SYNTHESIS OF DOUBLE WALL MICROCAPSULES OF M-F COMPOSITE, DETERMINING ITS ENCAPSULATION EFFICIENCY AND SHELL YIELD WITH SUITABLE PH

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1 Introduction

Throughout the evolutionary development of materials, specific and distinct functions are available to us now. However, such unique functionality result in various physical properties that limits us from reaching a higher goal. One of the promising techniques to achieve in order to maintain and apply these materials is encapsulation i.e. microcapsule.

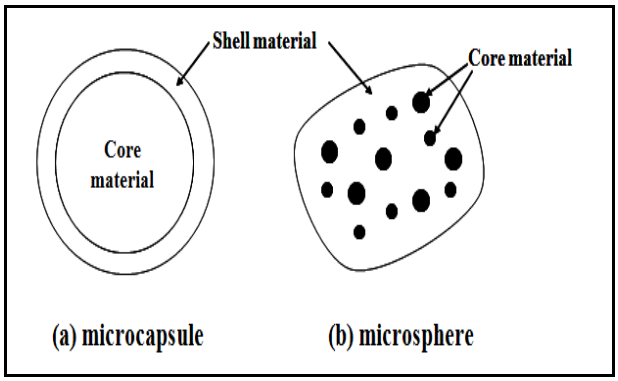

Fig. 1. Small particle that contain an active core material surrounded by a coating layer or shell

Advantages of microcapsule are that it can contain physically unusable functional materials and also the harmful materials safely away from the contact. By controlling the density and thickness of wall, the excretion of core materials can be adjusted. The wall materials can be given a function to target a desirable location.

Microcapsules have just a few ㎛ of diameter and it composites of core and shall materials. The core materials are the active components. Such as phase change materials and self healing materials.

Self-healing materials are one of promising smart material. It can be divided into two different groups, depending on the required trigger and the nature of the self-healing process: Non-autonomic and autonomic.

Non-autonomic self-healing materials require a modest external trigger, like heat or light. The (additional) energy for the healing process can be supplied by the prevailing operating conditions as well as by targeted external stimuli.

In contrast, autonomic self-healing materials do not require any additional external trigger; the damage itself is the stimulus for the healing. This concept corresponds to an adaptive structure, because the detection of the damage (by a sensor) as well as the repair (by an actuator) proceeds autonomically within the material structure. [1] In both group of self healing materials, it is necessary to isolate the materials from the trigger.

Phase change material was based on the idea of NASA research team in 1980s to protect the equipments and astronauts from exposure of extreme alteration of temperature and climate. In 1987, Triangle Research and Development Corporation (Raleigh, USA) proposed the idea of inserting PCM within the textile fiber and strongly contended that heat capacity of fiber containing PCM is not related to the suspended air layer. Triangle Research has exceeded their technology to Gateway Technology which now is known to be Outlast Technologies (Boulder, Colorado). [2]

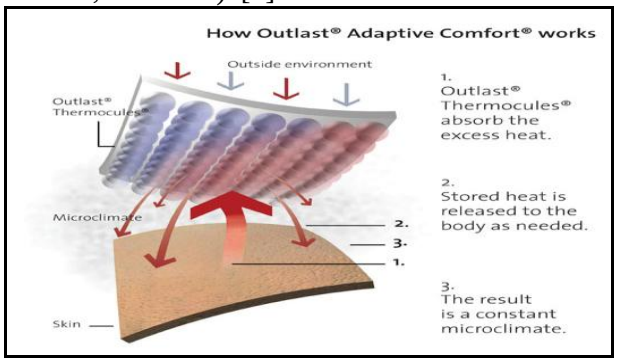

Fig. 2. Outlast Adaptive Comfort

PCM is a material that absorbs or radiates heat

through the physical phase change such as from solid to liquid and liquid to solid. When the surrounding temperature increases it absorbs heat as it melts and when the temperature is decreased it radiates heat as it crystallizes to solid. However, when the PCM reaches liquid phase it is difficult to apply on the fiber etc, therefore it is logically necessary to isolate PCM.

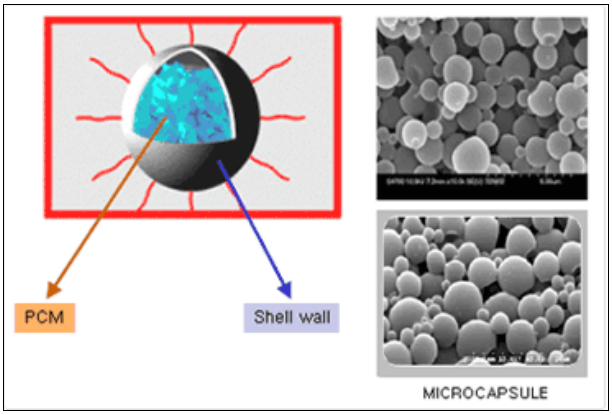

Fig. 3. Microcapsule containing PCM

This study specializes on the synthesis to optimize and also to verify the encapsulation efficiency and the shell yield by selecting suitable pH environment, using PCM as a functional core material.

2 Experiments

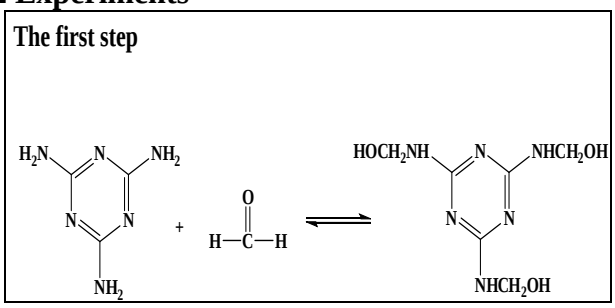

Fig. 4. First step of prepolymerization

In first step of the experiment, prepolymer of Melamine and Formaldehyde is used to form an oligomer under basic condition in order to prevent it from progressing polymerization.

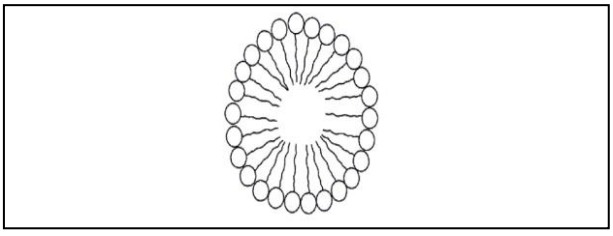

Fig. 5. Emulsion by water, emulsifier and octadecane

During the first step, emulsion of water, emulsifier and octadecane is formed. Octadecane, the core material, will be surrounded by nonionic surfactant, NP-9, forming micelle.

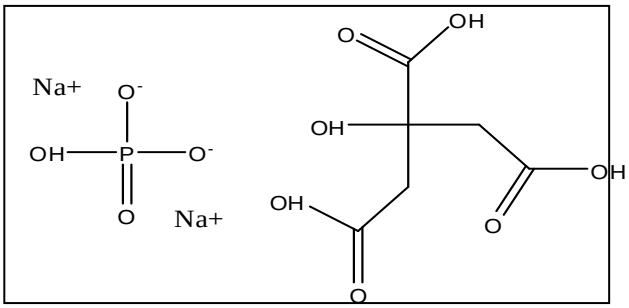

Fig. 6. Sodium phosphate dibasic anhydride and citric acid

Before adding emulsion into the prepolymer of melamine and formaldehyde, in order to set desired pH value, buffer solution of Phosphate and citric acid is prepared. Finding a certain ratio of phosphate and citric acid is crucial at this point as it is required to progress the polymerization in specific condition.

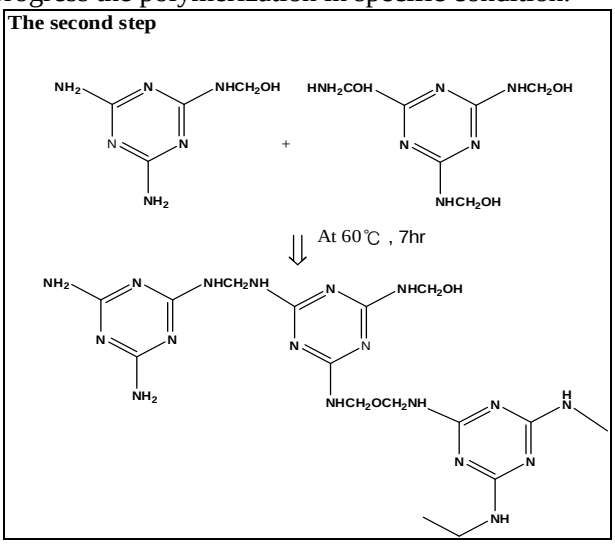

Fig. 7. Second step of forming crosslinked structure

The purpose of this experiment is to find the suitable pH condition during the polymerization. To encounter necessary buffer solution, wide range of pH is needed and also in large quantity in case of diverse outcomes of experiment.

The emulsion is then added into the prepolymer. The prepolymer forms a cross link structure within the micelle surrounding the core..

In this step the pH value of the system is measured at the addition of emulsion and the end of the polymerization. The temperature is constant at all times. After at least 7 hours of polymerization single wall microcapsule is formed.

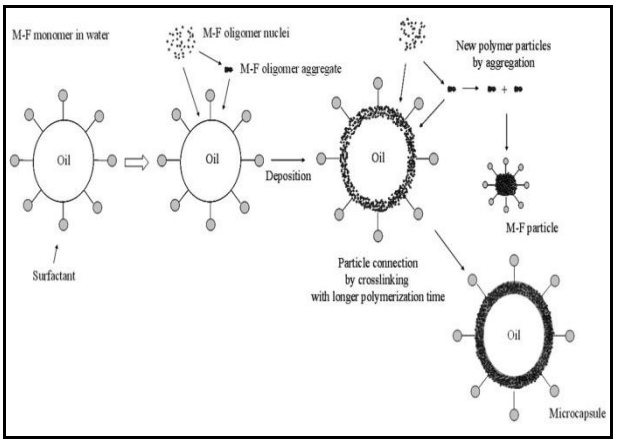

Fig. 8. Single wall microcapsule

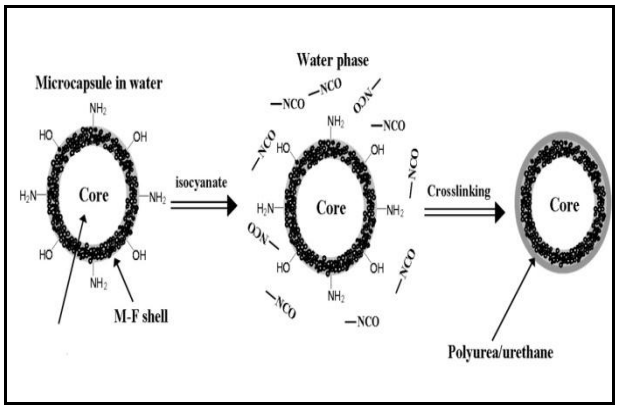

Fig. 9. Double wall microcapsule

Since the single wall can't withhold the octadecane from elution. The upcoming experiment in future is to crosslink the single wall into double wall. Using TDI, enhancing the physical property will result in efficiency improvement.

2.1 Materials

In prepolymerization Melamine (Samchun Pure Chemical Co., Ltd, 99%) and Formaldehyde (Aldrich®, 37%) was used in basic condition (3droplets of 5wt% of NaOH)

In Emulsification phase octadecane (Aldrich®, 99%) and Tergitol® NP-9 (Aldrich®) was used with SMT Process HOMOGENIZER.

At reaction the premade Phosphate-citric acid buffer solution which composites of Sodium phosphate dibasic, anhydrous (Aldrich®, 99.0%) and Citric acid (Aldrich®, 99.5%, ACS Reagent) was used. pH of solution is measured with METTLER DELTA 340. Washing was done by 3:1 ratio of methanol and water. Following equations and table is used.

The Henderson-Hasselbalch equation

$$pH = pK_a + \log (C_s/C_{ac}) \qquad (1)$$

Encapsulation efficiency (%)

$$= \frac{\frac{\Delta H_{sample}}{\Delta H_{octadecane}} \times \text{total sample weight}}{7.77g} \times 100 \qquad (2)$$

Shell yield (%)

$$= \frac{\text{total sample weight} - \left(\frac{\Delta H_{sample}}{\Delta H_{octadecane}} \times \text{total sample weight}\right)}{5.72g} \qquad (3)$$

2.2 Experiments

In emulsification step 2.5g of NP-9, which is emulsifier, is inserted in 50g of deionized water. Adding it with 7.77g of octadecane into homogenizer, agitation is done with given condition (2000rpm, 40℃, and 3min**).** The remaining 30 g of water is to be used at washing of the instrument.

In prepolymerization step, 3.5g of melamine is inserted into 3-neck flask with 20.5g of deionized water in given condition (60℃). Then 6.0 g of formaldehyde was put into the flask with 3 droplets of 5wt% of NaOH. The agitation is done as follows (400rpm, 60℃, 15~40min). At around 20~30minutes the solution becomes clear which will be the time that methyl melamine is formed.

It is crucial to start the microcapsulation step when the solution of Melamine-Formaldehyde becomes clear at which is just before the synthesis progression. PCM emulsion is mixed with the clear solution of prepolymer.

With various pH buffer solution (20 ml or more) injected, the condition of capsulation was set as given (400rpm, 60℃, 7hr).

After 7 hours of synthesis, flask is then cooled at room temperature. The contents of the flask is cleaned out to the 500ml beaker using deionised water. 1~2 days of the precipitation is followed at room temperature.

When clear precipitation is formed it is filtered with 7㎛ filter paper. Since octadecane is insoluble in water, remains of that isn't capsulated, is washed with 3:1 ratio of methanol and water.

3. Conclusion and expectations

We are expecting to distinguish the specific pH buffer

solution for the system to maximize the efficiency and the yield of single wall microcapsule. Also to compromise the set amount of the buffer solution and the molar ratio to evaluate the progression of this experiment, using following table.

0.2 M Na_2HPO_4 (ml)	0.1 M Citrate (ml)	pH
5.4	44.6	2.6
10.2	39.8	3.0
14.1	35.9	3.4
19.3	30.7	4.0
22.2	27.8	4.4
25.7	24.3	5.0
27.8	22.2	5.4
32.1	17.9	6.0
34.6	15.4	6.4

Table 1. Ratio table for phosphate-citric acid buffer solution [4]

4. Reference

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