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Emulsion stability and cross-linking of PMMA microcapsules containing phase change materials

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ABSTRACT

The microencapsulation of paraffin as a phase change material (PCM) using poly methyl methacrylate (PMM) as a shell was investigated by means of suspension polymerization. The increase in the emulsion stability by using mixed surfactants was studied. It was observed that a mixed surfactants system induces long-term emulsion stability and monodisperse droplets size distribution. Also, the use of mixed surfactants reduces significantly the buckles in microcapsules significantly. The effect of using pentaerythritol tetraacrylate (PETRA) as a cross-linker agent on the diverse properties of PCM microcapsules such as morphology, energy storage density, shell permeability and thermal stability has been investigated. Adding PETRA to the system improves the surface morphology and produces microcapsules with a much higher PCM content. For example, the core/shell mass ratio of 2:1 produces microcapsules with regular spheres having smooth surfaces. TGA results show two steps thermal degradation of microcapsules. The mass loss was similar to the non-encapsulated PCM until all the PCM was dissipated (step 1). Following that the microcapsules experienced lower rate of mass loss of the shell, which depends on its thickness (step 2).

1. Introduction

In an attempt to reduce the amount of energy consumption by heating and cooling in buildings, considerable efforts have been made to use phase change materials (PCMs) within the building envelope [1]. PCMs are organic or inorganic compounds, which melt and solidify with a melting range suitable for a given application. They have the ability to absorb and release large amounts of heat during their phase transition. The use of PCMs in buildings increases their thermal inertia, and therefore improves thermal comfort, reduces internal temperature fluctuation reduces heating and cooling requirements. However, in order to use them practically, they must be well contained to prevent them from leaking out when melted. Microencapsulation has been shown as the effective engulfing of PCM [2].

Microencapsulation is a well-known technology and has been developed in many fields such as pharmaceutical industry [3], food [4], cosmetics [5], textile industries [6] and thermal energy storage applications [7]. A number of articles have been published for microencapsulation of PCMs using different techniques with different shell materials [8–10]. A method was developed based on suspension free radical polymerization for microencapsulation hexadecane by using poly (styrene-co-N, N-dimethyl amino ethyl methacrylate) as shell [11]. Paraffin wax microcapsules were produced using gum arabic-gelatin mixture (as a shell material) by means of spray drying and complex coacervation methods [9]. Polycarbonate microcapsules containing stearic acid as PCM was fabricated using solution the casting method [12]. N-tetradecane-microcapsules with different shell materials were synthesized by using phase separation method [13]. Poly methyl methacrylate (PMMA) network-silica hybrid microcapsules containing PCM was fabricated via Sol–Gel process [14]. A series of PMMA microcapsules containing different kind of PCMs were prepared using emulsion polymerization method [15–18]. Tetradecane microcapsules using melamine formaldehyde as a shell material was prepared using in situ polymerization [19]. Polyurea microcapsules containing octadecane as PCM was fabricated using interfacial polymerization [8]. A facile and an effective approach for fabricating highly monodisperse PCM polyurea microcapsules were reported using a tubular microfluidic technique [20].

In all of microencapsulation methods that previously mentioned, the introduction of emulsifier to stabilize the emulsion has been critical. Different concentrations of polyvinylpyrrolidone (PVP) (K30, Mw 40,000 g/mol) as stabilizer were tested [21]. The average particle size decreased when the surfactant concentration increased. The highest mass percentage of paraffin in the microcapsules

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(46.5 wt%) was achieved at a core/shell mass ratio of 1.02 and PVP/monomer mass ratio of 0.091. The effect of different types of single surfactant on the PCM microcapsules properties (particle size distribution, morphology and thermal properties) were investigated [22]. Spherical microcapsules with smooth surface were obtained when polyvinylpyrrolidone (PVP) and gelatin was used. Nevertheless, Arabic gum and poly vinyl alcohol (PVA) shows irregular particles with a rough surface. PVP produced microcapsules with lowest value of mean particle diameter (204 μm) while Arabic gum produced microcapsules with the highest amount of PCM mass percentage content (67.9 wt%).

A prerequisite for manufacturing good characteristics PCM microcapsules is the ability to produce stable emulsion with a well-controlled droplets size. Literature survey clearly indicates that in the majority of the investigations of PCM microencapsulation single surfactant was used [22–24]. Improving the stability of the emulsion through the use of mixed surfactants was not reported in the literature. Therefore, in this work, the emulsion stability and PCM microcapsules characterizations (morphology and thermal properties) were investigated in the presence of a mixture of surfactants (sodium dodecyl sulfate (SDS) and poly vinyl alcohol (PVA)).

A number of articles in the literature reported that the cross linking of PCM microcapsules exhibits a great improvement in shell mechanical strength and PCM payload [25–27]. Therefore, the effect of adding pentaerythritol tetraacrylate (PETRA) as cross linking agent on the PCM microcapsules characteristics such as morphology, shell permeability and thermal properties was investigated.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) (99%, contains $\leq$30 ppm monomethyl ether hydroquinone (MEHQ) as inhibitor, Sigma Aldrich, NZ) and pentaerythritol tetraacrylate (PETRA) (contains 350 ppm (MEHQ), Sigma Aldrich, NZ) were used as monomer and cross-linking agent respectively. Commercially available Rubitherm®RT21 (T_{pm}=21 °C, ΔH_m=135 J/g, RUBITHERM® Technologies GmbH, Germany) was used as PCM. Polyvinyl alcohol (PVA) (Mw 85,000–124,000, Sigma Aldrich, NZ) and sodium dodecyl sulfate (SDS) (BioXtra, 99%, Sigma Aldrich, NZ) were used as non-ionic and ionic surfactant respectively. Luperox® A75, Benzoyl peroxide (BPO) (75%, contains 25% water, Sigma Aldrich, NZ) was used as free radical thermal initiator. All chemicals were used as it is without any further purification.

2.2. Synthesis of PCMs microcapsules

2.2.1. Emulsification

A standard procedure was used as reported elsewhere [28]. Wherein; an aqueous solution of surface-active agent (called aqueous phase) and a mixture of MMA, PETRA, BPO and PCM (called organic phase) were prepared separately. The organic phase was added to the aqueous phase and emulsified mechanically using a high shear mixer (Silverson L5M-A laboratory Mixer) equipped with a fine emulsor screen. A stirring rate of 3000 rpm for 5 min was chosen to achieve the required emulsification.

2.2.2. Polymerization

The produced emulsion was transferred to a 2-L four-neck glass reactor (LR-2.ST laboratory reactor- IKA-Werke Gmbh@Co.KG) consisting of EUROSTAR 200 control P4, Anchor stirrer LR 2000.1, HBR 4 digital heating bath as shown in Fig. 1. The agitation speed was set at approximately 300 rpm; and the temperature of the water bath was maintained at 70 °C for 2 h, and then adjusted to 85 °C for another 4 h. The water bath was then switch off and allowed to cool down naturally to room temperature. After cooling, the suspension of PCM microcapsules was transferred to a clean glass beaker and washed three times with distilled water to remove the unreacted monomers and the PCM, which is not encapsulated. The separated microcapsules were spread on a tray and placed in an oven at 50 °C for 48 h for drying. The dried microcapsules were then collected for testing.

Fig. 1. Schematic diagram of LR-2.ST laboratory polymerization reactor.

3. Characterization of microcapsules

3.1. Scanning electron microscope (SEM)

The microcapsules morphology was examined using a scanning electron microscope (SEM) (Philips XL30S FEG, Netherland) operating under low vacuum pressure of 0.9 Torr. All samples were coated with gold prior to the investigation.

3.2. Differential scanning calorimetry (DSC)

Phase change properties of the fabricated PCM microcapsules and the pure PCMs (such as melting and solidification temperatures and their phase change enthalpies) were determined using a SHIMADZU DSC-60 differential scanning calorimetry. The measurements were performed by varying the temperature from −15 to 40 °C with heating and cooling rate of 3 °C/min. Each sample was analyzed for three times and the average was taken.

Consequently, the ratio of encapsulated PCM (core material) to polymer (shell material) can also be determined using DSC results from the following equation [21]:

$$\%\ \text{PCM in microcapsules by mass} = \frac{\Delta H_{\text{microcapsules}}}{\Delta H_{\text{Pure PCM}}} 100\% \quad (1)$$