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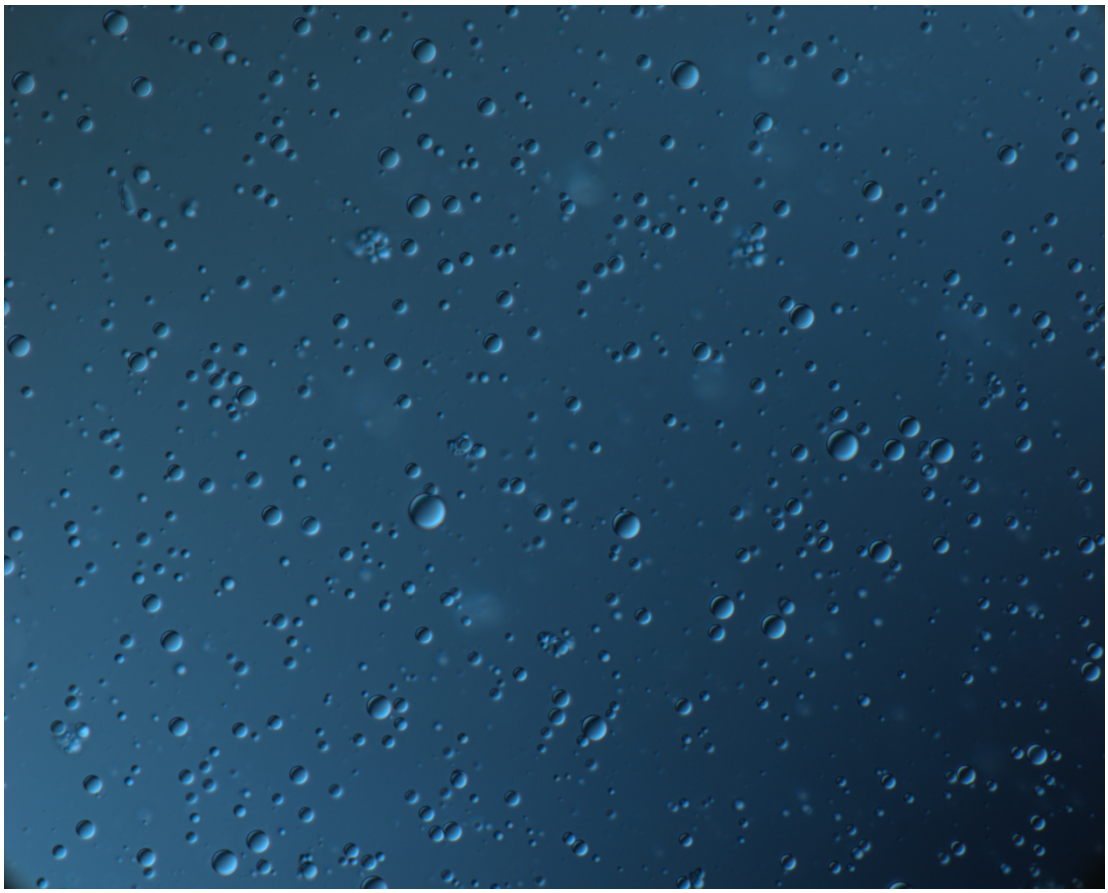

Formulation and Controlled Release – Titania Core-shell Particles with Biocide

Bachelor of Science Thesis

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Applied Surface Chemistry
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Cover:

Titania core-shell particles with biocide prepared by interfacial condensation

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Abstract

Anti-growth agents like biocides are commonly used to protect pained house facades and other exterior surfaces from biofouling like mold, lichens, mosses and algae. The biocides are normally directly mixed into the paint during formulation. The biocides are small molecules with high diffusivity which leads to fast leakage of biocide out from the painted coating matrix. When the concentration of the biocide in the coating matrix is too low there is no protection against biofouling. To maintain the concentration for as long as possible microencapsulation has been shown to be a promising method to slow down the diffusion rate. The biocide must then diffuse through the shell of the microcapsule before diffusing through the coating matrix. In previous studies various types of biocides have been encapsulated in microcapsules based on the polymer polymethylmethacrylate. In this study a titania core-shell was used for encapsulation of the biocide BHT (2,6-di-tert-butyl-4-methylphenol) via an interfacial condensation method. The release from the prepared microcapsules was studied. The release bath was 0.125 M aqueous solution of SDS (sodium dodecyl sulphate). The microcapsules did yield full encapsulation of the biocide through the purification. Samples were taken from the release bath and analysed with UV/Vis - spectroscopy. The results show an almost immediate release of BHT from the core-shell particles.

Sammanfattning

Växthämmande agens, så som biocider är vanligt använt för att skydda målade husfasader och andra ytor utomhus från mikrobiell påväxt som mögel, larvar, mossa och alger. Biociderna blandas normalt direkt ner i färgen under tillverkningen. Biocider är små molekyler med hög diffusivitet, vilket leder till snabbt läckage av biociden ut från den målade färgmatrisen. Är koncentrationen av biociden i färgmatrisen för låg, verkar inte längre dess skyddande effekt mot påväxt. För att behålla koncentrationen på en lagom nivå och för att ge ett långvarigt skydd har mikroinkapsling visat sig vara en lovande metod för att sakta ner diffusionshastigheten. Biociden måste då diffundera genom skalet på mikrokapseln innan den kan diffundera genom färgmatrisen. I tidigare studier har olika typer av biocider inkapslats i mikrokapslar baserade på polymeren polymethylmethacrylate. I denna studie används kärnskals kapslar av titan för att kapsla in biociden BHT (2,6-di-tert-butyl-4-methylphenol) via en interfacial condensation metod. Frisättningen från de tillverkade kapslarna studerades. Frisättningsbadet var 0.125 M vattenlösning av SDS (sodium dodecyl sulphate). Prover togs från frisättningsbadet och analyserades med UV/Vis-spektrometri. Resultaten visade på en nästan omedelbar frisättning av BHT från kärnskals kapslar.

ABBREVATIONS

BHT – 2,6-di-tert-butyl-4-methylphenol or butylated hydroxytoluene

Brij ®L23 – Polyoxyethylene(23)monododecyl ether

NMR – Nuclear magnetic resonance

PEG-PPG-PEG – Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)

PMMA – Poly(methylmethacrylate)

PVA – Poly(vinyl alcohol)

$Ti(OBu)_4$ – titanium tertbutoxide

$Ti(OEt)_4$ – titanium tertethoxide

SDS – sodium dodecyl sulphate

UV/Vis – ultraviolet visible

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1. Introduction

Different kinds of coatings, like paint, varnish and lacquers are well used in different areas in today's society. The different coatings have a large variety of functions and can be divided into decorative, protective and functional coatings. Antifouling and antimicrobial coatings are a typical example of functional coatings. Functional coatings also include functions as self-cleaning, lubricating, self-polishing and flame-retardant [1].

Growth of mold, mosses, lichens and algae on exterior surfaces like house facades and ship hulls is a critical problem. Discoloration and rotting of the wall, especially the wood material is a few results of the biofouling. It also results in society costs because of reparation cost and it has been found that the growth of an especially fungi has a serious impact on the human health. These impacts can lead to respiratory diseases like asthma and bronchitis. The marine biofouling may increase the fuel consumption of the ship by as much as 40% because the biofouling leads to an increased friction drag. Higher fuel consumption leads to more pollution of the environment [1,2,3,].

To prevent higher fuel consumptions, respiratory diseases and other health problems, discoloration and potential damage of the painted surface antifoulants are used [1]. These antifoulants prevent biofouling and are normally mixed directly in the paint during formulation. Earlier toxic metal based compounds have been used as antifoulants but due to the negative impact on the environment they are now prohibited [2]. Nowadays, biocides, a more environmentally friendly substance is used. Even though the biocides are friendlier than the metal compounds there is a limit on the legal concentration in the paint. Biocides are small molecules with a high diffusivity [2,4,5]. The high diffusivity leads to premature loss of the biocides because of diffusion through the coating matrix to the coating surface, where the biocide is flushed away by the rain water. Thereby the protection against biofouling is lost, that is the biocidal action is over before the lifetime of the coating. Depending on the paint system the porosity in the dry-film coating matrix differ and thereby the diffusion rate of the biocide through the coating matrix. This leads to a quick loss of protection and repainting and cleaning of the coating is necessary [1,2,3].

The biocides protection activity is only effective at the action of growth, which is at the coating surface. The biocide has a toxic function and inhibits the cellular activity within the

biofouling organisms. Therefore the concentration of the biocide at the coating surface must be above the critical threshold to protect against biofouling. A concentration too low will not give any protection and a concentration too high can involve environmental impacts, regulatory aspects and material modification.

A way to overcome the problem of premature biocide leakage is to encapsulate the biocide. Encapsulation will reduce the release rate from the coatings and by that prolong the protection [3].

Encapsulation of specific substances is already used in different areas with different applications. Food industry, agricultural applications, cosmetic and pharmaceutical products are common areas for application of microencapsulation [3,6]. The reason for encapsulating materials is to ensure that the substance reach the target of action without getting negatively affected by the environment or released before reaching this specific target [6]. Depending on the area of application, different release mechanism of the encapsulated materials can be used. The substance can be released by diffusion through the wall of the capsule, dissolution or melting of the wall or by mechanical rupture. These release mechanisms cause different types of release and release rate from the microcapsule. Triggered release, immediate release or sustained release are to mention a few.

2. Purpose

The purpose of this project was to gain understanding of the release properties from titania core-shell particles. This project was partly carried out in cooperation with a group of bachelor students' project, where the aim was to optimize the formulation of the titania core-shell particles and prolong their stability.

3. Theory

3.1 Surface-active substances

Surface active substances like surfactants and surface active polymers will be described in the following section. In this project surface active polymers are used as stabilizer.

3.1.1 Surfactants

Surfactants are amphiphilic compounds having a polar group and a nonpolar hydrocarbon chain. The polar group is often referred as the head and the chain as the tail of the surfactant molecule. This amphiphilic structure makes it possible for the surfactant to concentrate at the interfaces when it is added to a solution. This absorbance at the interface is a significant behaviour for the surfactant. If the concentration of the surfactant in the solution gets too high, there will not be enough space for all the surfactant molecules at the interfaces. The molecules in excess are forced to aggregate in the solution, which is another typical behaviour. The form of these aggregations are usually micelles or other forms of aggregates [7,8]. The driving force for this phenomena is to minimizing the contact between the hydrocarbon chain and the surrounding water. Due to this aggregation process the total free energy will increase [8].

The concentration of surfactants when the first micelles starts to form is called the critical micelle concentration, often shortened CMC. If more surfactants are added to the solution more micelles will form. The concentration of free surfactant molecules is constant above CMC. The value of CMC is of significance because a low value indicates that the surfactant rather will form micelles then being a free molecule. The micelles are formed by a characteristic number of surfactant molecules, it is also known as aggregation number. The aggregation number depends on the surfactant geometry. The hydrophilic head is in contact with the surrounding solution and therefore forms the shell/outer surface of the micelle. The hydrophobic tail is orientated to the centre of the micelle [7].

The hydrophilic head can be classified into non-ionic and ionic due to the nature of polar groups. If the head is classified as ionic it can be either cationic or anionic and amphoteric or zwitterionic. The non-ionic surfactant are amphiphilic compounds and does not dissociate into ions and therefore has no charge. Depending on the pH value some non-ionic surfactant can acquire charge, especially tertiary amine oxides. The main part of non-ionic surfactant

does not have any charge in the predominant working range of pH and are classified into alcohols, polyether and esters [8].

The classification of an anionic surfactant is an amphiphilic compound with an anionic group, either attached directly to the hydrocarbon chain or through an intermediates. The most characteristic properties of anionic surfactants are dispersing ability, high foaming and sensitivity to water hardness and protein denaturation. When dissociated in water the anionic surfactant do form surface-active anions and hydrated cations. The anionic surfactants are also called “detergents” as they are often used in cleaning products. Most of the anionic surfactants are based on synthetic raw material [8].

Cationic surfactant do form a surface-active cation and a normal anion then dissociated in water. The main groups of cationic surfactants are alkyl amines, ethoxylated amines, alkyl imidazolines and quaternaries [8].

Amphoteric surfactants are amphiphilic surfactant and can forma both cationic and anionic charges. They are referred to compounds that show amphoteric properties depending on the pH-value. If the surfactant is independent of the pH it is called a zwitterionic surfactant. Usually this show both anionic and cationic properties, because of the strongly acidic and basic groups in the structure of the surfactant [8].

3.1.2 Surface active polymers

Surface active polymers are commonly used as stabilizers in dispersed systems like emulsions and suspensions. They are used as additives in paint, ink and in food because of their ability to affect the flow properties and viscosity and thereby optimize the rheology of the formulation. Hydrophobically water soluble polymers are an example on compounds that are used for optimizing the rheology. They consist of a polymer backbone with hydrophobic groups attached along the backbone chain. The hydrophobic tails do associate with eachother and a spare network is created which increase the solubility of the solution. When stirring the paint the network is broken and the viscosity decreases, this is called shear thinning and is of high importance when it comes to paint. The network is fast recreated when the paint is no longer under stirring conditions [7].

Is a surface active polymer and a surfactant is combined in a solution so called mixed-aggregations can be formed. The surfactant enhances the interaction between the polymer

chains that is formed by the hydrophobic tails. The mixed-aggregations starts to form at a lower concentration of the surfactant when a surface active polymer is present compared to the CMC. The concentration is called critical association concentration, CAC. At a certain concentration the surface active polymer will start to interact with the surfactant rather than being absorbed at the interface between air and solution. This leads to a decrease in the surface tension and within this interval the surfactant creates aggregation with the hydrophobic tails on the polymer. When no more tails are free the surfactant is again absorbed at the interface and the surface tension will decrease even more [7].

3.2 Emulsions

Emulsions are dispersions of two immiscible liquids. One liquid is dispersed in the other liquid [9,10,11]. The dispersed liquid is called the dispersed phase and the other liquid the continuous phase [10]. There are two main types of emulsions, oil-in-water (O/W) and water-in-oil (W/O). To be able to create an emulsion one must diminish the interfacial tension between the phases. Surface active polymers or surfactants are components that are used for the purpose, to decreases the interfacial tension and to facilitate the decomposition of the system, to form small droplets [11]. The polymer and is often added to facilitate the formation of the emulsion or form a protective film to prevent the emulsion from fragmentation [9]. The polymer is absorbed on the droplets and produces a either electrostatic or steric repulsions [10]. By time, all emulsions will separate into two phases but the surface active polymer (stabilizer) will stabilizes the emulsion so it will take much longer time before separation.

3.3 Suspensions

Suspensions are in many cases similar to emulsions. Like emulsions one liquid is dispersed in another and have a dispersed and a continuous phase. The difference is they are not thermodynamically stable and the stability of the suspension decreases with increasing size at the particles. Normally the particle size is about a few micrometres but there are suspensions with a particle size as small as nanometres [12].

3.4 Biocides

Biocides are commonly used to protect painted exterior surfaces against micro-organic growth such as mold, lichens, mosses and algae [1]. Earlier more hazardous substances has been used, but due to the high impact on the environment biocides are now used, but to

excessive amounts of biocide can be a risk of impact due to pollution on the environment. The biocide may be inconsistent with the used binder-solvent system which can lead to technical problems like macroscopic phase separation [1]. They are small molecules with a high diffusivity. The diffusion to the coating-surface gives protection against the growth because the biocide is only active at the action of the growth which is the material exterior surface. The high rate of diffusion also leads to leakage of the biocide. When the coating is rinsed by the rain the biocide flows with the rain water and therefore the protection diminish because of the leakage of biocide. The protection against growth is only active above a certain critical concentration of the biocide in the coating matrix [1,2].

The biocide used in this project was BHT (2,6-di-tert-butyl-4-methylphenol or butylated hydroxytoluene) and is shown in Figure 1.

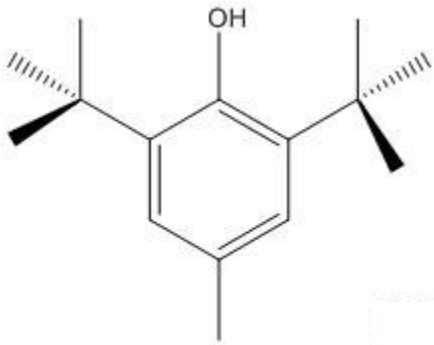


Figure 1: The structure of BHT (butylated hydroxytoluene).

3.5 Microencapsulation

Microencapsulation has a wide range of applications, from chemicals and pharmaceuticals to cosmetics and printing [1,4,6]. Microencapsulation is used for the purpose to shield an active ingredient from a surrounding environment. The active ingredient, which is dissolved in the core material can either be a solid, liquid droplets or gas bubbles. The active ingredient is embedded in a coating or shell material. The size of the microcapsules can differ from below µm to a few mm. Sometimes they can be as small as a few nanometres, then called nanocapsules [6,13,14].

There are a numerous of different methods for encapsulating an active substance (biocide). Depending on the intended release profile and the physicochemical properties of the biocide like polarity, size and charge different methods are used [1]. Internal phase separation,

double emulsion, emulsion polymerization and interfacial polycondensation are a few common methods that are used today. All these methods can be categorized into two main categories. The first technique is the ones that have monomers or pre-polymers as a starting material. This technique involves chemical reactions and do form microspheres. The other technique have polymers as starting material and unlike the first category these techniques do not involve chemical reactions and only form the shape [6]. Starting material and microencapsulation methods are decided depending on the desired compositional and morphological characteristics at the microcapsules.

3.5.1. Internal phase separation by solvent evaporation

The internal phase separation by solvent evaporation method developed by Loxley and Vincent [2,15] is most suitable for encapsulation of hydrophobic actives in liquid oil cores [1,2,16]. The method gives almost full encapsulation yield of the active substance [17]. An o/w emulsion is prepared and formed by high shear stirring. To create the suspension of core-shell particles the emulsion is poured into an aqueous solution with a volatile solvent. The method is based on coacervation which is induced by solvent evaporation from the emulsion.

The emulsion consist of an oil- and water phase which is mixed together. The oil phase contains of a shell-forming polymer, low-boiling (volatile) solvent, a high-boiling poor solvent for the polymer (core-oil) and the active substance. The volatile solvent is to provide that the polymer is completely dissolved. The aqueous phase consist of a suitable stabilizer, which is often a water-soluble and surface-active polymer [2,15].

When the solvent evaporates the polymer-rich phase migrate to the interface of the droplets and starts forming the shell while the core-material accumulate in the centre of the forming shell [1,15,17].

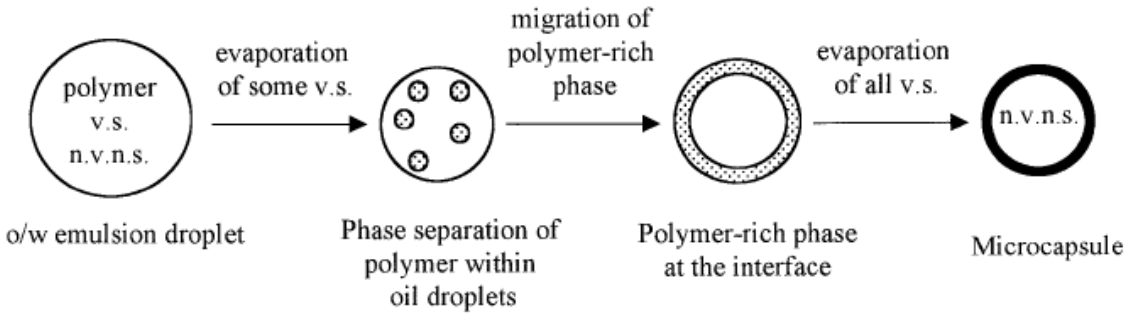


*Figure 2: Schematic picture of Loxley and Vincent method; internal phase separation, for preparing of microcapsules [*15*].*

3.5.2 Double emulsion

Like the name reveals the double emulsion route starts with creating a double emulsion, often a water-oil-water ($W_1/O/W_2$) emulsion. To create the double emulsion a two-step homogenization method is used. A pre-emulsion W_1/O is formed under high shear and then dispersed in the continuous W_2 phase. The aqueous phase consist of the active substance and the oil phase of the shell forming polymer and a volatile solvent. The solvent is slowly evaporated when the pre-emulsion is dispersed in the W_2 phase under moderate shearing [1].

3.5.3 Emulsion polymerization

An aqueous polymerisation medium containing core material and an emulsifier is stirred around and a monomer is dropwise added. The polymerization begins and a nuclei is formed and entraps the core material as they grow gradually as the polymerization proceeds. The nuclei is formed by initially formed polymer molecules. Common materials for this technique is lipophilic materials [6].

3.5.4 Interfacial polycondensation

This reaction occurs at the interface of a two phase system and therefor the name interfacial. The polycondensation is between two monomers. The two-phase system should form small droplets of one phase in the other one and must therefore be mixed under very carefully and controlled conditions. The small droplets represents the dispersed phase and the other phase is the continuous phase. It is necessary that the material that to be encapsulated can form droplets and that the concentration of the stabilizer is not too high because of the high risk of droplet coalescence and particle coagulation. Depending of the solubility of the polycondensation the droplets phase two types of microcapsules can be formed, monocore and matrix. If the polymer is soluble in the droplets, matrix microcapsules are formed and if not the monocore microcapsules are formed [6].

3.5.4.1 Titania core-shell particles

Titania core-shell particles were used in this project and the formulation was prior to this work by a group of bachelor students based on an earlier study by Collins, Spickermann and Mann [18].

These microcapsules are made by a non-aqueous emulsion with the precursor $Ti(OEt)_4$ (titanium tertethoxide) and hexadecane as core-oil. Hexadecane has been used in earlier studies and do satisfy the requirement for core-oils. The core-oil should not react with the precursor but dissolve the precursor and the biocide [3,5,18].

3.6 Release mechanisms

Encapsulation of different material can provide controlled, sustained or targeted release of an active substance and the release mechanism is used in many different areas. Depending on the area of use and the desired rate of release, different mechanisms for encapsulated material to be released are active. Mechanical rupture of the capsule wall, diffusion through the wall and dissolution or melting of the wall are a few examples of release mechanisms [6,17].

3.6.1 Release from microcapsules

Studies of the release from microcapsules to an external medium can be performed in many different ways and by using several different methods. The studies can cover all steps from the setup to the time when all of the active substance is released. Although there are three main steps that are to be considered that is; setup, analysis and evaluation.

The setup includes the laboratory equipment and materials needed to perform the release studies. Essentially for the release studies is to know the saturation concentration of the biocide in the chosen release medium and the distribution for the biocide. The distribution is explained by the partition coefficient, K, and by that information the distribution between of the biocide in the microcapsule and the releasing medium is known [17].

The release studies in this project was performed by dispersing the microcapsule suspension in the release medium during stirring conditions. The release of the active substance starts immediately when the microcapsules are dispersed. Small samples are taken using a syringe and then filtrated through a syringe filter. The filtrate is analysed using UV/Vis-spectrophotometry. Only the active substance that is released passes through the filter, and so this method only permits the concentration of the released active to be analysed.

The analysing part, like the setup step, include all the equipment that is necessary but in this case for the analysis, like equipment for data sampling and analytical technique to quantify the time-dependent concentration of the active.

Last in the evaluation step all the collected data and results are put into perspective by the application of release models [17].

3.6.2 Sustained release

The use of rate determining release systems in coating have both shown benefits from an economical and environmental point of view [1]. The focus in this project is sustained release from core-shell particles.

The release rate of the active substance is determined by the penetration though the shell and through the coating matrix. The diffusion coefficient and the solubility of the active substance in the barrier affects the kinetics and thermodynamic parameters, which are determining for the penetration of the active substance [1,16,17]. The partition coefficient, *K*, describes partition of the active between the core and shell or between the microcapsule and release medium. It is affected by the solubility of the active substance in and the interaction with the core and shell materials [16].

$$K^i = \frac{C_A^i}{C_B^i} \qquad (1)$$

K^i – partition coefficient for active *i*

C_A^i – equilibrium concentration of active *I* in phase A

C_B^i – equilibrium concentration of active *I* in phase B [1]

3.7 Previous studies about release from microcapsules

In previous laboratory studies about microencapsulated biocides, several biocides have been studied and their release from PMMA-capsules. The aim of one study was to evaluate the release of OIT from microcapsules dispersed in an aqueous solution. The release medium, 6-wt% Brij® L23, was used and the content of increases the aqueous solubility of OIT. The microcapsules were prepared by internal phase separation [2.16]. Also release of BHT have been studied from microcapsules based on PMMA using a solid and liquid core. The core-shell particles were prepared with internal phase separation with PMMA as shell-material and dodecane (liquid) or octadecane (solid) as core-oil [19]. The BHT used was labelled with ^{14}C so the radioactivity could be measured.

At time zero 10ml of the suspension with microcapsules was added to a beaker containing 190ml of 0.125 M SDS solution. The release bath was kept at room temperature under

continuous stirring. At specific times samples of 5ml was removed using a syringe and immediately pressed through a syringe filter. 3ml of the filtrate was then mixed with 18ml Ultima Gold^{TM} and the radioactivity of the samples was recorded [19].

4. Materials and Methods

In this section the materials and methods used will be described. When optimizing the formulation of titania core-shell particles no biocide was added and the first verification before creating the microcapsules was to check that the biocide is totally dissolved in the core-oil and that a phase separation still occur between the core-oil and the shell material.

After the verification, a batch with microcapsules containing the biocide was made and the stability, structure and the microcapsules ability to maintain all the biocide within the shell.

4.1 Pre-studies

As mentioned in section *3.5.1.1* a necessity for creating core-shell particles is that the oil phase do not react with the precursor but still dissolve the precursor and the biocide.

Phase separation between the core-oil and shell material is also a necessity for creating the emulsion. The addition of biocide to the core-oil was not tested by the group of bachelor students. Interesting when introducing the biocide, BHT, in the core-shell particles is the distribution of BHT between the core-oil and solvent. The distribution of BHT between the phases was investigated by mixing BHT with the core-oil, hexadecane and with the solvent, formamide with the volumetric ratio 1:1 and 1:5 (hexadecane:formamide), see Appendix I. When the mixtures reaches equilibrium a phase separation occurs and a top and bottom phase is visible. Samples were taken from the top phase and the bottom phase and analysed with NMR-spectroscopy. The top phase would contain only BHT and hexadecane and the bottom phase only formamide. The results from the NMR analysis were used to calculate the distribution factor or partition coefficient from equation (1) to see that basically no BHT was in the bottom phase. The precursor was also added in a separate study to see that it did not affect the result of distribution of BHT.

Two other compounds ($Ti(OBu)_4$ and oleyl alcohol) similar to $Ti(OEt)_4$ and hexadecane was also tested to see if they gave a similar outcome and therefore could be an option for the

formulation of core-shell particles. $Ti(OBu)_4$ would be a substitute for $Ti(OEt)_4$ and oleyl alcohol a substitute for hexadecane.

4.2 Formation of the microcapsules

The microcapsules were created by the interfacial condensation method described in section *3.5.4*. For the formation of the microcapsule, titania and hexadecane constituted the shell and the core oil. The biocide was encapsulated and dissolved in the core oil.

To create the microcapsules a continuous and a dispersed phase was used. The continuous phase was prepared with 0.625g PEG-PPG-PEG and 25g formamide which was left with a magnet stirrer until totally dissolved. The dispersed phase was made of 1.786g hexadecane, 0.1786g BHT and 0.714g $Ti(OEt)_4$.

The continuous phase was held in a round bottom flask which was placed in a cool-water bath with a stirrer, SilentCrusher M. The stirrer was started and sheared the continuous phase at 5000rpm while the dispersed phase was added dropwise for two minutes. Then the solution was left to shear for 60 minutes so an oil-in-water emulsion was formed. All the areas exposed against air was covered with parafilm to prevent air to get in the system since $Ti(OEt)_4$ reacts very quickly with water vapour in the air.

The emulsion was then poured into a beaker with a magnetic stirrer and a water phase was added dropwise to create a suspension. The water phase was made of 6.25g milliQ-water and 12.5g formamide. It was left for a few minutes then the suspension was divided into two centrifuge tubes and centrifuged for 30 minutes at maximum effect. During the centrifugation the microcapsules were separated from the formamide and the capsules created a white foam on top of the formamide which was easily separated and put in a new centrifuge tube with a continuous phase. The continuous phase was prepared by water and a few weight-% of a surfactant, either PEG-PPG-PEG or PVA. This was repeated twice to ensure that all the formamide was gone. Thus the solvent were removed and replaced by another continuous phase. Accordingly to the pre-studies the microcapsules had shown to be more stable in a continuous phase containing a surfactant compared to water phase. The microcapsules had also proved to be more stable in water than in formamide. The pre-studies, capsules with $Ti(OBu)_4$ and oleyl alcohol gave promising results. The $Ti(OEt)_4$ was

substituted with $Ti(OBu)_4$ in one batch and an emulsion and a whole batch was made with oleyl alcohol as core-oil.

4.3 Construction of standard curve

The standard curve were constructed by preparing samples with known concentrations of BHT and then analysed with UV/Vis. The measured absorbance was plotted against the known concentrations to get the standard curve, see Appendix II. Using the curve the maximum release concentration could be read and by that calculations for the release bath could be done.

A stock solution containing 250 mg/l BHT in 0.125M SDS-solution was made and by diluting this stock solution the other samples were made. The used concentration (mg/l) was 250, 125, 75, 50, 30, 15, 5 and 2,5. By a linear fit to the curve, the equation was found and according to Lambert Beer's law (2) the absorbance is directly proportional to the absorbance.

Lambert Beer's law $A = \varepsilon * c * l$ (2)

l – length of the cyvett

c – concentration

ε - molar absorbtivity

A – measured absorbance

The equation of the standard curve showed to be A=7.96 * c and by this the measured absorbance from the release studies could be calculated.

4.4 Stability tests

To see if the capsules could be used in a release study the stability of the microcapsules were examined in different continuous phases. The examined phases were 6.25 weight-% PEG-PPG-PEG, 2.5 weight-% PEG-PPG-PEG and 2.5 weight-% PVA. The stability was analysed using microscope examinations repeatedly over time. The analysis were made at different times by taking samples from the batches. The samples were analysed by light microscopy and the pictures were compared to the earlier ones. Important observations was for how long and how well the microcapsules kept their shape, no broken microcapsules or that no flocculation has occurred.

Another important aspect before starting with the release studies is to examine if there is any leakage of the biocide out of the microcapsules. A sample was taken from the suspension with a syringe and then filtered through a syringe filter and analysed with UV/Vis-spectroscopy. This should not show any absorbance because if it gave a result that would indicate that the biocide would have diffused out of the microcapsules and that the shell were not stable enough to maintain all of the biocide inside.

4.5 Release studies of BHT

The release medium used was 0.125M of aqueous SDS-solution. The SDS increase the solubility of BHT in water from 1ppm to 500 ppm.

At release time zero the 20 ml of suspension was added to the 70 ml of SDS-solution, which was kept under stirring conditions. At specific time samples of 5 ml was taken using a syringe. Immediately the samples was filtered through a syringe filter. The samples was then analysed using UV/Vis-spectrophotometry at 277nm. With a constructed standard curve, the measured absorbance and Lambert Beer's law (2) the concentration of BHT could be calculated.

4.5.1 Encapsulation yield

To get an idea of the release rate the fraction of the release is calculated. The release fraction tells how much of the biocide that is release. It is calculated by dividing the released amount of biocide with the amount of biocide that could be released.

$$\frac{concentration\ of\ released\ biocide}{total\ concentration\ of\ biocide} = release\ fraction \qquad (3)$$

The concentration of released biocide is calculated from the measured absorbance from the UV/Vis analysis. The total concentration of biocide is reached when all the biocide is released from the microcapsules. To find out the total concentration of the biocide 1 ml of the suspension was diluted with microcapsules with 9 ml of 0.125 SDS-solution. From this mixture 2.5 ml was mixed with 2.5 ml of methanol. This mixture of suspension, SDS and methanol was analysed with UV/Vis-spectroscopy at 277nm. When the suspension is diluted with methanol all of the biocide is released from the microcapsules and measuring the absorbance when all the biocide is released one can compare the value with the values from the real release bath and calculate the release fraction.

4.6 Size distribution

To determine the size distribution of the titania core-shell particles an image processing program, Image J was used. A representative picture of the capsules used for the release studies (from batch 2) were chosen, see Appendix III. The diameter of the capsules were measured and a histogram over the size distribution were constructed.

5. Results and Discussion

In this section the results from the pre-studies, preparation of microcapsules and the release studies will be presented and discussed included the microcapsules with oleyl alcohol.

5.1 Pre-studies

The phase separation between BHT, hexadecane and formamide was stable and samples showed that the bottom phase, mostly consisting formamide, did contain negligible amounts of BHT. This results speaks for the basically all of the added BHT will be in the core-oil, except the loss during the formulation.

The phase separation test with $Ti(OBu)_4$ and oleyl alcohol gave promising results with a clear separation between the two phases but no NMR analysis was made for these tests.

5.2 Microcapsules

The microcapsules were then centrifuged with water and a polymeric surfactant. Batch 1 was centrifuged with 6.25 weight% PEG-PPG-PEG and did gave a promising result. After a few days some flocculation made this batch unusable for release studies, see Appendix IV.

Batch number 2 were split in two where one half was centrifuged with 2.5 weight% PEG-PPG-PEG and the other half with 2.5 weight% PVA. These two were compared with and checked regularly. First there was no major difference between them but one could tell that the microcapsules in PVA were a bit more flocculated than the microcapsules in PEG-PPG-PEG.

The phase separation test with oleyl alcohol did gave a promising result so an emulsion was made to examine the stability and structure at the microcapsules. The emulsion droplets did look very nice with smooth and round shapes. The emulsion did not show any flocculation over time and the microcapsules contain their shape, see Appendix V. Therefore a batch of microcapsules with oleyl alcohol was made (batch 7). The suspension did look nice but the size of the microcapsules did differ a bit and the centrifugation was a bit more difficult than with the capsules with hexadecane. The foam of microcapsules were much thinner and harder to separate from the formamide.

Together with the bachelor students a batch with $Ti(OBu)_4$ as precursor was made, the microcapsules were unfortunately broken which made $Ti(OBu)_4$ as no longer an option for the formation of microcapsules.

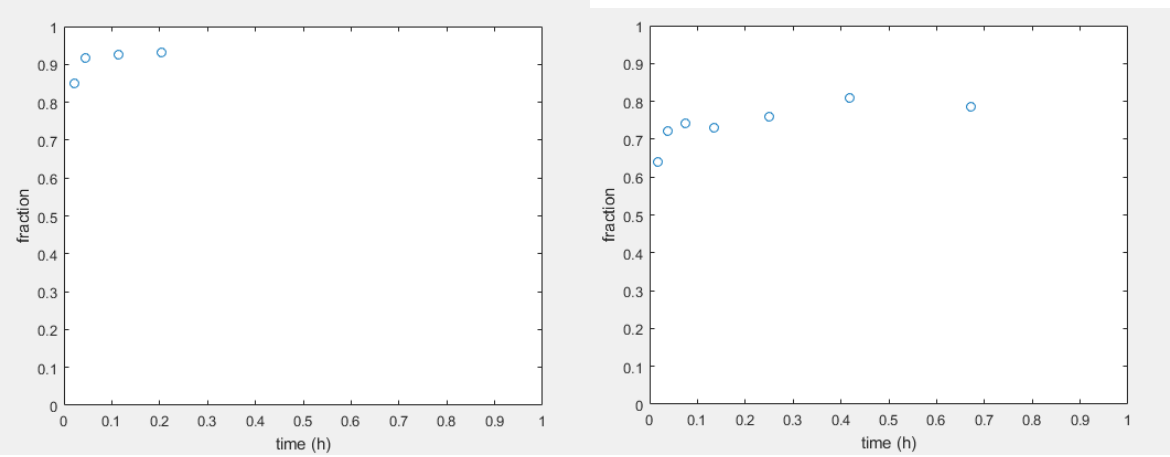
5.3 Release studies and sustainability

The titania core-shell particles centrifuged with 2.5 weight% PEG-PPG-PEG (batch 2 and bath 5) and the microcapsules with oleyl alcohol as core-oil, also centrifuged with 2.5 weight% PEG-PPG-PEG (batch 7) were used for the release studies.

Batch 2 were the first release study performed. The first sample were taken 30 seconds after the suspension was release in the release bath and the last one 4 days after. The samples were analysed in UV/Vis and shown really high absorbance already after 30 seconds. The following samples showed a plateau of maximum release which means that the release of BHT from the microcapsules was next to immediate. Therefore a new batch was made (batch 5) in the same way as batch 2. The suspension of batch 5 was checked so there was no leakage of the BHT. The results did not show any leakage so a “quick and dirty”-test was made, that means a release study with a about 5-8 time intervals. This to see if the results are similar and to get an idea how much of the BHT that has been released. This batch also show an almost immediate release of the active substance.

Since the results from the release studies of the microcapsules with hexadecane as core-oil was not so promising the microcapsules with oleyl alcohol was tested. The release study were performed in the same way, with a quick and dirty test. These capsules also showed an almost immediate release. The suspension did show a leakage of the biocide as well but the amount of leakage only correspond to about 10% of the added amount of BHT during formulation. The small amount of leakage was able to overlook during the release studies since the release from the microcapsules seemed to be immediate.

The release fraction of the microcapsules from batch 5 and batch 7 were calculated from equation (3) and the results is shown in figure 3 below.



(i) *(ii)*

Figure 3: The release of BHT from (i) microcapsules from batch 5 with hexadecane as core-oil and (ii) microcapsules from batch 7 with oleyl alcohol as core-oil.

5.5 Size distribution

The result of size distribution of titania core-shell particles from batch 2 centrifuged with PEG-PPG-PEG is presented in Figure 4. Most of the microcapsules have a diameter in the range of 1,5-3,5 µm. But there is also a few microcapsules with a diameter between 4-5,5 µm. The picture of the microcapsules used for determine the size distribution is presented in appendix III.

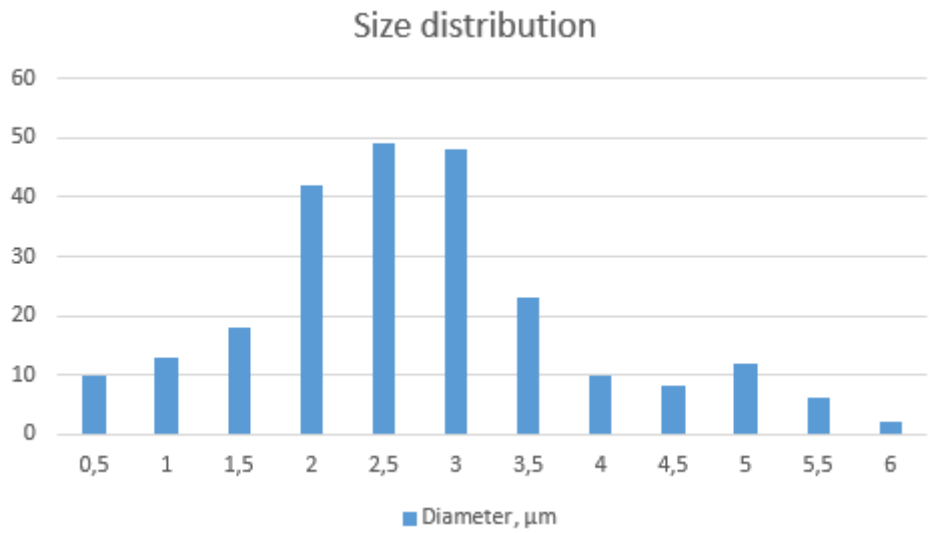


Figure 4: Size distribution of titania core-shell particles with hexadecane as core-oil.

6. Conclusion

The titania core-shell particles seemed to be a promising solution for encapsulation of biocides since there was no leakage of the biocide in the suspension and since the suspension did show a good stability and no flocculation. When it comes to the release studies the microcapsules showed an almost immediate release of the biocide from the microcapsules which is not promising in this content. The stability of the oleyl capsules were not examined for as long as the hexadecane capsules, but they showed immediate release like the hexadecane capsules, which also made them not to be an option to apply in coatings.

7. Future perspectives

Since the microcapsules with hexadecane as core-oil did show good stability and no leakage of the biocide, they can be promising for future studies. Modification of the added amount of shell material may be a possibility for future studies.

8. Acknowledgments

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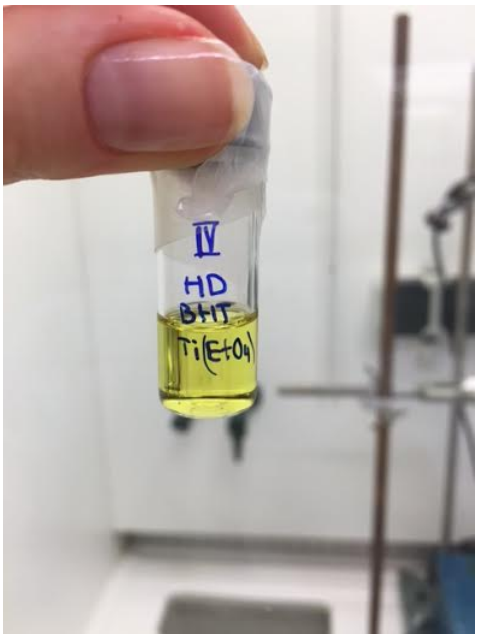
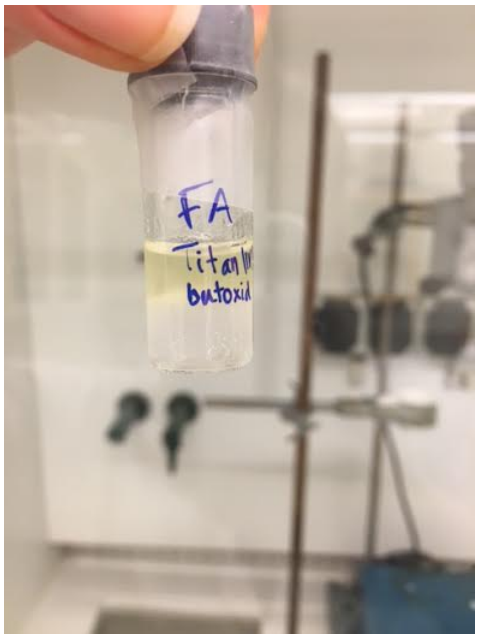
Appendix I: Phase separation from pre-studies



(i)



(ii)

(iii)

(iv)

Figure 1: (i) Core-oil, hexadecane, dissolve the precursor, $Ti(OEt)_4$ and the biocide, BHT. (ii) Phase separation between the solvent, formamide and the precursor, $Ti(OBu)_4$. (iii) Phase separation between the core and shell material with the volumetric ratio 1:1 and (iv) volumetric ratio 1:5.

Appendix II: Standard curve

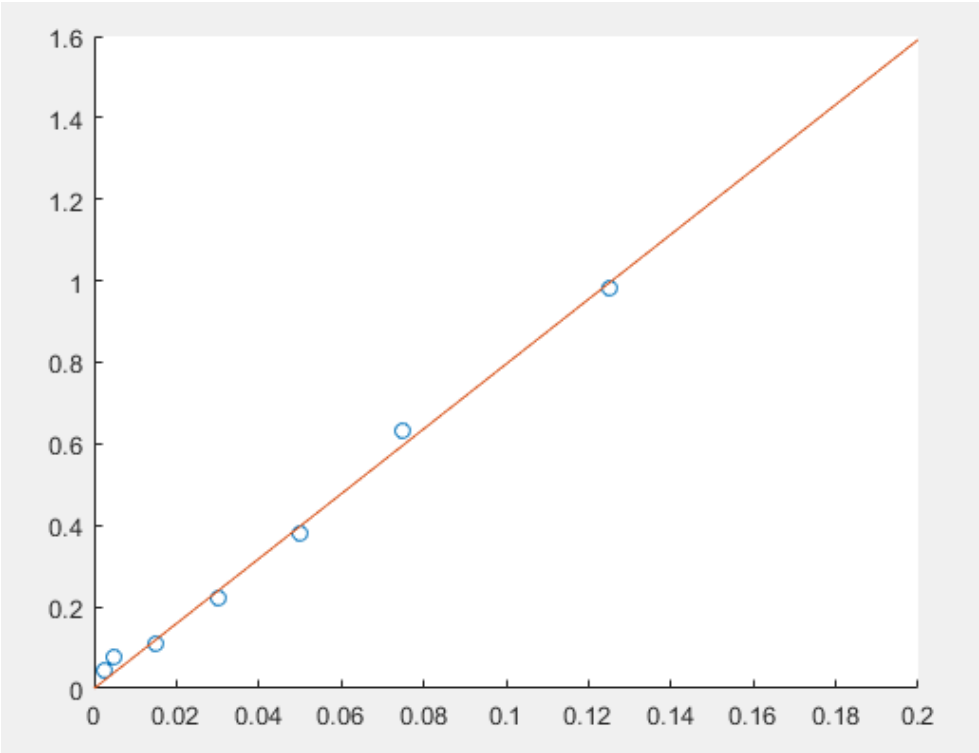


*Figure 2: The constructed standard curve with the equation, A=7.96*c.*

Appendix III: Size distribution

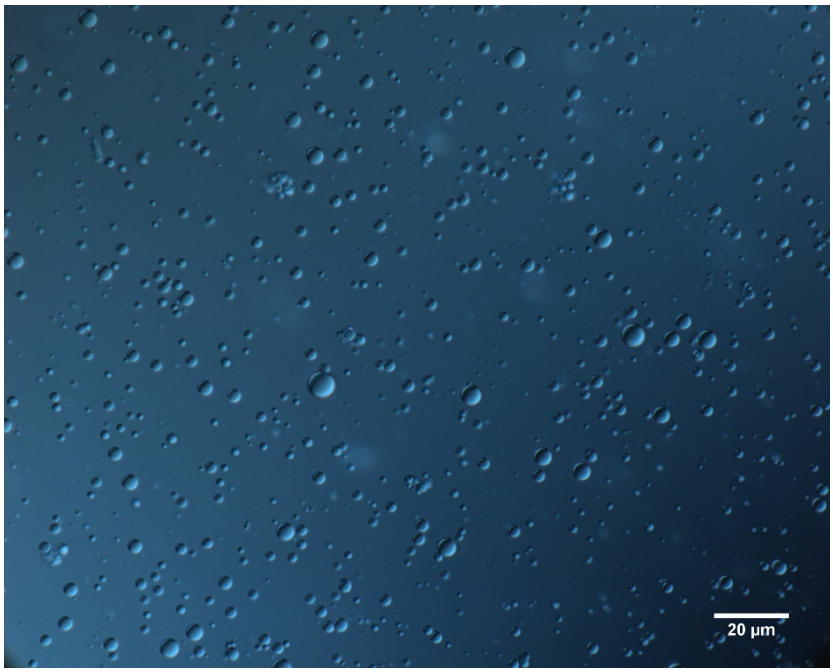
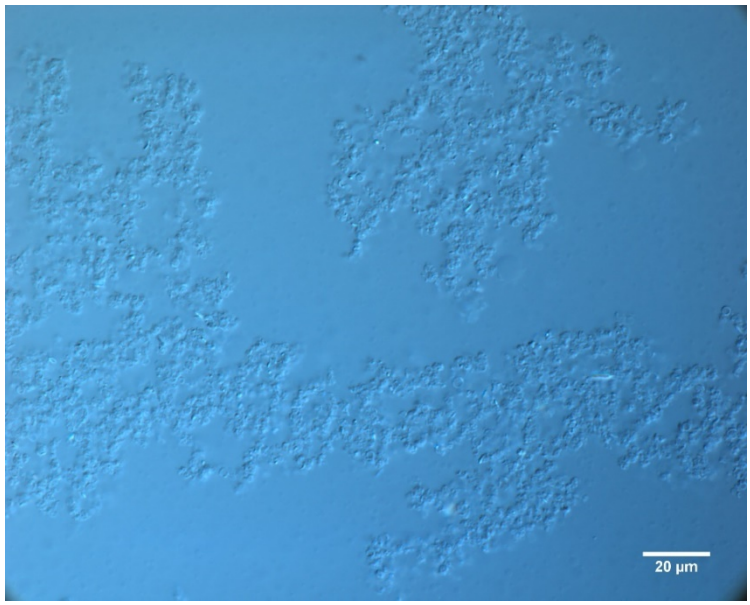
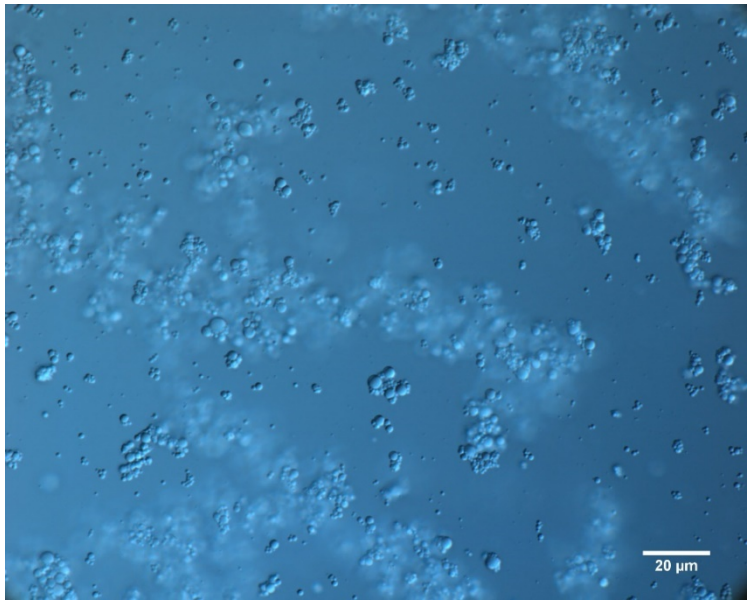


Figure 3: The microcapsules from batch 2 after centrifugation with 2,5 weight-% PEG-PPG-PEG. Theses microcapsules with hexadecane as core-oil were used for the release studies.

Appendix IV: Stability test

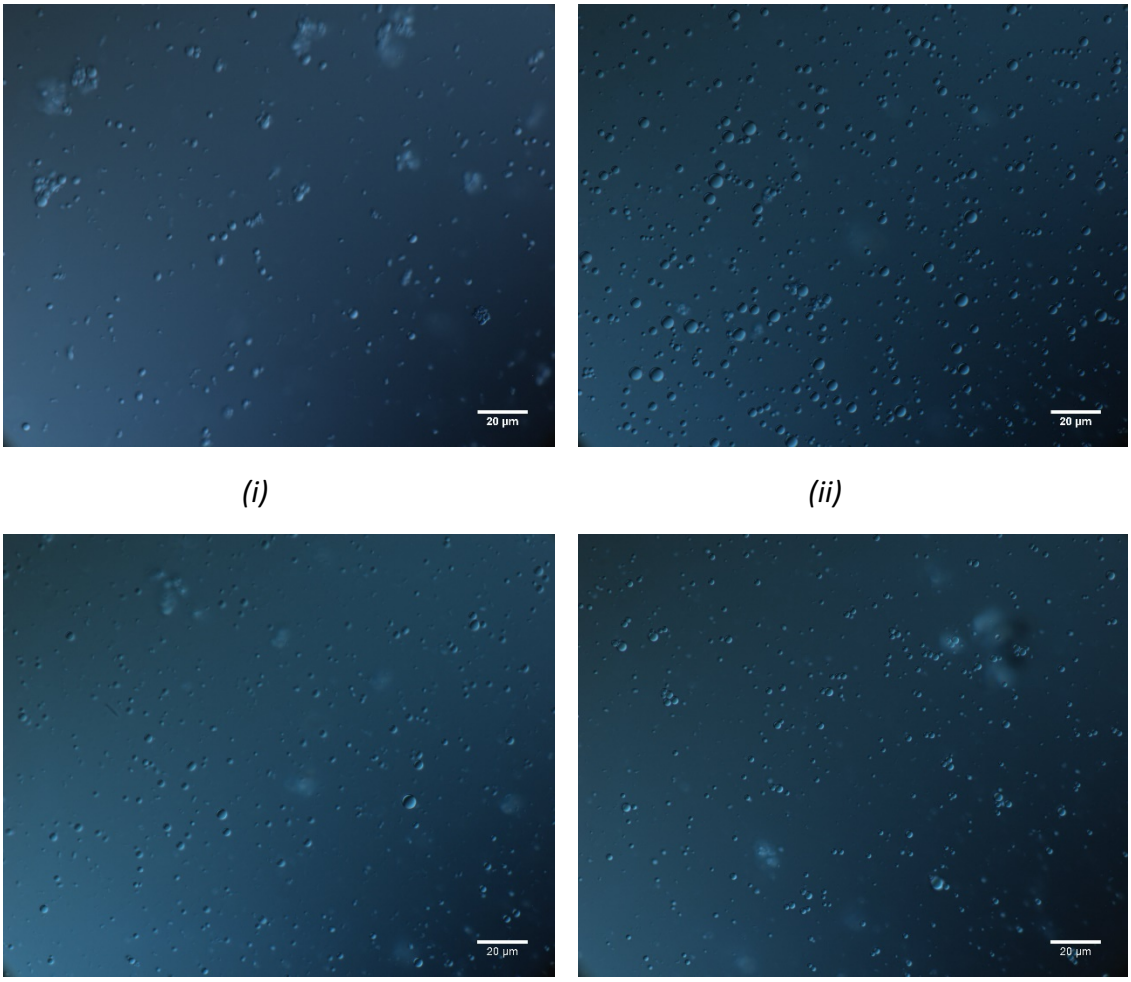


(i)



(ii)

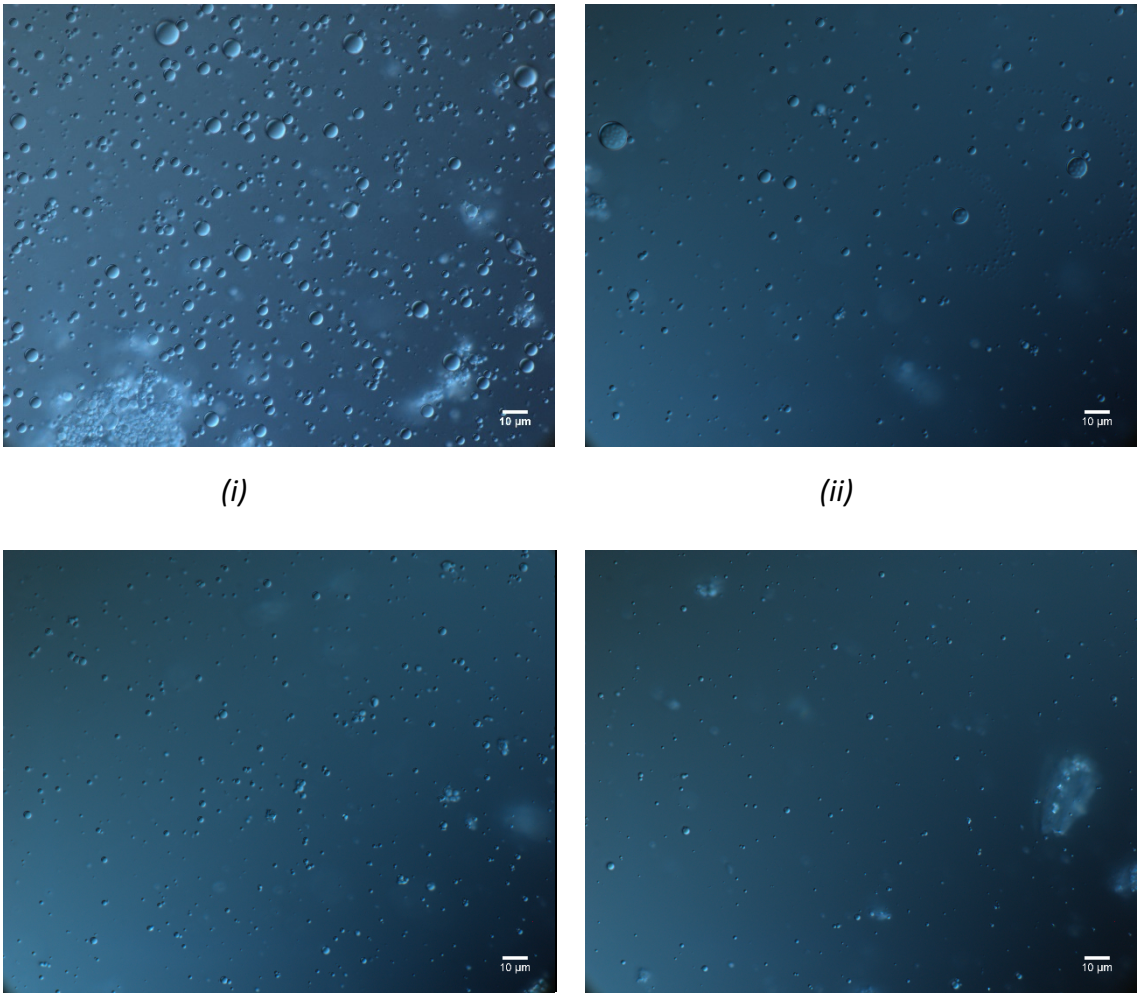
Figure 4: Batch 1. (i) Suspension before centrifugation and (ii) suspension directly after the centrifugation. The solvent has been substituted to a continuous phase containing 6.25 weight-%. Some flocculation has occured and the capsules have very different sizes but their shapes are even.



(i) *(ii)*

(iii) *(iv)*

Figure 5: Batch 2 centrifuged with 2.5 weight-% PEG-PPG-PEG. (i) Suspension directly after the centrifugation. Picture (ii) and (iii) shows the suspension two respectively five days after the centrifugation. It is not until after one week (picture (iii)) that it shows small hints of flocculation. The flocculation part are still so small that the suspension still looks good.

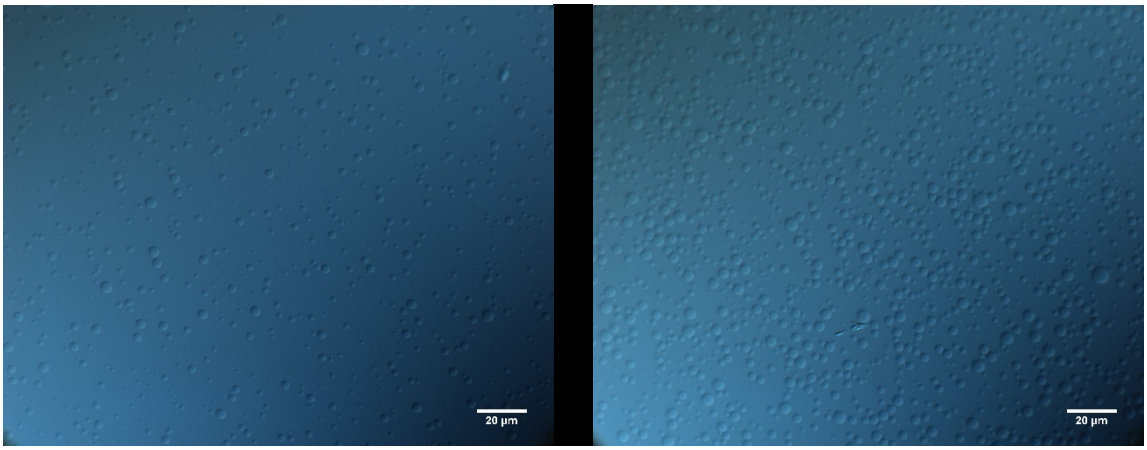


(i) *(ii)*

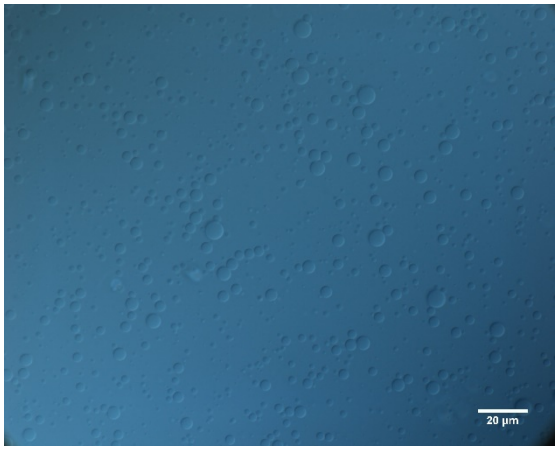
(iii) *(iv)*

Figure 6: Batch 2 centrifuged with 2.5 weight-% PVA. (i) Suspension directly after the centrifugation. Picture (ii) and (iii) shows the suspension two respectively five days after the centrifugation. It is not until after one week (picture (iii)) that it shows small hints of flocculation. The flocculation part are still so small that the suspension still looks good.

Appendix V: Emulsion with oleyl alcohol



(i) *(ii)*



(iii)

Figure 7: Emulsion made with oleyl alcohol as core oil. (i) Emulsion directly after the shearing, (ii) Emulsion three days after and (iii) Emulsion 18 days after.