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Functional Nano/Microcapsules: Synthesis And Characterization

Gbewonyo Spero
North Carolina Agricultural and Technical State University

Functional Nano/Microcapsules: Synthesis and Characterization

Spero Gbewonyo

North Carolina A&T State University

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Approved by:

Dr. Lifeng Zhang Major Professor	Dr. Shyam Aravamudhan Committee Member
Dr. Sung-Jin Cho Committee Member	Dr. Ajit D. Kelkar Department Chair

Dr. Sanjiv Sarin
Dean, The Graduate School

Biographical Sketch

Spero Gbewonyo was born on May 16, 1989 in Aflao, Ghana. He received his Bachelor of Science in Material Science and Engineering from the University of Ghana, Legon in 2010. In 2013, he joined the master program in Nanoengineering at the North Carolina Agricultural and Technical State University, Greensboro, North Carolina.

While pursuing his degree, Spero Gbewonyo served as a Research Assistant at the Joint School of Nanoscience and Nanoengineering of North Carolina A&T State University. His thesis entitled *Preparation of Functional Nano/Microcapsules: Synthesis and Characterization* was supervised by Dr. Lifeng Zhang.

Dedication

This work is dedicated to my parents, Mr. Dela Gbewonyo and Mrs. Esi Gbewonyo and the entire Gbewonyo family.

Acknowledgement

Foremost, I would like to express my sincere gratitude to my advisor Dr. Lifeng Zhang for the continuous support of my masters' study and research, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my masters' study.

Besides my advisor, I would like to thank the rest of my committee members: Dr. Shyam Aravamudhan and Dr. Sung-Jin Cho for their encouragement, insightful comments and questions.

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Abstract

Microencapsulation is a technique by which solid, liquid or gaseous active ingredients are enclosed within a shell material for the purpose of shielding the active ingredient from surrounding environment. The product therefrom is valuable as an active ingredient carrier and controlled release vehicle. In this research, polymer micro/nanocapsules with enclosed aqueous solution were synthesized through O/W emulsion-solvent evaporation technique. Specifically a commercial textile dye was encapsulated in poly (methyl methacrylate) (PMMA) micro/nanocapsules for an innovation of textile dyeing.

A variety of synthesis parameters were studied including concentration of polymer, amount of dye, amount of surfactant, volume of surfactant aqueous solution, solvent evaporation temperature, and stirring speed. The obtained PMMA/dye capsules had average diameters from hundreds of nanometers to tens of micrometers with encapsulation efficiency ranging from 58% to 76%. FTIR and DSC results further confirmed the capsule structure of PMMA/dye. This work demonstrated a promising approach to enclose solution of active reagent in polymer micro/nanocapsules with good encapsulation efficiency.

CHAPTER 1

Introduction

1.1 Background

The textile and clothing industry these days have evolved towards more groundbreaking and high quality products in order to distinguish themselves and also to enhance competitiveness. The new products are not only different for their designs but also for their uses. Recently, microcapsules have been applied to many functional and technical textiles. Examples of this include fragrances, aromatic deodorants, cosmetics, insect repellents, antibiotics, polychromic and thermochromic dyes, drug delivery and thermo-regulating systems. Microencapsulated fabrics should introduce new functionalities or enhance already present functionalities without affecting the look and feel of the textile [1]. Microencapsulation technique offers the possibility of producing novel textile products with many advantages compared to traditional textiles.

Although microencapsulation has found applications in other business sectors such as food, cosmetics and pharmaceuticals during the last few decades, a significant number of microcapsule-based commercial products in the textile industry did not appear until the 1990s, while many potential new products are still in the research and development stage [2]. The most attractive examples are fabrics with durable fragrances, garments with UV-ray absorbing microcapsules, fabrics with thermo-changeable dyes, military uniforms with microencapsulated insecticide, thermo-regulation vehicle seats, ski suits, gloves, and etc. In spite of some success in developing new products, there is a lot of room for further research especially in order to improve the mechanical strength of the obtained microcapsules and the kinetics and the mechanism of the release of active compounds. Numerous research focused on the development

of new methods of applying of microcapsules on textile, new immobilization techniques and materials are underway [3].

1.2 Objectives

The objective of this study is to investigate the encapsulation of an active ingredient in polymer micro/nanocapsules, particularly indigo dye solution is used as an application example for an innovative dyeing process. One important feature of these microcapsules is their stability, i.e. no dye release during stocking. An oil-in-water (O/W) emulsion-solvent evaporation technique was employed to allow encapsulation of the dye. The dye was mixed into a PMMA matrix in the composition range of 5-20% and Cetrimonium Bromide (CTAB) was used as surfactant to lower interfacial tension between oil and water phases and also prevent aggregation of newly formed drops. The synthesized micro/nanocapsules were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS), differential scanning calorimetry (DSC) and Fourier-transform infrared spectroscopy (FTIR).

1.3 Significance

Indigo is a challenging dye because it is not soluble in water. In conventional dyeing process, Indigo undergoes a chemical change (reduction). Reduction converts indigo into white indigo (leuco-indigo). When a submerged fabric is removed from the dye bath, white indigo quickly combines with oxygen in air and reverts to insoluble and intensely colored indigo. The dying process also requires several chemical manipulations, involving toxic materials and chances to injure workers [4]. PMMA Micro/nanocapsules with encapsulated indigo dye provides an alternative efficient way to dye fabrics. With this technique the dye in the capsules is

kept intact (no reduction and air-oxidation is required) during normal hours and can attach to fabric and release the dye at desired time through heat treatment.

CHAPTER 2

Literature Review

2.1 Introduction

In recent years, the use of several types of colloidal systems to encapsulate active ingredients has received considerable scientific attention and interest due to the numerous advantages of encapsulated systems [2]. Microencapsulation is the process of enclosing a substance inside a shell of a different material. Extremely tiny droplets or particles of solid, liquid or gaseous material are packed within a second material or coated with a continuous film of polymeric material for the purpose of shielding the active ingredient from the surrounding environment. The microcapsules range in size from one micron to several hundred micrometers and may or may not release their contents later by means appropriate to the application [5]. Depending on the state of the active ingredient encapsulated i.e. solid, liquid and gases the size and shape of the capsules can be affected. If a solid or a crystalline material is used as the core, the resultant capsule may be irregularly shaped. However, if the core material is a liquid, spherical capsules containing a single or numerous droplets of encapsulate may be formed. The capsulated particles produce their required effect when their core material is released [5, 6].

Microencapsulation prevents probable chemical reactions between the core and the surrounding environment. Having control over the release of the active material in the core is also another advantage of microencapsulation. Sometimes the term nanocapsules is used to emphasize that such microcapsules are in the size range of 10 – 1000 nm. Microencapsulation offers great opportunities for the improvement of the textile industry by the application of additional compounds such as fragrances, dyes, insect repellents, antimicrobials or phase changing materials [3, 7]. There has since been propulsive research of techniques for obtaining

products that can fulfil even the most demanding customer wishes which resulted in several commercial products and many more in the research and development stage. Consequently, nowadays products which were just a few decades ago considered to be science fiction are available in almost every market. The most illustrative examples are fabrics with durable fragrances, shirts with thermo-changeable dyes, military uniforms with microencapsulated insecticides, thermoregulation vehicle seats, ski suits and gloves [8].

2.2 Techniques to Manufacture Microcapsules

There are various techniques available for the encapsulation of core materials. Broadly the methods are divided into three types.

1. Chemical methods
2. Physico-chemical methods
3. Physico-mechanical methods

Table 1.

Different techniques used for microencapsulation

Chemical methods	Physico-chemical methods	Physico-mechanical methods
Interfacial Polymerization	Coacervation and Phase Separation	Spray drying and congealing
Poly Condensation	Sol-Gel Encapsulation	Fluid bed coating
In Situ Polymerization	Super critical fluid assisted microencapsulation	Pan coating
		Solvent Evaporation

2.2.1 Chemical methods

2.2.1.1 Interfacial polymerization (IFP). In this technique the capsule shell is formed at or on the surface of the core material by polymerization of the reactive monomers. The substances used are multifunctional monomers. Generally used monomers include multifunctional isocyanates and multifunctional acid chlorides. They are used either individually or in combination. The multifunctional monomers are dissolved in a liquid core material and then dispersed in water-based phase containing a dispersing agent. A co-reactant multifunctional amine could also be added to the mixture. This results in a rapid polymerization at interface and generation of capsule shell takes happens.

A polyurea shell will be formed when isocyanate reacts with amine, poly nylon or polyamide shell will be formed when acid chloride reacts with amine. When isocyanate reacts with hydroxyl containing monomer it produces a polyurethane shell [9].

2.2.1.2 In situ polymerization. Like IFP the capsule shell formation occurs because of polymerization monomers added to the encapsulation reactor. In this process no reactive agents are added to the core material, polymerization only happens in the continuous phase and on the continuous phase side of the interface formed by the dispersed core material and continuous phase. At first a low molecular weight prepolymer will be formed, as time goes on the prepolymer grows in size, it deposits on the surface of the dispersed core material thereby generating solid capsule shell [10].

2.2.1.3 Poly condensation. This process involves the polycondensation of two complementary monomers in a two phase suspension system. Each of the two complementary monomers dwells in one of the two immiscible phases in the suspension system. The resulting polycondensate, which is formed either at or on one side of the interface, may or may not be

soluble in the droplet phase. If the polymer is soluble in the droplets, particulate microspheres or monolithic microcapsules are formed, i.e. particle forming interfacial polycondensation. If the polymer is insoluble in the droplets, it forms a membrane around them and the droplets are consequently encapsulated by the polymer. This leads to the formation of capsular microspheres or reservoir microcapsules, and hence capsule forming interfacial polycondensation [11]. A major example of particle forming polycondensation is that of phosgene with bisphenol A, recently developed for the production of polycarbonate resins in particle form [12]. This technique is commonly used to synthesis polyamide microcapsules containing proteins for use in the pharmaceutical industry.

2.2.2 Physico-chemical methods

2.2.2.1 Coacervation and phase separation. This process involves a partial desolvation of a homogeneous polymer solution into a polymer-rich phase (coacervate) and the poor polymer phase (coacervation medium). This was the first reported process to be adapted for the industrial production of microcapsules [5, 9]. Currently, two methods for coacervation are available, namely simple and complex processes. The microcapsule formation procedure for both processes is identical except the phase separation step. In simple coacervation a desolvation agent is added for phase separation, whereas complex coacervation involves complexation between two oppositely charged polymers. The three basic steps in complex coacervation are: (i) formation of three immiscible phases; (ii) deposition of the coating; and (iii) rigidization of the coating.

The first three immiscible phases include; liquid manufacturing phase, core material and coating material. The core material is dispersed in a solution of the coating polymer. The coating material phase, an immiscible polymer in liquid state can be formed by; (i) changing temperature of polymer solution (ii) addition of salt (iii) addition of non-solvent, (iv) addition of incompatible

polymer to the polymer solution (v) inducing polymer – polymer interaction [13-15]. The second step involves the deposition of liquid polymer upon the core material. Finally, the prepared microcapsules are stabilized by crosslinking, desolvation or thermal treatment.

Crosslinking is the formation of chemical links between molecular chains to form a three-dimensional network of connected molecules.

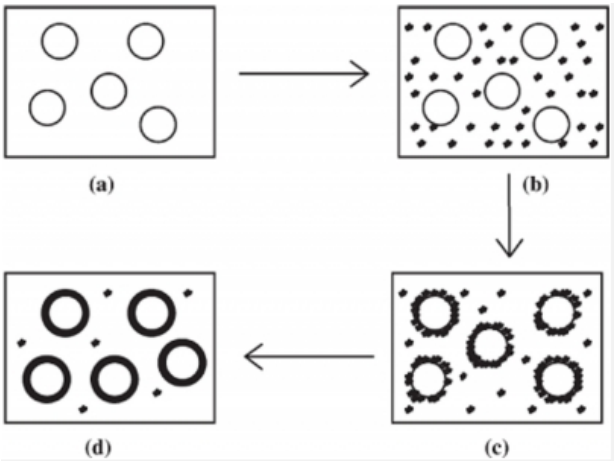

Figure 1. Schematic representation of the coacervation process [9].

(a) Core material dispersion in solution of shell polymer; (b) separation of coacervate from solution; (c) coating of core material by microdroplets of coacervate; (d) coalescence of coacervate to form continuous shell around core particles.

2.2.2.2 Polymer encapsulation by rapid expansion of supercritical fluids. Supercritical fluids are highly compressed gases that possess several advantageous properties of both liquids and gases. The most widely used being supercritical carbon dioxide (CO_2), alkanes (C_2 to C_4), and nitrous oxide (N_2O). A small change in temperature or pressure causes a large change in the density of supercritical fluids near the critical point. Supercritical CO_2 is widely used for its low critical temperature value, in addition to its nontoxic, non-flammable properties; it is also readily available, highly pure and cost-effective [9]. The most widely used methods are as follows:

- Rapid expansion of supercritical solution (RESS)

- Gas anti-solvent (GAS)
- Particles from gas-saturated solution (PGSS)

2.2.2.2.1 Rapid expansion of supercritical solution. In this process, supercritical fluid containing the active ingredient and the shell material are maintained at high pressure and then released at atmospheric pressure through a small nozzle. The sudden drop in pressure causes desolvation of the shell material, which is then deposited around the active ingredient (core) and forms a coating layer. The hindrance of this process is that both the active ingredient and the shell material must be very soluble in supercritical fluids. In general, very few polymers with low cohesive energy densities are soluble in supercritical fluids such as CO_2. The solubility of polymers can be enhanced by using co-solvents. In some cases non-solvents are used and this increases the solubility in supercritical fluids, but the shell materials do not dissolve at atmospheric pressure.

A group of researchers recently carried out microencapsulation of TiO_2 nanoparticles with polymer by RESS using ethanol as a non-solvent for the polymer shell such as polyethylene glycol (PEG), poly(styrene)-b-(poly(methyl methacrylate)-copoly (glycidal methacrylate) copolymer (PS-b-(PMMA-co-PGMA) and poly(methyl methacrylate) [16].

2.2.2.2.2 Gas anti-solvent process (GAS). This process is also called supercritical fluid anti-solvent (SAS). Here, supercritical fluid is added to a solution of shell material and the active ingredients and maintained at high pressure. This leads to a volume expansion of the solution that causes super saturation such that precipitation of the solute occurs. Thus, the solute must be soluble in the liquid solvent, but should not dissolve in the mixture of solvent and supercritical fluid. On the other hand, the liquid solvent must be miscible with the supercritical fluid. This process is unsuitable for the encapsulation of water-soluble ingredients as water has low

solubility in supercritical fluids. It is also possible to produce submicron particles using this method [17].

2.2.2.2.3 Particles from a gas-saturated solution (PGSS). This process is carried out by mixing core and shell materials in supercritical fluid at high pressure. During this process supercritical fluid penetrates the shell material, causing swelling. When the mixture is heated above the glass transition temperature (T_g), the polymer liquefies. Upon releasing the pressure, the shell material is allowed to deposit onto the active ingredient. In this process, the core and shell materials may not be soluble in the supercritical fluid [9].

2.2.3 Physico-mechanical process

2.2.3.1 Spray drying and congealing. Microencapsulation by spray-drying is a low-cost commercial process which is mostly used for the encapsulation of fragrances, oils and flavors. Core particles are dispersed in a polymer solution and sprayed into a hot chamber. The shell material solidifies onto the core particles as the solvent evaporates such that the microcapsules obtained are of poly core or matrix type [9].

Spray congealing can be done by spray drying equipment where protective coating will be applied as a melt. The core material is dispersed in a coating material melt rather than a coating solution. Coating solidification is accomplished by spraying the hot mixture into cool air stream. Waxes, fatty acids, and alcohols, polymers which are solids at room temperature but can be melted at reasonable temperature are applicable to spray congealing. Albertini B et al. prepared mucoadhesive micro particles and designed an innovative vaginal delivery systems for econazole nitrate (ECN) to enhance the drug antifungal activity [18].

2.2.3.2 Fluidized-bed technology. In this technique, a liquid coating is sprayed onto the particles and the rapid evaporation helps in the formation of an outer layer on the particles. The

thickness and formulations of the coating can be obtained as desired. Different types of fluid-bed coaters include top spray, bottom spray, and tangential spray.

In the top spray system the coating material is sprayed downwards on to the fluid bed such that as the solid or porous particles move to the coating region they become encapsulated. Increased encapsulation efficiency and the prevention of cluster formation is achieved by opposing flows of the coating materials and the particles. Dripping of the coated particles depends on the formulation of the coating material. Top spray fluid-bed coaters produce higher yields of encapsulated particles than either bottom or tangential sprays [9].

The bottom spray is also known as "Wurster's coater" in recognition of its development by Prof. D.E. Wurster [9, 19]. This technique uses a coating chamber that has a cylindrical nozzle and a perforated bottom plate. The cylindrical nozzle is used for spraying the coating material. As the particles move upwards through the perforated bottom plate and pass the nozzle area, they are encapsulated by the coating material. The coating material adheres to the particle surface by evaporation of the solvent or cooling of the encapsulated particle. This process is continued until the desired thickness and weight is obtained. Although it is a time consuming process, the multilayer coating procedure helps in reducing particle defects.

The tangential spray consists of a rotating disc at the bottom of the coating chamber, with the same diameter as the chamber. During the process the disc is raised to create a gap between the edge of the chamber and the disc. The tangential nozzle is placed above the rotating disc through which the coating material is released. The particles move through the gap into the

spraying zone and are encapsulated. As they travel a minimum distance there is a higher yield of encapsulated particles [9, 19].

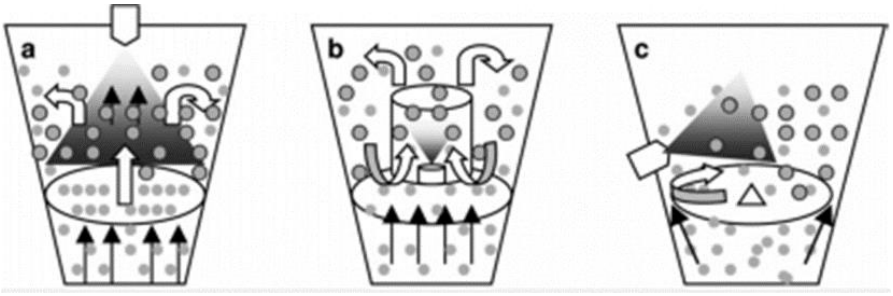

Figure 2. Schematics of a fluid-bed coater. (a) Top spray; (b) bottom spray; (c) tangential spray

2.2.3.3 Solvent evaporation. The coating material is dissolved in a volatile solvent, which is immiscible with the liquid manufacturing vehicle phase. A core material to be encapsulated is dissolved or dispersed in the coating polymer solution. This mixture is added to the liquid manufacturing vehicle phase with agitation, the mixture is heated to evaporate the solvent for polymer. Here the coat material shrinks around the core material and encapsulate the core.

Pseudoephedrine HCl, a highly water-soluble drug, was entrapped within poly (methyl methacrylate) microspheres by a water/oil/water emulsification-solvent evaporation method. An aqueous drug solution was emulsified into a solution of the polymer in methylene chloride, followed by emulsification of this primary emulsion into an external aqueous phase to form a water/oil/water emulsion. The middle organic phase separated the internal drug-containing aqueous phase from the continuous phase. Microspheres were formed after solvent evaporation and polymer precipitation [20].

2.2.3.4 Pan coating. For the microencapsulation of relatively large particles, pan coating has become wide spread in the pharmaceutical industry. With respect to microencapsulation, solid particles greater than 600 microns in size are generally considered essential for effective

coating and the process has been extensively employed for the preparation of controlled release beads. In practice, the coating is applied as a solution or as an atomized spray to the desired solid core material in the coating pan. Usually, to remove the coating solvent, warm air is passed over the coated materials as the coatings are being applied in the coating pans [21].

2.3 Mechanism of Microcapsule Shell Formation

As previously discussed in this chapter, there are many different ways in preparing microcapsules with aqueous cores.

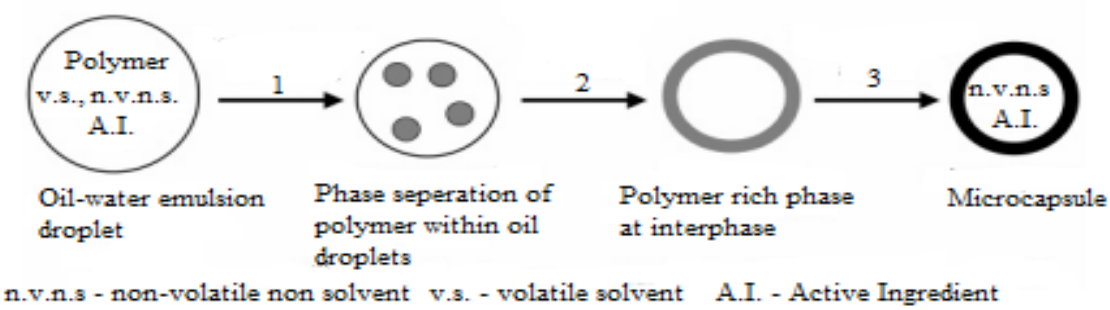

Figure 3. Schematic diagram of the shell formation mechanism (redrawn from [22])

1. Evaporation of the volatile solvent (v.s.); 2. Migration of the polymer-rich phase;

3. Evaporation of all volatile solvents (v.s.), and the formation of a microcapsule with a non-volatile, non-solvent (n.v.n.s.) core.

Figure 3 above shows schematically the basis of the various methods used for preparing the microcapsules. It illustrates that the dispersed oil phase involves dissolving the wall-forming polymer in a mixture of a volatile good solvent and a high boiling point poor solvent. When the good solvent is removed, the previously dissolved polymer separates from the remaining poor solvent, following which the polymer creates a shell at the oil droplet/water interface when the balance of interfacial tensions is correct [22].

Frequently, the encapsulation of water-soluble active components in microcapsules is achieved through the use of oil-in-water (o/w) emulsions. By considering different interfacial tensions between the polymeric shells (p), the oil phase (o), and the continuous water phase (w), i.e., γ_{op}, γ_{ow} and γ_{pw}, conditions required for microcapsule formation can be determined. Torza and Mason [23] evaluated the possible equilibrium morphologies adopted by droplets of immiscible liquids (oil (o) and polymer (p) phases) when brought into contact with a third mutually immiscible liquid (water phase (w)), in terms of the various interfacial tensions between the phases (γ_{op}, γ_{ow} and γ_{pw}). The spreading coefficients (S_i) for each phase can be determined by applying the following equation:

$$S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik}) \quad (1)$$

and defining the oil phase (o) to be that for which $\gamma_{ow} > \gamma_{op}$, in which case the spreading coefficient for the oil phase (S_o) is $S_o < 0$. In this way, there are only three possible combinations of S_i:

$$S_o < 0;\ S_w < 0;\ S_p > 0 \quad (2)$$

$$S_o < 0;\ S_w < 0;\ S_p < 0 \quad (3)$$

$$S_o < 0;\ S_w > 0;\ S_p < 0 \quad (4)$$

Core–shell morphology particles will form when conditions in Equation (2) are satisfied, with the oil phase being the core within a polymer phase shell. Particles with an acorn-shaped

morphology will be formed when Equation (3) is satisfied. And finally, when Equation (4) is satisfied, two separate droplets or hetero-aggregates will be formed [6].

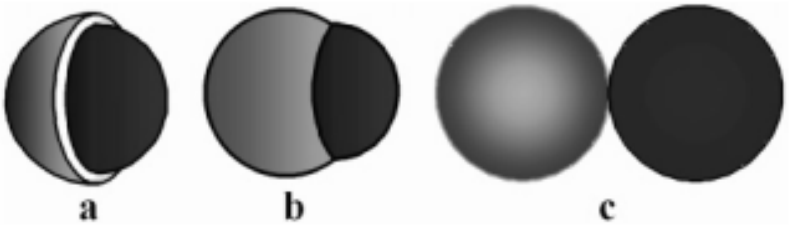

Figure 4. Three particle morphologies: (a) Core-shell microcapsule; (b) acorn; (c) two separate droplets (hetero-aggregates).

2.4 Applications of Microencapsulation

2.4.1 Microencapsulation in biological applications. Throughout these few decades, many new uses of the microencapsulation system have been investigated for pharmaceutical, chemical, food processing and biological applications. The advantages of microencapsulation technology as means of storing materials at microscopic level raise scientists' interest to further explore its potential application in drug delivery i.e. handling free suspended powder, masking tastes and smells, as well as providing an inert environment especially for medicinal applications for patients.

When considering microcapsules for drug delivery applications, their safety in use, site-specificity and release mechanism of a given active ingredient under different conditions such as pH value, enzymatic action, formulation (coating or shell material) are all well thought out. Natural or semi-synthetic polymers such as polysaccharides, cellulose, proteins, lipids, polyesters and inorganic sulfate and silicates can also be employed as coating or shell for producing microcapsules [24]. Researches on pharmaceutical applications for anti-inflammatory drugs, antibiotics and anti-tumor drugs have been reported [25]. For medicinal or health product applications, applied formulation with edible and nutrition beneficial oil, such as soybean oil,

castor oil, shark liver oil, tuna oil, orange peel oil or corn oil have been encapsulated in various biodegradable polymer shells [26].

2.4.2 Microencapsulation in textile applications. Recently, it can be seen that there are increased appeal and uses of microencapsulation in the textile industry. The main uses include phase change materials, aromatherapy, photochromic and thermochromic dyes, flame retardants and cosmetic textiles [7, 27]. Microcapsules can be applied to textiles by padding, coating, spraying or immersion without altering their feel or color. For all these methods a binder is required. It may be acrylic, polyurethane, silicone, starch, etc. Its role is to fix the capsules onto the fabric and to hold them in place during washing and wear. Microcapsules can be applied to silk, cotton, synthetic fiber, etc. and may contain perfumes, cosmetic products, antimicrobials, thermochromes, flame-retardants, dyes, phase change materials, etc. [28]. The textile support may be cotton, silk, nylon, polyester, natural and artificial leather, etc.

The main challenge in the process of developing microcapsules with application in the textile industry is producing a capsule with adequate mechanical strength to endure the process of application to the textile. Also, the obtained microcapsules have to provide the desired mechanism and the rate of release of encapsulated compounds, stability and non-toxicity [3].

2.4.2.1 Phase-change materials. The development of microencapsulation with the integration of phase-change materials was originally developed by the US National Aeronautics and Space Administration (NASA) in the 1980s. The development achieved the thermo-regulatory property in the extreme variation of temperature encountered by the astronauts when it was applied in the space suits. Although the technique was not taken up ultimately, the potential of using the microencapsulation technique was recognized.

Phase change material (PCM) is a substance with a high heat of fusion. It can melt and solidify at a certain temperature and is capable of storing and releasing a large amount of energy. Heat is absorbed or released when the material changes from solid to liquid and vice versa. Hence, PCMs are classified as latent heat storage units. The microcapsules provide a relatively large surface area for heat transfer. The rate at which the PCM reacts to the external temperature changes is very fast. The PCM is mostly beneficial to the part of the body where there is the greatest impact due to the extreme temperature. Many researchers have concentrated their studies on encapsulating phase change materials and further applying them to textile materials.

Shin et al. [29] prepared melamine-formaldehyde microcapsules containing eicosane by in situ polymerization. The microcapsules were spherical and strong enough to secure capsule stability under stirring in hot water and alkaline solutions. The prepared microcapsules were added to polyester knit fabrics by a conventional pad-dry-cure process to develop thermo-regulating textile materials. The thermo-regulating fabrics had heat storage capacities of 0.91-4.44 J/g, depending on the concentration of the microcapsules. The treated fabrics were capable of retaining 40% of their heat storage capacity after five launderings.

Researchers Fallahi et al. prepared phase change material microcapsules containing solid paraffin or camel fat as core materials synthesized by in situ polymerization using melamine-formaldehyde as shell material. The shell resin was strong and stable enough to prevent the liquid oils from seepage and leaking at 80 °C. The effect of prepared camel fat microcapsules on the delay of heat was determined through examining a covered polyester/ viscose-fiber fabric. The loaded fabric samples with 10% (w/w) camel fat microcapsules delayed the rise of temperature of the covered thermometer when exposed to heat at 50 °C oven [30].

Similarly, Salaun et al. also studied microcapsules containing phase change material for textile thermal insulation. The stability and phase change behavior of paraffin mixture were studied in order to define an optimum formulation with a wide temperature range. The addition of approximately 4 wt% tetraethyl orthosilicate in n-haxadecane-n-eicosane mixture was found to improve latent heat of phase change [31].

2.4.2.2 Fragrant textiles. Aromatherapy is a form of alternative medicinal treatment that uses plant materials known as essential oils. Similar aromatic compounds can be extracted from the plants for the purpose of improving a person's mood, cognitive function or health. Preliminary scientific evidence is growing in all these areas. In recent years, aromatherapy has been introduced into this stressful ambience of the modern world. The controlled release of the fragrance can give the well-being and comfort feeling among the users. Some of the fragrances used for aromatherapy are applied to performance apparel.

The addition of fragrance to textiles has been carried out for many years. The most commonly used method is to use fabric conditioners in the wash during tumble drying. However, the effect of the fresh aroma is relatively short-lived. Although later there are some technologies invented to apply fresh aroma to the textile, the outcome is still short lived. It is only through microencapsulation that the fragrances are able to remain on a garment or textile during a significant part of its lifetime and withstand a number of washing cycles. The studies of microencapsulated fragrance in textile applications have been investigated over the years.

Researchers Hwang et al. prepared melamine resin microcapsules containing Migrin oil by in-situ polymerization method. The structure, mean particle size and size distribution, morphologies, thermal properties and released behavior were characterized and discussed [32]. Korean researchers Hong and Park also prepared poly (L-lactide) microcapsules for fragrant

fiber by interfacial precipitation method through solvent evaporation from water-in-oil-in-water emulsion. The microcapsules were then uniformly printed on the cotton fabrics and the resulted fabric could withstand 15 cycles of washing durability [33].

Specos et al developed fragrance microcapsules with complex coacervation using gelatin and Arabic gum or by encapsulation in yeast cells and made the comparison. The microcapsules increased the durability of the fragrance on the treated fabrics and withstood one wash [34]. Wang et al. developed natural fragrant microcapsules with ethyl cellulose (EC) as a shell and lavender oil as a core which were prepared by emulsify-solvent diffusion method. The microcapsules were in spherical shape and most of their particle size were about 1µm. Encapsulation efficiency and the oil loading capacity were high with a satisfied fragrant releasing rate [35].

2.4.2.3 Photochromic and thermochromic dyes. There are two major types of color-changing systems namely thermochromatic and photochromatic. Thermochromatic changes its color in response to temperature and photochromatic changes color in response to UV light. Today the manufacturers can make the dyes which are capable of changing color at the specific temperature in response to the body heat. Many photochromics and nearly all thermochromics require microencapsulation for protection. New technologies of color changing are on the way like microencapsulated hydrochromic dyes in response to water and also piezochromic dyes which change color in response to pressure [36].

2.4.2.4 Flame retardant. The conventional flame retardant treatments on garments or fabrics mostly do not have the durability once they are sent to wash. The solubility of flame-retardant substances used is also very dangerous to people who work under severe condition like firemen. Hence, the microencapsulation can provide the flame retardant with protection within

the shell of a suitable polymer coating. As a result, the flame retardant can last longer inside the capsules and the durability is also enhanced. Sometimes the shell of some specific polymers can also act as adhesive to attach themselves to the textiles or clothing.

Giraud et al. prepared two types of microcapsules of di-ammonium hydrogen phosphate (DAHP) with polyether-polyurethane shell and polyester-polyurethane shell respectively. They were evaluated as intumescent flame retardant (FR) in a commercial polyurea coating for textiles. The reaction to the fire of cotton fabrics coated by FR polyurea and loaded with neat or microencapsulated DAHP was studied with a cone calorimeter as the fire model. It was found that coatings containing microcapsules with polyester-polyurethane shell evolved the smallest quantity of smoke and carbon monoxide [37].

Chinese researchers, Lin et al. also encapsulated water-soluble flame retardant containing organophosphorous using interfacial reaction and conventional multiple-emulsion processes and conducted its application on fabric. The microcapsules were synthesized with the water soluble dimethyl methyl phosphorate (DMMP) acting as the core material and the acetal product of polyvinyl alcohol (PVA) and glutaraldehyde (GA) acting as the shell material. The microcapsules with the core of organophosphorous claimed to have promising application in inflaming retardant of cotton fabric [38].

Wang and his co-workers prepared melamine-formaldehyde resin microencapsulated red phosphorus for the first time using montmorillonite as a stabilizer. Particle size analysis showed that montmorillonite could function as an effective stabilizer during the microencapsulation process of red phosphorus, and montmorillonite had the similar effects of the common surfactant sodium dodecyl sulfate (SDS). Moreover, the obtained montmorillonite stabilized microcapsules also exhibited lower water absorption (0.3%) and higher ignition point (360 °C) compared with

the common red phosphorus microcapsules stabilized with surfactant SDS (the water absorption is 1.2% and the ignition point is 350 °C) [39].

2.4.2.5 Cosmetic textiles. Cosmetic textiles are the functional garments which come into direct contact with the skin. Some active substances which are used for cosmetic purposes are then introduced to the skin through friction or other trigger mechanisms, in particular, to combat ageing effects in order to promote a younger look. In cosmetic textiles, the major interest in microencapsulation is currently in the application of vitamins, essential oils, skin moisturizing agents, skin cooling agents and anti-ageing agents. However, only a few studies regarding techniques of producing microcapsules containing cosmetic substances have been found in literature.

Yamato et al. patented microcapsules comprising the active substances to improve physiological conditions of the human skin. The microcapsule would not be broken during production but was gradually released when the textiles structure was subjected to light pressure created by the movement of the human body [40].

Nelson introduced the use of waste yeast cells in the microencapsulation process. After encapsulating the core material, the yeast cells were attached to both cotton and wool fiber by using cross linking agents and binders. The use of yeast cells as wall material generally provided several advantages such as, high loading, protection from light, oxygen and hazardous environment and cost effectiveness [7].

A commercial company, Cognis has developed Skintex Care System which uses chitosan to encapsulate the active ingredients to form an ‘active wellness garment’. Cognis has devised Skintex ingredients for moisturizing and relaxing, anti-cellulite, hair retardant and tanning. The active ingredients present in the Skintex Care System are mainly released by three different

mechanisms which are friction between fabric and skin, biodegradation of the natural biopolymer membrane of the microcapsules and the dissolution of the membrane when the pH condition is changed [41].

2.4.2.6 Others. Many researchers have also done a lot to improve the durability of microencapsulated products. Li et al. investigated the effect of UV curing for encapsulated aroma finish on cotton. The aroma function was prolonged to 50 wash cycles whereas the traditional curing method could only withstand half of that. They also studied the durability of microencapsulated aroma textiles with respect to different binders, for example polyurethane and acrylic binders and different curing apparatus; conventional hot air tender, infrared lamp and microwave oven [42, 43].

Salaun et al. also investigated the efficiency of binders that linked microcapsules onto textile surface. The result revealed that a polyurethane-based binder was the most suitable one to link up melamine formaldehyde microcapsules. Furthermore, the adhesion of microcapsules was closely dependent on the chemical nature and structure of the textile [31].

Monllor and his group also studied the effect of resin on the adhesion of microcapsules to cotton fabrics. The results showed the influence of resin quantity on the microcapsule resistance to washing out of the fabrics during washing treatments [44].

CHAPTER 3

Methodology

3.1 Materials

3.1.1 Shell polymer. Poly (methyl methacrylate) (PMMA) was chosen as the polymer to encapsulate the dye.

PMMA is the polymer of methyl methacrylate, with chemical formula $(C_5H_8O_2)_n$. It is a clear, colorless polymer and is commonly called acrylic glass or simply acrylic. PMMA is a linear thermoplastic polymer. It has a glass transition temperature (T_g) around 105°C and it can be varied for different molecular weight. It is insoluble in water but soluble in organic solvents. It has high mechanical strength, high Young's modulus and low elongation at break. It does not shatter on rupture. It is one of the hardest thermoplastics and is also highly scratch resistant. It exhibits low moisture and water absorbing capacity due to which products made with them have good dimensional stability. It is also one of the polymers that is most resistant to direct sunshine exposure. Its strength characteristics exhibit fairly small variations under the effect of UV radiation. These properties make it suitable for products intended for long open air use. PMMA with average molecular weight ~120,000 acquired from Sigma-Aldrich was used for this work.

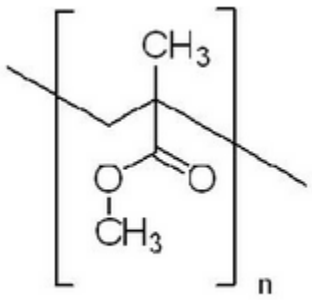

Figure 5. Chemical structure of poly (methyl methacrylate) (PMMA)

3.1.2 Active ingredient (core). When the polymer contains a liquid core it should have some very important properties. First, it should have water solubility as small as possible. Second, a very high interfacial tension between the core liquid and aqueous phase is needed. Also, the core oil should have a very high boiling point and very low vapor pressure not to be removed during solvent evaporation. Besides, it is preferable that the solubility of the core oil in the polymeric shell is as small as possible.

Considering all the requirements above a liquid dye received from Dystar was used for the interior core. Dystar Indigo ($C_{16}H_{10}N_2O_2$) is an odorless, blue liquid with density = 1.1 g/cm^3 and boiling point around 100 $^{\circ}$C They have restrictive miscibility or solubility in organic solvents, but very low solubility in water.

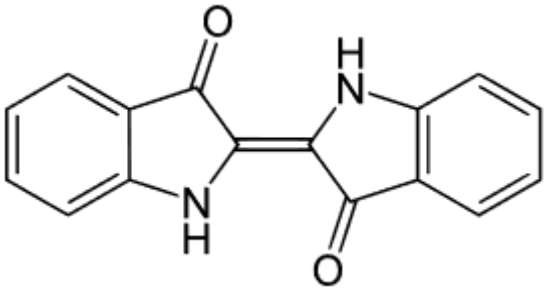

Figure 6. Chemical Structure of Indigo Dye

3.1.3 Solvent. In the o/w emulsion solvent evaporation method the solvent selection plays a very vital role in the evaporation stage. Therefore, some requirements need to be met by the solvent when used for preparing microcapsules with this method. The first requirement is the immiscibility of the solvent with water but solvent diffusion into the aqueous phase is also needed to get a control of the rate of evaporation. The diffusion of the solvent depends on its water solubility; very low water soluble solvents would diffuse very slowly into the aqueous phase and evaporate slower and on the other hand a highly water immiscible solvent slows down the evaporation rate. Another important requirement is for the solvent to allow the complete

dissolution of both polymer and dye. Additionally, a high vapor pressure is required to enhance and speed up the removal of the solvent from the water/air interface by evaporation [45].

The solvent used in this work is dichloromethane (DCM; Sigma-Aldrich)), which is miscible with organic solvents, has a very low miscibility with water (17.5g/l at 25°C), a boiling point of 40°C and vapor pressure of 57.3kPa at 25°C.

3.1.4 Surfactant. A surfactant lowers the surface tension at the interface between materials. The capsules can only grow bigger than a few tens of nanometers by successfully growing larger than their Kelvin barrier. This barrier is determined by the available surface energy and the radius of curvature of the particle. So when the particle is too small and doesn't have enough surface energy to exceed the Kelvin barrier, the low surface tension due to the high radius of curvature won't allow the particle to grow any larger. The surfactant modulates the available surface energy of the particles so that the surface tension decreases, and the Kelvin barrier moves, allowing more particles to escape the aggregation process and generally lowering the mean particle size. The surfactant is dissolved in the disperse phase rather than the continuous phase as this often leads to smaller droplets [46].

Cetrimonium Bromide ($(C_{16}H_{33})N(CH_3)_3Br$, CTAB)(Sigma-Aldrich) with a solubility of 36.4 g/l in water was used as the surfactant in this work.

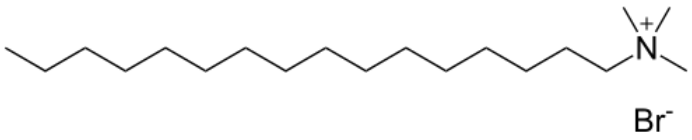

Figure 7. Chemical structure of Cetrimonium Bromide (CTAB)

3.1.5 Other Materials. Isopropyl alcohol (Sigma Aldrich, boiling point = 80 °C) was used as the extraction solvent.

3.2 Synthesis of Microcapsules

PMMA-dye microcapsules were prepared by an oil-in-water emulsion solvent evaporation procedure according to this specific description: PMMA was dissolved in DCM and then mixed with dye as a homogenous solution (organic phase) under the conditions listed in Table 2. Next, an aqueous surfactant (CTAB) solution is also prepared. The aqueous phase was stirred mechanically at 1200 rpm and the organic phase was added drop-wise over 60 seconds to form an oil-in-water emulsion. The agitation was kept at the same speed for 3 hours. After the evaporation of DCM, dye encapsulated in PMMA shells were obtained. Finally, they were centrifuged four times at 2000 rpm for 10 minutes each time discarding the supernatant and adding distilled water to get rid of as much surfactant and dye on the surface of the microcapsules as possible following which the microcapsules were dried at room temperature in the fume hood.

Several batches of microcapsules were prepared by varying the concentration of PMMA; the amount of dye, the amount of surfactant, volume of the aqueous phase, solvent evaporation temperature and agitation speed.

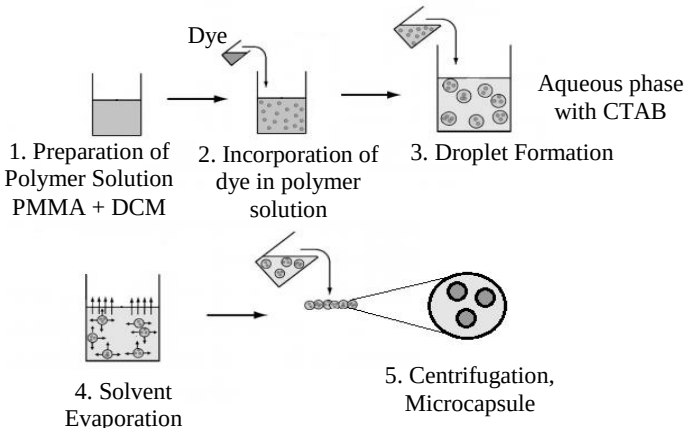

Figure 8. Schematic representation of the preparation of microcapsules.

Table 2.

Different conditions used for preparing PMMA microcapsules

Sample Number	PMMA (g)	DCM (ml)	Dye (g)	Water (ml)	CTAB (g)
1	1	10	0.5	50	0.5
2	1	10	1	50	0.5
3	1	10	2	50	0.5
4	2	10	0.5	50	0.5
5	4	10	0.5	50	0.5
6	1	10	0.5	50	0.1
7	1	10	0.5	50	1
8	1	10	0.5	50	2
9	1	10	0.5	75	0.5
10	1	10	0.5	100	0.5

3.3 Characterization

3.3.1 Microscopy. The surface morphology of the microcapsules was examined by scanning electron microscope. SEM analysis was carried out using a Carl Zeiss Auriga-BU FIB FESEM. Prior to examination, the samples were sputter with gold-palladium using Leica EM ACE200 sputter coater to render them electrically conductive. The internal structure of the microcapsules was also studied with a Carl Zeiss Libra 120 Plus TEM.

3.3.2 Dynamic light scattering. Size distribution of the microcapsules was determined using dynamic light scattering (DLS), Malvern Instruments-Zetasizer ZS. Dynamic Light

Scattering (DLS) works by measuring the intensity of light scattered by the molecules in the sample as a function of time. When light is scattered by a particle some of the incident light is scattered. Since all molecules in solution diffuse with Brownian motion in relation to the detector there will be interference (constructive or destructive) which causes a change in light intensity. Using the scale of light intensity fluctuations, DLS can provide information regarding the average size, size distribution, and polydispersity of particles in solution by measuring the diffusion of particles moving under Brownian motion, and converting this to size and a size distribution using the Stokes-Einstein relationship. The DLS was run on 1mL of very dilute microcapsules dispersed in water. Reproducibility was checked by running the sample in triplicate.

3.3.3 Differential scanning calorimetry. Differential scanning calorimetry (DSC) is a thermal analysis technique which measures the temperature and heat flow associated with transitions in materials as a function of temperature and time. Such measurements provide quantitative and qualitative information about physical and chemical changes that include endothermic/exothermic processes or changes in heat capacity.

The DSC analysis of the dye, blank PMMA microcapsules and dye-loaded PMMA microcapsules was carried out using TA Q200 DSC to evaluate any possible dye-polymer interaction. The three samples were accurately weighed using an electronic balance and heated in sealed aluminum pans at a rate of 10 °C/min from 40 °C to 300 °C temperature range under a nitrogen flow of 50 mL/min.

3.3.4 Fourier transform infrared spectroscopy. All materials above absolute zero emit infrared (IR) light. However, when molecules are radiated by infrared light, the IR light can be absorbed and the absorbed energy causes vibration in the atomic bonds. Specific atomic groups

tend to absorb infrared light at particular wavelengths, regardless of the response of other chemical bonds in the rest of the molecule. The fact that different atomic groups absorb at different IR wavelengths can be used to identify the structure of molecules. PMMA-dye interactions were also studied by FTIR spectroscopy. The spectra were recorded for dye, void PMMA microcapsules and dye encapsulated PMMA microcapsules using Varian 670 FTIR/610 Spectrometer with Single Point Detector.

3.3.5 Amount of dye encapsulated. The amount of encapsulated dye was also evaluated via an extraction method using isopropyl alcohol as the extracting solvent [47]. 50mg of the microcapsules were ground with a pestle on a filter paper and then inserted in an oven for 5 hours at 120 °C. Afterwards, the microcapsules were crushed again to ensure the PMMA shell was broken. The crushed microcapsules were collected and washed with 20 mL of Isopropyl alcohol and dried overnight in an oven at 80 °C. The percentage of the microcapsule made up of shell (W_{shell}) and core contents (W_{core}) could be calculated by knowing the initial weight of intact microcapsules (W_i) and the weight of the residual shell (W_s).

$$W_{shell} = \frac{W_s}{W_i} \times 100\% \quad (5)$$

$$W_{core} = \left(1 - \frac{W_s}{W_i}\right) \times 100\% \quad (6)$$

CHAPTER 4

Results

4.1 Morphology of Microcapsules

The morphology of the microcapsules was observed by scanning electron microscopy. The SEM images show regular spherical shapes with various size ranges.

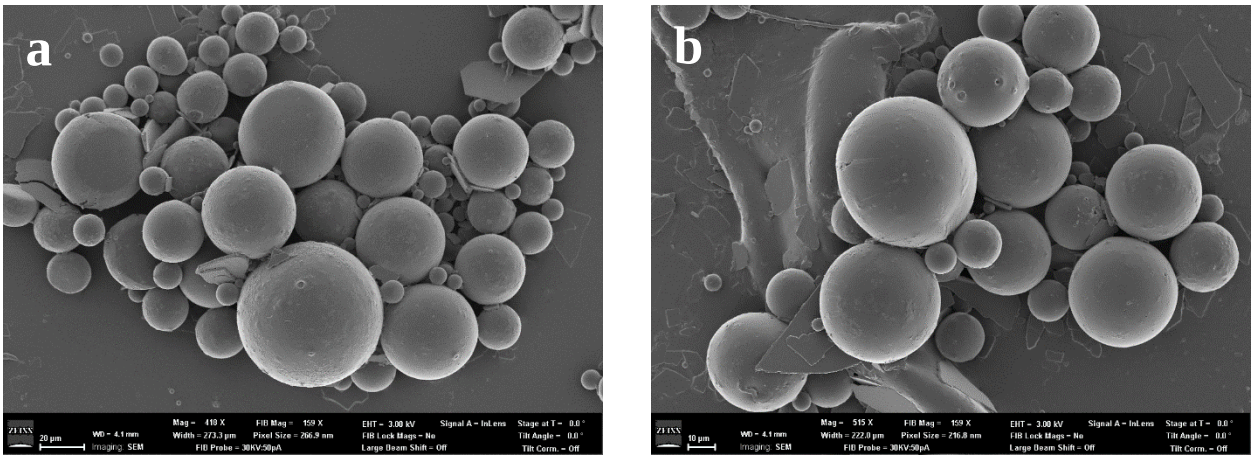

Figure 9. SEM micrographs of PMMA:Dye microcapsules ((a) 420x magnification & (b) 515x magnification)

Figure 10 below shows the SEM images of the PMMA:Dye microcapsules at different compositions. The microcapsules are fairly well dispersed with broad particle size distributions and they are mostly intact. Few of the images show a microcapsule with a broken shell. This may be attributed to the high speed (1200 rpm) at which the solution was stirred. The presence of a shell is clear from the images, indicating the successful encapsulation of the dye. Teeka et al. [48], who studied micro-encapsulated of jasmine oil in PMMA also observed that most of the microencapsulated particles were still intact, though some of them were ruptured.

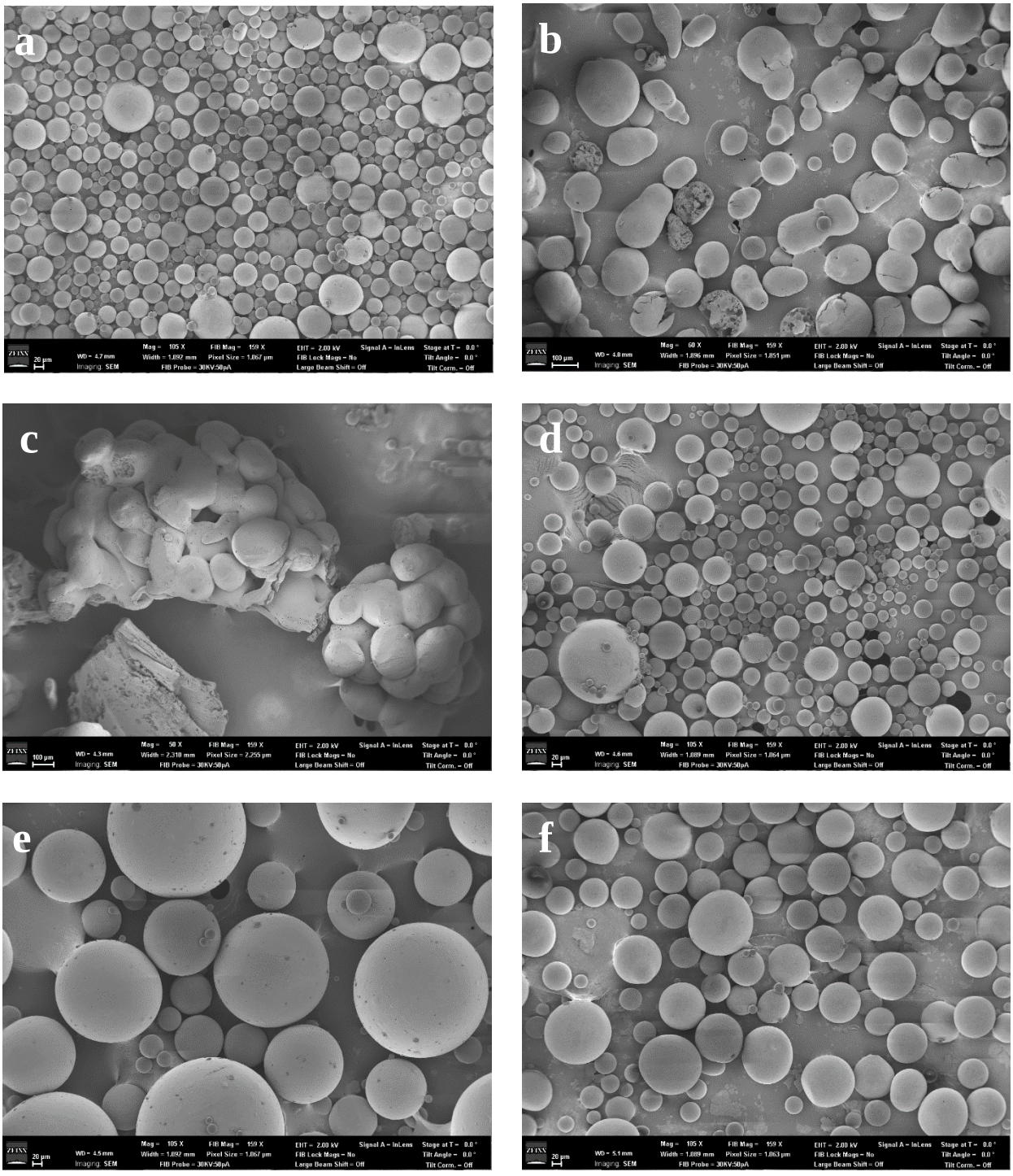

Figure 10. SEM micrographs of PMMA-dye microcapsules

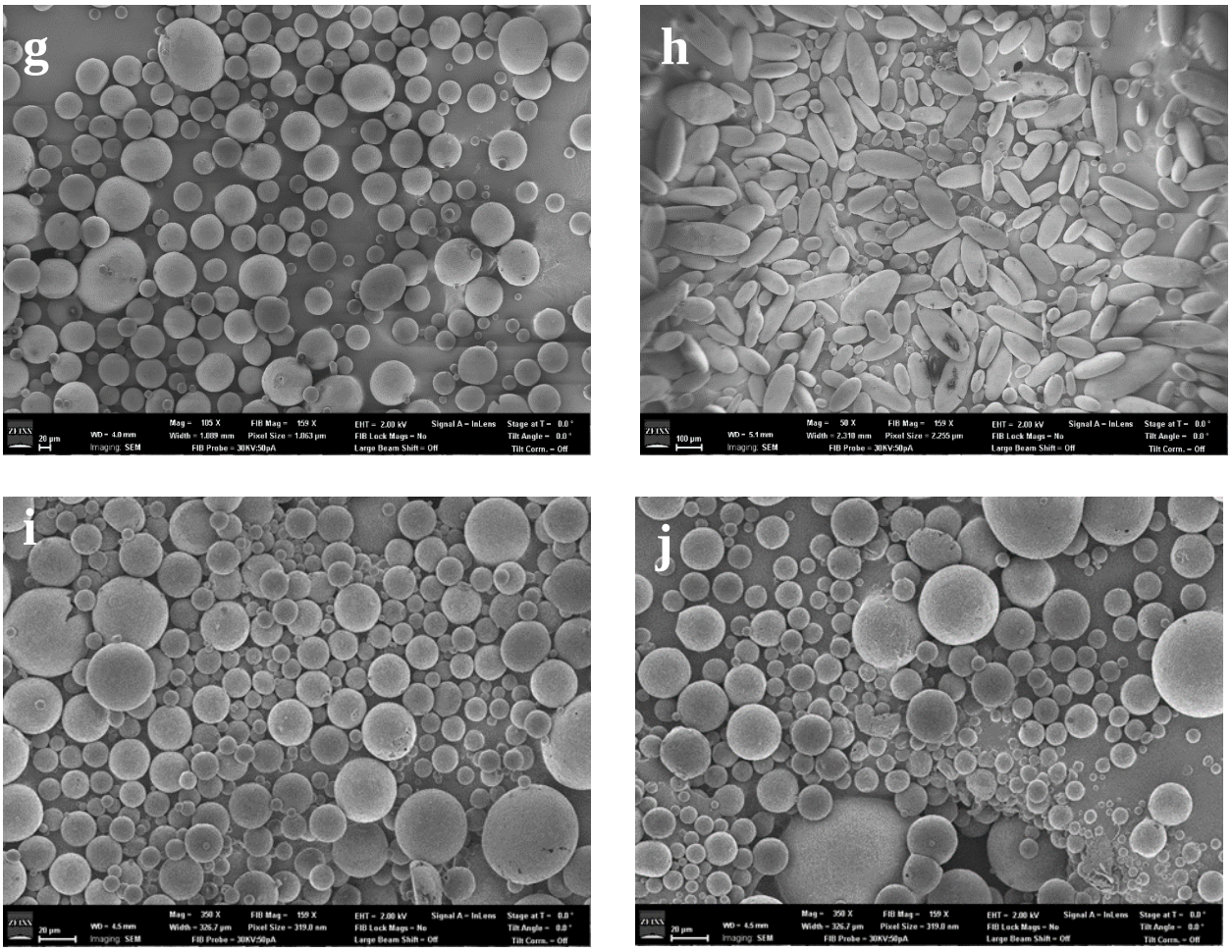

Figure 10. Cont.

(a) Sample 1 (b) Sample 2 (c) Sample 3 (d) Sample 4 (e) Sample 5 (f) Sample 6 (g) Sample 7 (h) Sample 8 (i) Sample 9 (j) Sample 10 (Sample numbers from Table 2)

The hard surface of the prepared microcapsules confirmed our assumption that PMMA shells were formed. It is interesting to note that the microcapsules present many internal cavities, corresponding to the type B of the droplet classification according to Dobey et al. [49]. Thus the synthesized microcapsules can be classified as multi compartmental microcapsules or multicore microcapsules. SEM images of fractured microcapsules reveal a multi internal cavity.

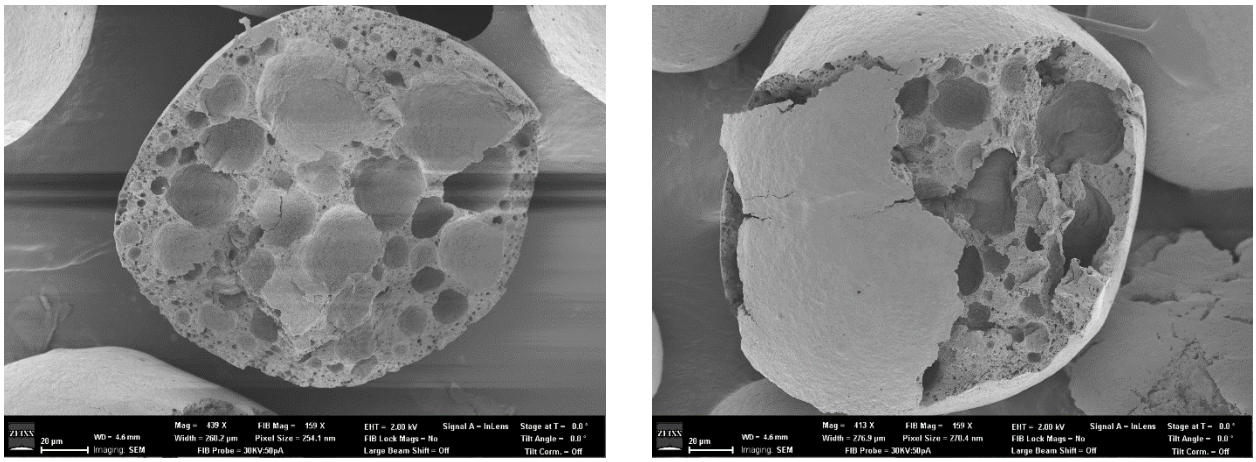

Figure 11. SEM showing interior structure of fractured microcapsules.

This was further illustrated using Transmission Electron Microscope (TEM), Figure 11 showing many lighter regions surrounded with darker areas. The lighter portions are assumed to be the encapsulated dye regions and the darker areas the hard PMMA shell.

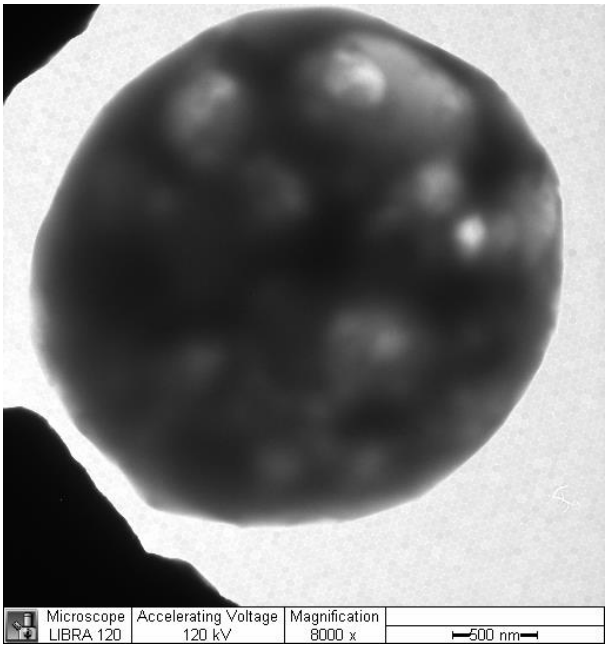

Figure 12. TEM image showing multi internal cavities

The behavior and the distribution of the surfactant at the PMMA-dye interface is most likely the reason for the multicore morphology. The CTAB will accumulate at and stabilize the interface between the polymer-rich and the dye-rich phase. However, CTAB is cationic in nature and the surfactant-decorated oil droplets will repel each other and prevent coalescence. The stabilized and dispersed oil droplets will ultimately freeze inside the glassy PMMA phase once all DCM has evaporated, thereby maintaining the original multicore–shell morphology from the initial stages of the coacervation (see Figure 1).

Figure 13. Photograph of PMMA capsules with indigo dye encapsulated

CHAPTER 5

Discussion and Future Research

5.1 Effect of Various Processing Parameters on the Particle Size Distribution and Encapsulation Efficiency of PMMA-dye Microcapsules

In this section, the influence of the concentration of PMMA, variation of the dye content, amount of surfactant used, the volume of aqueous phase, solvent evaporation temperature and stirring speed on the diameter and encapsulation efficiency of the microcapsules were evaluated. It will be concluded that the interaction between the indigo dye in the solvent (DCM) or PMMA and CTAB in the aqueous phase is key for the core–shell formation as well as for the colloidal stability.

Table 3.

Effect of Processing Parameters on the Particle Size Distribution of PMMA-dye Microcapsules

Processing Parameters		Particle Size Distribution (nm)
PMMA-dye Ratio	1:0.5	1473±110
	1:1	2674±49
	1:2	17372±141
	2:0.5	3770±85
	4:0.5	5261±142
Percentage of CTAB in 50 mL aqueous phase	0.2%	1480±63
	2%	1264±17
	4%	10028±382

Table 3.

Cont.

Volume of Aqueous Phase (mL)	75	3540±196
	100	4330±29
Temperature for Solvent Evaporation (°C)	40	993±59
Stirring Speed (rpm)	800	5714±160
	1000	4882±37

Table 4.

Effect of Various Processing Parameters on the Encapsulation Efficiency of PMMA-dye Microcapsules

Processing Parameters		Encapsulation Efficiency (%)
PMMA-dye Ratio	1:0.5	68.62±1.05
	1:1	71.13±0.67
	1:2	76.42±0.59
	2:0.5	70.33±0.70
	4:0.5	75.25±1.32
Percentage of CTAB in 50 mL aqueous phase	0.2%	64.91±1.08
	2%	69.27±0.49
	4%	76.33±1.70
Volume of Aqueous Phase (mL)	75	69.25±0.71
	100	73.89±0.77

Table 4.

Cont.

Temperature for Solvent Evaporation (°C)	40	58.00±1.06
Stirring Speed (rpm)	800	64.29±2.33
	1000	66.95±0.27

5.1.1 The effect of concentration of PMMA. Microcapsules with multicores are produced using the O/W emulsion solvent evaporation technique. From the results obtained, although the microcapsules had similar surface morphology, the sizes of the microcapsules and their encapsulation efficiency were controlled by changing the concentration of the polymer dissolved in an organic solvent. The increase in the polymer concentration shows increase in the size of the microcapsule. The reason being with increase in the concentration of PMMA the viscosity of organic phase also increases which makes it difficult to form smaller emulsion droplets and thus leads to the formation of bigger microcapsules.

Also, microcapsules made at higher polymer concentrations have higher encapsulation efficiency compared to those fabricated at lower concentrations. This may be because with high polymer concentration, viscosity of the solution increases resulting in faster hardening of the polymer and this reduces dye diffusion into the aqueous phase.

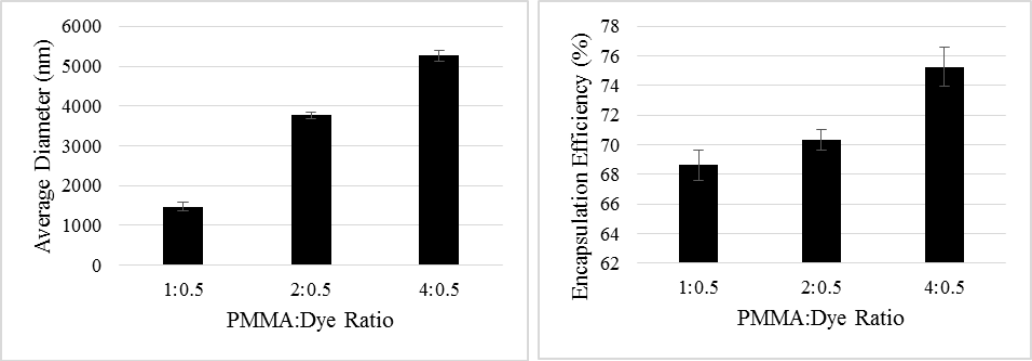

Figure 14. Graphs showing effect of PMMA:Dye Ratio on Average diameter (left) and Encapsulation Efficiency (right)

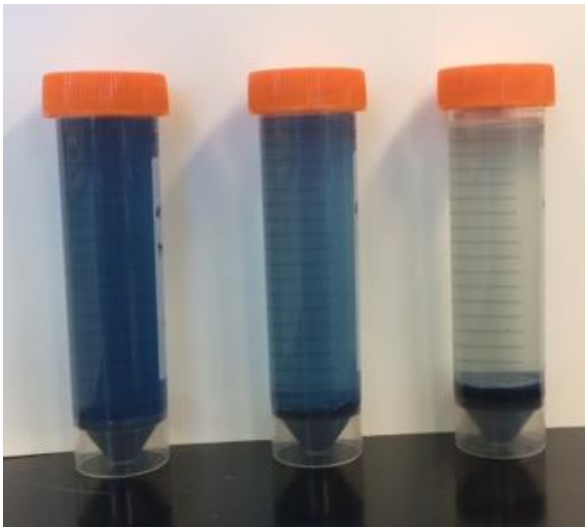

Figure 15. Photograph of PMMA-dye microcapsules in the aqueous phase after centrifugation showing amount of dye used in encapsulation. From left to right 1:0.5, 2:0.5, 4:0.5 PMMA:Dye ratio

5.1.2 Variation of dye content. As the quantity of dye increased in the microcapsule sample formation, the size of the microcapsules also changed. For 1:0.5 PMMA:Dye weight ratio sample (Figure 10a) and 1:1 PMMA:Dye weight ratio sample (Figure 10b), smooth polymer shells were observed. This may be due to the utilization of enough amount of PMMA which is adequate to completely encapsulate the dye. In contrast, irregular and large aggregated

microcapsules were formed due to the formation of unstable emulsion using the 1:2 weight ratio of the PMMA:Dye (Figure 10c).

During the course of the coacervation process depicted in Figure 1, the emulsion droplet becomes increasingly hydrophobic. This leads to an accumulation of CTAB at the dye–water interface and a subsequent PMMA solidification at the CTAB tail (PMMA is hydrophilic), which increases in magnitude during the solvent evaporation. The CTAB layer at the interface of the emulsion droplet prevents immediate migration of the dye and maintains the integrity of the PMMA droplet. It is clear that amount of dye facilitated by the strong interaction with CTAB at the emulsion droplet is also important for the colloidal stability. Therefore, the increase in dye leads to a very small adsorption of CTAB which cannot keep the polymer droplets dispersed which in turn eventually leads to complete aggregation of the PMMA microcapsules after solvent evaporation in the dispersed phase. Increase in the PMMA:Dye ratio is accompanied with increase in average size of the microcapsules and higher encapsulation efficiency.

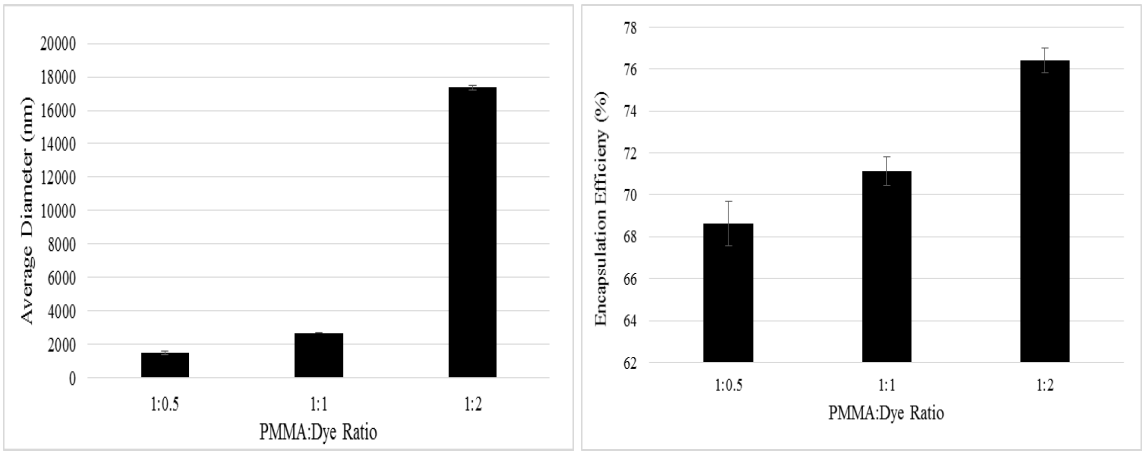

Figure 16. Graphs showing effect of dye content variation on average diameter (left) and Encapsulation Efficiency (right)

5.1.3 Amount of surfactant (CTAB). Microcapsules prepared with low amount of CTAB are overall larger, which was expected considering that they will show a weakened steric

hindrance. First, it was experimentally proven in this work that without CTAB it is impossible to produce the microcapsules. An increase in CTAB leads to a reduction in the particle size and a narrower size distribution but a further increase (4%) increased the size and also changed the shape of the microcapsules (Figure 10h). The addition of CTAB to the emulsion aqueous phase reduces the surface tension between the various components in the solution and had a strong effect on the emulsification which results in a decrease in size of the emulsion droplets. Also, by increasing CTAB concentration from 0.2 to 2.0%w/v, the emulsion droplets were stabilized to avoid coalescence, resulting in smaller microcapsules. After reaching the critical micelle concentration (CMC), 0.00092M, all CTAB molecules added form micellar aggregates around the hydrophobic sites (indigo dye). As a result, increase in the concentration causes binding of CTAB molecules until all adjacent PMMA chains are connected. CTAB in the aqueous phase helps stabilize emulsion droplets and prevents coalescence resulting in smaller droplets. With a further increase in surfactant concentration, droplet size of emulsion increases, which indicates instability of emulsion. This could be due to low dilution effect which results in multiple surfactant association. Aggregated surfactant micelles is possible as in the case of Figure 9h where the capsules are not only bigger but the shape also changed from spherical to ellipsoidal.

All microcapsule formulations prepared with a higher concentration of surfactant showed higher encapsulation efficiency [0.2% w/v CTAB=64.91%, 1% w/v CTAB= 68.62, 2%w/v CTAB= 69.33, 4% w/v CTAB=76.33]. This may be due to the increase in the insolubility of the dye in the aqueous phase or the increase in CTAB adsorption at the dye interface on increasing the concentration of the surfactant.

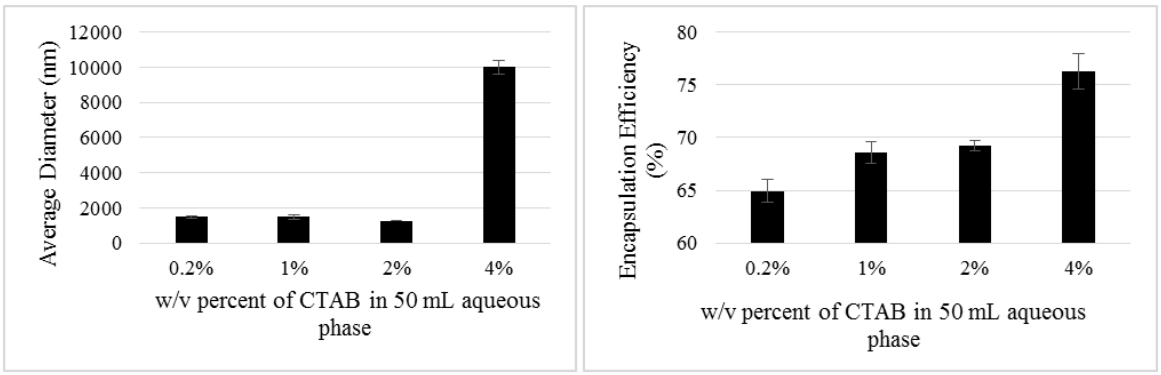

Figure 17. Graphs showing effect of amount of CTAB on average diameter (left) and Encapsulation Efficiency (right)

5.1.4 Volume of aqueous phase. Microcapsule size is also affected by the volume of aqueous phase. It was established that an increase in the volume of the aqueous phase led to an increase in the particle size of microcapsules. It is possible that a large volume of the aqueous phase produces a high dilution gradient of the organic solvent leading to fast solidification of the microcapsules. Another possible explanation is that with the increase of aqueous phase, the number of dispersed droplets generated from a fixed volume of organic phase increases and the probability of coalescence between the dispersed droplets increases. This results in an increase in size of the microcapsules. Also, associated with the increase in aqueous phase volume is an increase in dye encapsulation. Comparatively with large volume of aqueous phase (50ml to 100ml), encapsulation efficiency increased from 68.62% to 73.89%.

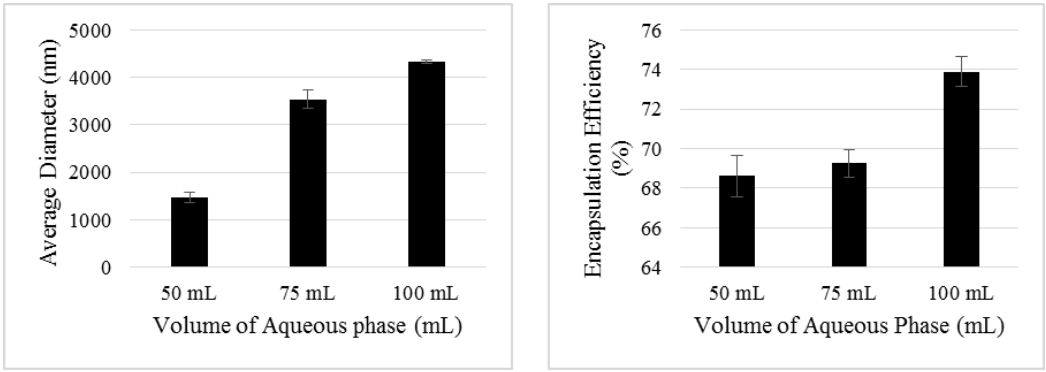

Figure 18. Graphs showing effect of volume of aqueous phase on average diameter (left) and Encapsulation Efficiency (right)

5.1.5 Temperature. Two temperatures were studied: room temperature and 40 °C (boiling point of DCM) to compare their effects on microcapsule structure and encapsulation efficiency. All microcapsules were spherical with a smooth outer skin. Increase in preparation temperature with all other parameters kept constant decreased average microcapsule size by 33%. The reason assigned to this is that the viscosity of the organic phase in the emulsion decreases with increasing temperature and therefore can more easily form smaller droplets at the same mixing speed.

Increase in temperature also reduced the encapsulation efficiency by 15.48%. With faster solvent evaporation, microcapsule shell formation at 40 °C is faster than at room temperature but there is also an increase in mobility of the dye molecules resulting in increased diffusion of the dye into the aqueous phase giving rise to lower encapsulation.

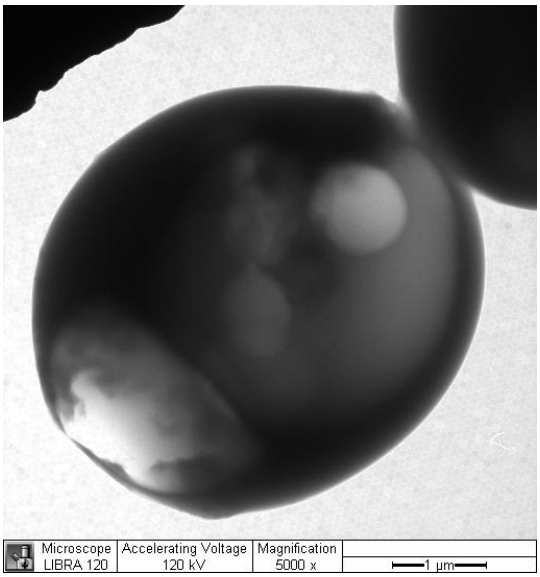

Figure 19. TEM image showing interior of PMMA-dye microcapsule synthesized at 40 °C. (Compare to Figure 12)

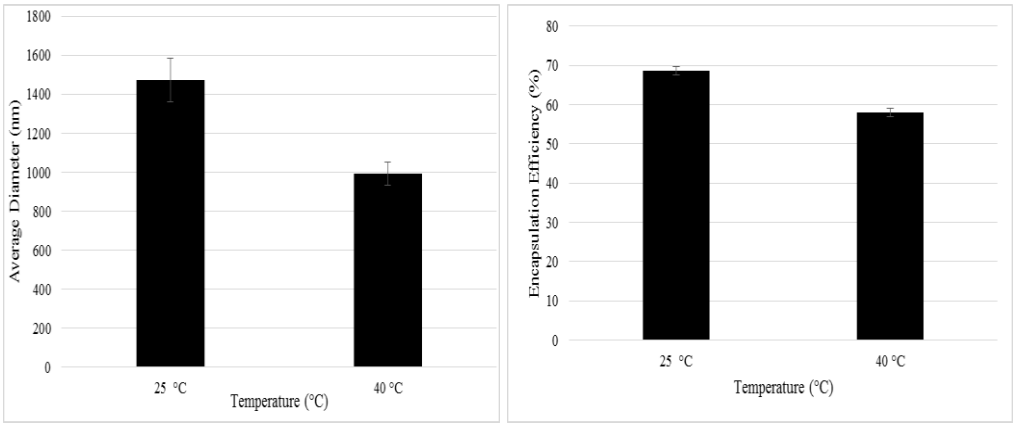

Figure 20. Graphs showing effect of temperature on average diameter (left) and Encapsulation Efficiency (right)

5.1.6 Stirring speed. Stirring is the most straightforward method to generate droplets of the PMMA-dye dispersion in the aqueous phase for subsequent solvent removal. In the simplest approach, a beaker is filled with the aqueous phase and agitated by a magnetic stir bar. The PMMA-dye dispersion is then added, drop wise under agitation at a speed sufficient to form droplet size. During droplet formation step, the stirring speed used is also a dominating parameter for controlling the PMMA-dye dispersion's droplet size in the aqueous phase. Increasing the mixing speed generally results in decreased microcapsule mean size as it produces smaller emulsion droplets through stronger shear forces and increased turbulence.

Encapsulation also increases with increasing stirring rate because there will faster solvent evaporation hence faster hardening of the polymer shell resulting in less diffusion of dye into the aqueous phase.

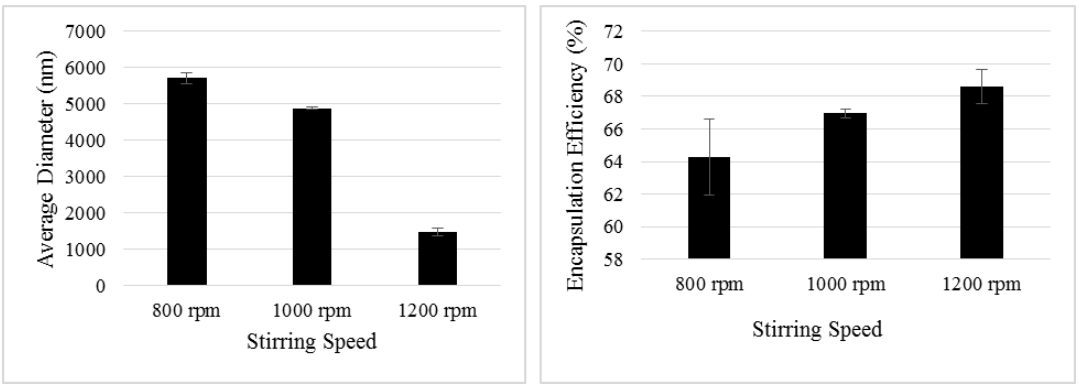

Figure 21. Graphs showing effect of stirring rate on average diameter (left) and Encapsulation Efficiency (right)

5.2 Differential Scanning Calorimetry

The thermal curves of individual components and the PMMA-dye microcapsules are shown in Figure 23. Any radical change in the thermal behavior of either the individual components or the PMMA-dye microcapsule may indicate a possible dye-polymer interaction. DSC confirms the amorphous nature of PMMA with a glass transition of 103 °C close to the theoretical value of 105 °C. The DSC results on PMMA-dye microcapsules after synthesis confirm that the polymer behavior does not change much after the encapsulation process with the glass transition measured at 102 °C.

An endotherm (160 °C) was observed for PMMA-dye microcapsules. This could correspond to the evaporation of the dye encapsulated in the microcapsules. The difference between this value and the experimental evaporation temperature of the indigo dye (102 °C) can be attributed to the entrapment of the dye in the PMMA shell. The flow temperature of PMMA, 130 °C coupled with its low thermal conductivity (0.19 - 0.24 W/mK) makes the evaporation temperature of the entrapped dye higher. This phenomenon has already been observed by other researchers [50, 51].

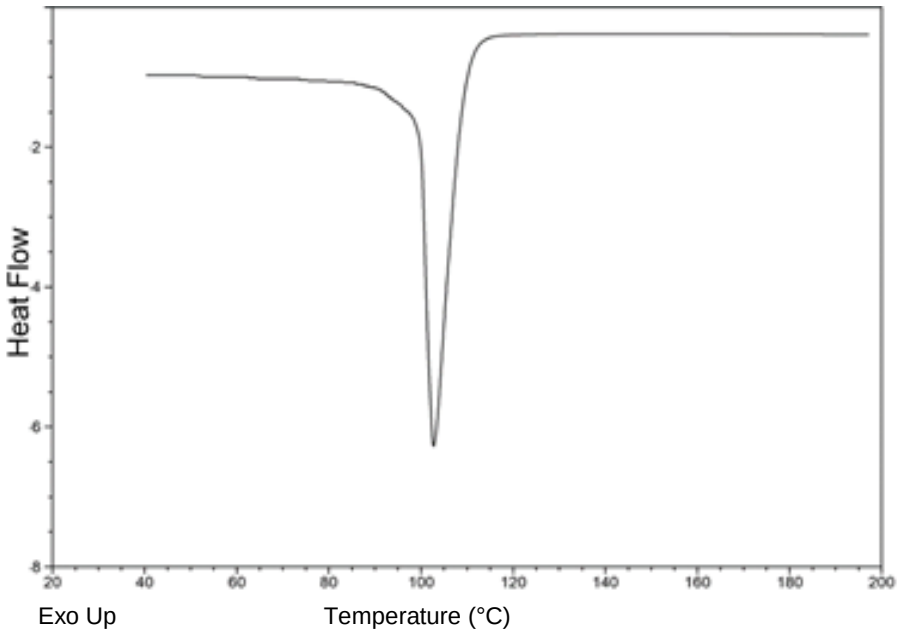

Figure 22. DSC to showing evaporation temperature of liquid indigo dye

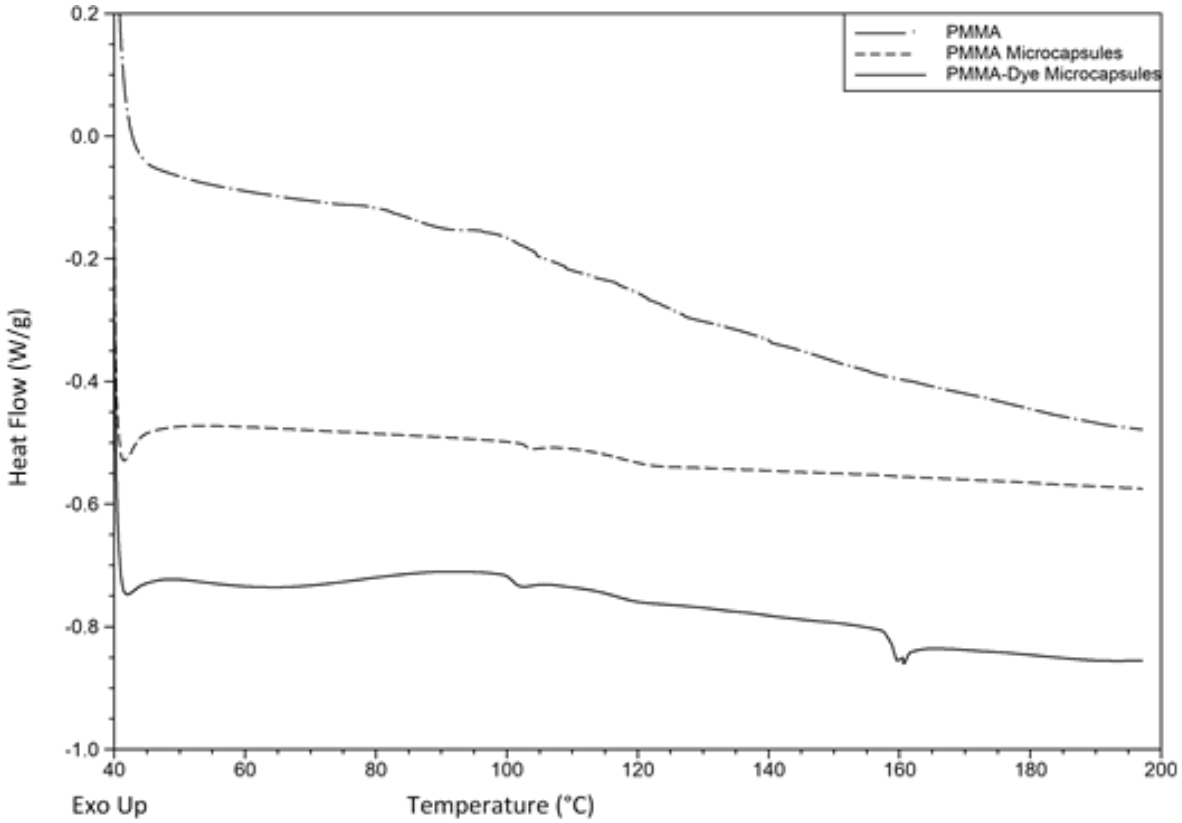

Figure 23. Thermal behavior of PMMA, PMMA microcapsules and PMMA-dye microcapsules.

5.3 Fourier Transform Infrared Spectroscopy

The FTIR spectra of Dye, PMMA and PMMA-dye microcapsules are shown in Figure 24. The FTIR spectrum indicates the details of functional groups present in the synthesized PMMA-dye microcapsules. There was no significant difference in the FTIR spectra of the dye and PMMA as well as the dye encapsulated PMMA capsules. A peak appeared at 1730 cm^{-1} due to the presence of ester carbonyl group, C=O stretching vibration. The peak at 1458 cm^{-1} is assigned to the aromatic (in-ring) C-C stretching present in the indigo dye. We also observe that the bands at 3265 cm^{-1} and 1140 cm^{-1} corresponding to the N-H amine and the aliphatic amine C-N stretching respectively of the indigo dye is still present in the synthesized microcapsules. The peak from 2850 to 2923 cm^{-1} can be assigned to the C–H bond stretching vibrations of the CH_3 and CH_2 groups present in the PMMA. The microcapsules were washed with distilled water three times and then dried under vacuum before the FTIR analysis so the presence of all these absorption peaks indicate that the indigo dye is indeed in the core of the PMMA microcapsule and not just on the surface. In the meantime, there is not much CTAB residue in the final capsule product. See the Appendix for the complete data on infrared absorption spectrum ranges for various functional groups.

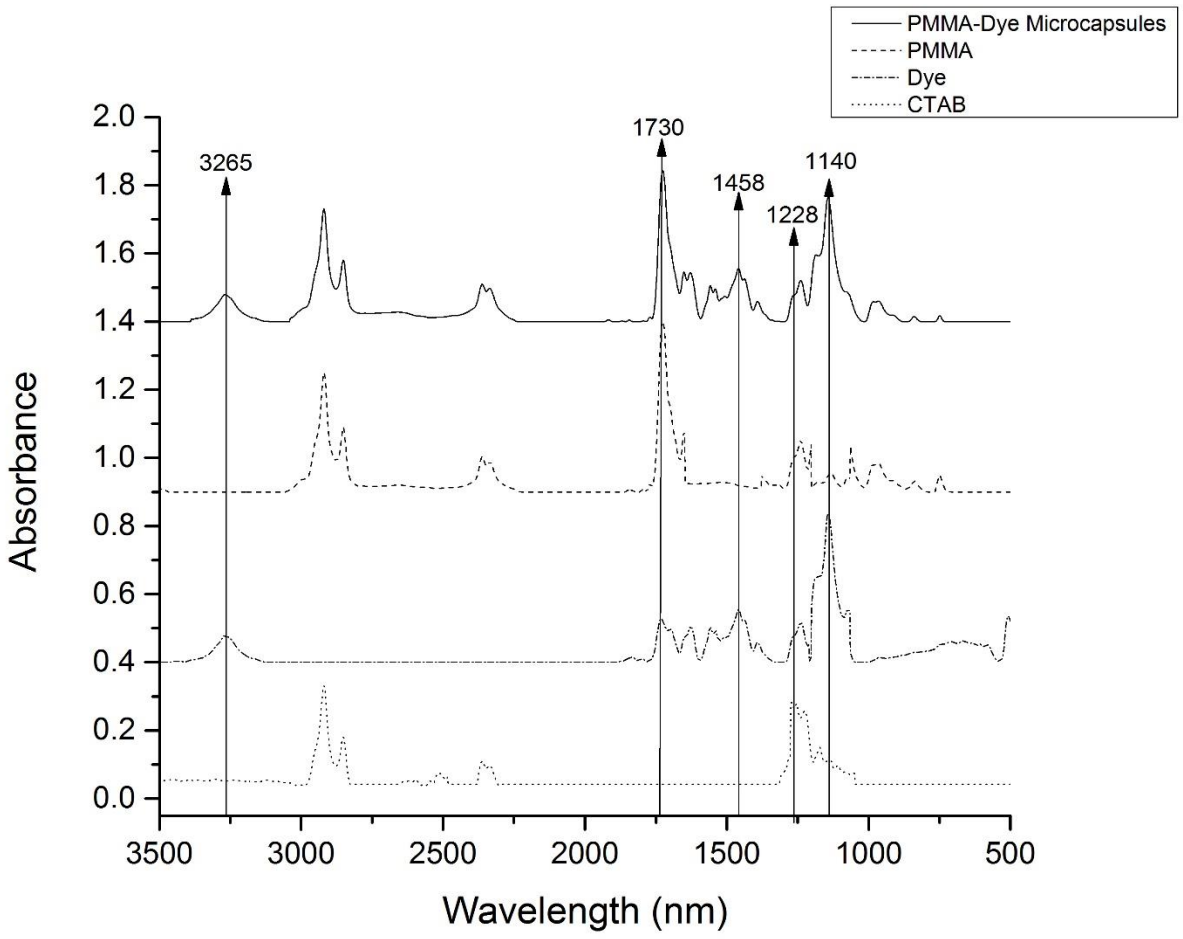

Figure 24. FTIR spectra of Dye, CTAB, PMMA and PMMA-dye Microcapsules.

5.4 Conclusion

The encapsulation of indigo dye by O/W emulsion-solvent evaporation was investigated using PMMA as polymer shell. The efficacy of this microencapsulation process is dependent on many factors, including varying the concentration of PMMA, the amount of dye, the amount of surfactant, volume of the aqueous phase, solvent evaporation temperature and stirring speed. These variables must be considered in order to develop a successful PMMA microcapsule containing indigo dye. The encapsulation efficiency ranged from 58% to 76% and the average diameter ranged from hundreds of nanometers to tens of micrometers. It was shown that the dye

color and also the chemical structure of the dye and PMMA were not changed nor damaged during the encapsulation process.

Overall, this work presents a promising possibility for encapsulation of aqueous solutions as active ingredient in polymer nano/microcapsule with good encapsulation efficiency.

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Appendix

Table 5.

IR Absorption Spectrum Table

Frequency, cm^{-1}	**Bond**	**Functional group**
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C=C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (w)	C=N stretch	nitriles
2260–2100 (w)	–C=C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes

Table 5

Cont.

1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H “oop”	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C=C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp