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Predicting microcapsules morphology and encapsulation efficiency by combining the spreading coefficient theory and polar surface energy component

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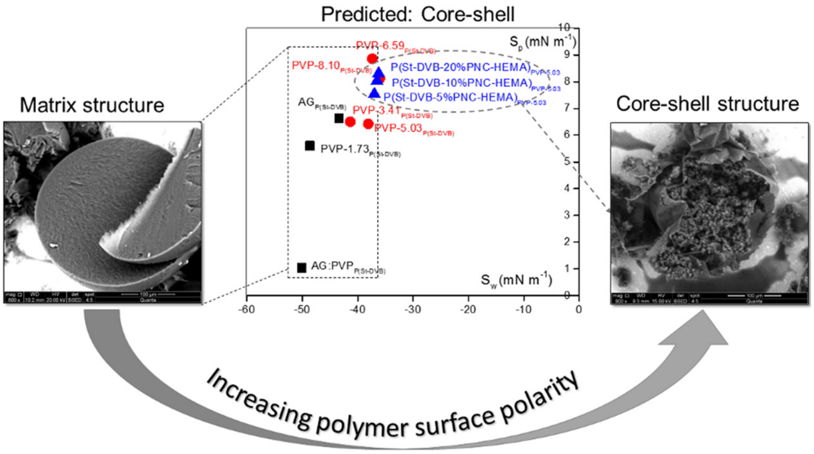
GRAPHICAL ABSTRACT



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ABSTRACT

The morphology and encapsulation efficiency of thermoregulating microcapsules based on a spreading coefficient theory and polar surface energy component were evaluated. For this purpose the microencapsulation of phase change materials (PCMs) with different copolymer shells and using different suspending agents by the suspension-like polymerization technique has been carried out. Contact angles and interfacial tensions were measured, and results were discussed with respect to the internal structure as well as encapsulation efficiency of the microcapsules. A core/shell structure was expected as the equilibrium morphology, whereas the experimental structure exhibited a matrix morphology. A core-shell structure was favored by increasing the polarity of the polymer and decreasing the solubility between the core and shell. The type and amount of suspending agent do not have a significant influence on the final characteristic of the microcapsules. Shells with various polarities were synthesized from styrene (S), divinylbenzene (DVB) and hexa(methacryloylethylenedioxy)

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cyclotriphosphazene (PNC-HEMA), and it was found that a core-shell structure was only obtained for microcapsules with a high polar surface energy component.

1. Introduction

One of the main problems observed over a last several decades is a high and quickly growing energy demand, which result in supply difficulties, resources depletion and destructive environmental impact such as climate change, global warming, and ozone depletion. To reduce these problems, thermal energy storage systems using phase change materials (PCMs) can be used to store the excess heat during the day (melting) and release it back during nighttime (solidifying). PCMs are chemically classified as organic and inorganic compounds or eutectics materials [1]. Among them, paraffin are usually selected for energy saving applications due to its excellent thermal properties, long-term reliability, chemical stability, easy and large availability, and relatively low price [2]. Nevertheless, they exhibit some disadvantages for further applications such as interactions with surrounding materials, leakage, volume change during the phase transition, and high flammability. To deal with a more suitable material, microencapsulated PCMs are often used, where a microscopic droplet of PCM is covered by a polymeric shell (capsule) [3,4]. The development of microcapsules with a liquid core is of considerable practical interest for a wide range of industries, however the manufacturing of core-shell structures is not as straight forward as the theory predicts.

There are few scientific studies reporting a theoretical framework to explain the relation between microencapsulation conditions, the microencapsulation efficiency and particle structure. The pioneer theory developed by Torza and Mason [5] established a relationship between the engulfing process, and define the final morphology of the particles by means of spreading coefficient values. Their theory stated that the morphology of microcapsules can be determined by the interfacial energies of three phases in contact. van Zyl et al. [6] were trying to predict the morphology of nanocapsules synthesized by an *in situ* miniemulsion polymerization reaction based on this thermodynamic approach. However, they found that the morphology was mainly influenced by the kinetic of the reaction (anchoring effects, chain mobility, and viscosity). Morphology and encapsulation efficiency in microencapsulation can also be dependent on the polar surface energy component of the discontinuous and continuous phases, and consequently on their ability to separate them. Furthermore, the type and concentration of suspending agents and the viscosity of the organic phase with respect to the shear imposed on the reaction system is important [7]. Decreasing the polarity of the aqueous phase decreases the interfacial tension causing an easier diffusion of monomers though this phase.

Other authors have tried to develop a general rule for predicting the physical properties of the microcapsules with respect to the chemical structure of the suspending agent (gelatin, Arabic gum (AG), polyvinylpyrrolidone (PVP), and poly(vinyl alcohol) (PVA)) but the results were not successful [8]. A decreasing particle size of microencapsulated PCM has been observed when the amount of stabilizer was increased, due to reduction of the oil/water interfacial tension [9]. The encapsulation mechanism is strongly dependent on the production methods (physical or chemical). However, for both methods the thermodynamic theory is the most used theoretical approach. The theory works well on some systems but fail for others, sometimes depending on the type of suspending agents used.

As examples, of physical methods, Loxley et al. [10] have investigated encapsulation of *n*-hexadecane in a poly(methyl methacrylate) shell dissolved in dichloromethane in presence of PVA, poly(methacrylic acid), sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide by oil-in-water emulsion. A core-shell structure was predicted for poly(methacrylic acid), and acorn shape for the other surfactants. However, for PVA the morphology was not in agreement with the prediction. Tasker et al. [11] used the same polymer and core while changing the surfactant chain length, and observed that the morphology were in agreement with the predictions. Feczko et al. [12] used ethyl cellulose to entrap *n*-hexadecane utilizing PVA, Tween80, and poly(methacrylic acid sodium salt) as emulsifiers in emulsion-solvent evaporation method. The structure of the microparticles were successfully predicted from interfacial tension and spreading coefficients for poly(methacrylic acid sodium salt) but failed for PVA and Tween 80. Utilizing chemical methods, Shirin-Abadi et al. [13] investigated a series of nanocapsules containing *n*-hexadecane as a core inside a shell of a copolymer of methyl methacrylate with 2-ethylhexyl acrylate and methacrylic acid through an *in situ* miniemulsion polymerization. SEM images confirmed that the morphologies predicted from the spreading coefficients were obtained. Accordingly, the success of the morphology prediction and the microencapsulation process is strongly dependent on the kind of suspending agent utilized, and on the polarity of both the aqueous and organic phases.

In this study, microcapsules containing Rubitherm®RT27 were prepared by a suspension-like polymerization technique. Three different monomers were used (styrene (S), divinylbenzene (DVB) and hexa(methacryloylethylenedioxy) cyclotriphosphazene (PNC-HEMA)) in order to change the polarity of the organic phase. In addition, different suspending agents were used to change the polarity of the aqueous phase. This chemical technique was selected due to the low cost, and simple and robust procedure. Styrene and divinylbenzene copolymers have been used previously for obtaining chemically and mechanically resistant materials. PVA can be used to decrease the interfacial tension between styrene and the water phase, thereby reducing the particle size [7]. However, sometimes the morphology of the microcapsules are not smooth, with large "concaves" [14] and dimples [15]. Addition of a third monomer has been found to improve the morphology [15]. Microcapsules combining S, DVB and PNC-HEMA have not been reported previously. PNC-HEMA is a new monomer obtained from the reaction between the HEMA and the PNC. Cyclotriphosphazene provides good flame retardant properties to polymers [16–18]. PNC-HEMA has therefore been selected for its high polarity and high flame retardant properties [19].

The morphology of the core-shell is defined by the spreading coefficients as well as the polarity of the surface. However, when the calculations were carried out, the engulfing theory is not able to distinguish between core-shell and matrix structures. It is therefore interesting to find an approach to a correct prediction of the morphology when a combination of both spreading coefficients and polar surface energy components are considered. Accordingly, the aim of this study is to evaluate the thermodynamic factors and the effect of type and concentration of the suspending agent and the polymer polarity on the morphology and efficiency of the microencapsulation process. Different microencapsulation experiments that satisfy the interfacial tension inequality for core-shell morphologies and that also exhibit different values of polar surface energy components of the continuous and discontinuous phases were performed.

2. Experimental

2.1. Material

Styrene of reagent grade (99 wt%, Sigma– Aldrich Chemical Co.) and divinylbenzene of technical grade (containing 80% DVB isomers, Sigma–Aldrich Chemical Co.) were used as monomers. Before use, the