering for their particle size and size distribution, and dynamic laser scattering for its surface charge measured as zeta potential. The RHC nanoparticle sample prepared dry in air was dispersed