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Fabrication of Microcapsules through Surfactant-Free Emulsification

Abdulwahed Shglabow

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THÈSE DE DOCTORAT
DE L'UNIVERSITÉ PSL

Préparée à l'ESPCI - Ecole Supérieure de Physique et Chimie
Industrielles de la ville de Paris

**Fabrication de microcapsules par émulsification sans
tensioactif**

Soutenue par

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*Everything flows
and nothing abides;
everything gives way
and nothing stays fixed.*
Heraclitus (535–475 BCE)

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*The significance of a man
is not in what he attains,
but in what he longs to attain.*
Khalil Gibran (1883–1931)

Fabrication of Microcapsules through Surfactant-Free Emulsification

This thesis presents a new process for the fabrication of microcapsules which is based on emulsification of non-miscible fluids, without using any surfactant. The only requirements are favorable interfacial energies, a viscosity ratio close to 1 between the inner phase (phase 1) and the liquid polymer that is used to make the shell (phase 2), and a viscosity ratio close to 1 between this liquid polymer (shell, phase 2) and the outer phase (phase 3).

In this work, we designed capsules with a core made either of an aqueous solution of sodium alginate or of poly alpha olefin 40 oil. The shell is made of a free radical cross linkable aliphatic or epoxy urethane acrylate liquid polymer. These capsules are dispersed in an aqueous solution. We focus on their synthesis.

In a first step, we characterize the physical properties of the fluids that are used to make the emulsions: density, interfacial tension and viscosity vs shear rate. Next, we determine experimentally the fragmentation diagram for single and the double emulsions by varying the viscosity ratios and the shear rates. We find that there is an optimum viscosity ratio η_1/η_2 between phase 1 and 2: this ratio = 0.8, which is close to 1. We also find that for the double emulsion the optimum viscosity ratio η_2/η_3 between phase 2 and 3 = 1.24, which is close to 1. We present microscope images and movies of the fragmentation of double emulsion droplets for both types of capsules.

We used osmotic swelling to study the polymerization of the acrylate shell and we show how it depends on UV exposure time and initiator concentration. We characterize the microcapsules by measuring their size distribution. We determine the encapsulation efficiency for both types of capsules. In the case of capsules with an aqueous core it is 70%. This loss of efficiency is due to the fact that phase 1 and phase 3 have no interfacial tension since they are chemically identical. In the case of capsules with an oil core, it is 100%. This stability of the double emulsion originates from the high interfacial tension between the oil core (phase 1) and the glycerol (phase 3). Finally, we present four methods that make it possible to trigger the rupture of the capsules and the release of encapsulated material. These methods use different chemical or physical properties of the encapsulated material and of the polymer shell.

Keywords: Emulsion, Interfacial Energy, Viscosity, Surfactant- Free, Overhead stirrer, UV curable polymer, Microcapsules, Optical rheology system, Osmotic pressure, Efficiency, Encapsulation.

Fabrication de microcapsules par émulsification sans tensioactif

Cette thèse présente un nouveau procédé de fabrication de microcapsules basé sur l'émulsification de fluides non miscibles, sans utilisation de tensioactif. Les seules conditions sont des énergies interfaciales favorables, un rapport de viscosité proche de 1 entre la phase interne (phase 1) et le fluide qui sert à faire la coque (phase 2), et un rapport de viscosité entre ce fluide (phase 2) et la phase externe (phase 3) qui est également proche de 1.

Dans ce travail, nous avons fabriqué des capsules avec un cœur qui est une solution aqueuse d'alginate de sodium ou qui est une huile polyalphaoléfine 40. La coque est fabriquée à partir d'un polymère aliphatique ou époxyuréthane acrylate liquide qui est ensuite réticulé par irradiation au rayon UV. Ces capsules sont dispersées dans une solution aqueuse. Nous nous concentrons sur la synthèse de ces microcapsules.

Dans un premier temps, nous caractérisons les propriétés physiques des fluides qui sont utilisés pour faire les émulsions : densité, tension interfaciale, viscosité en fonction de la vitesse de cisaillement. Ensuite, nous déterminons expérimentalement le diagramme de fragmentation des émulsions simples et doubles en faisant varier les rapports de viscosité et les vitesses de cisaillement. Nous trouvons qu'il existe un rapport de viscosité optimal η_1 / η_2 entre les phases 1 et 2 : ce rapport vaut 0,8, proche de 1. Nous constatons également que pour la double émulsion le rapport de viscosité optimal η_2 / η_3 entre les phases 2 et 3 vaut 1.24, également proche de 1. Nous présentons des images de microscopie et des vidéos de la fragmentation des gouttelettes d'émulsion double pour les deux types de capsules.

Nous avons utilisé le gonflement osmotique des capsules pour étudier la polymérisation de la coque d'acrylate et nous montrons comment ce gonflement dépend du temps d'exposition aux UV et de la concentration en initiateur. Nous caractérisons les microcapsules en mesurant leur distribution de tailles. Nous déterminons l'efficacité de l'encapsulation pour les deux types de capsules. Dans le cas des capsules à cœur aqueux, l'efficacité de l'encapsulation est de 70%. Cette perte d'efficacité est due au fait que la tension interfaciale entre les phases 1 et 3 est nulle. Dans le cas des capsules à cœur huileux, ce taux est de 100%. Cette stabilité de la double émulsion était due à la tension interfaciale élevée entre le cœur huileux (phase 1) et le glycérol (phase 3). Enfin, nous présentons quatre méthodes qui permettent de déclencher la rupture des capsules et la libération du matériau encapsulé. Ces méthodes utilisent différentes propriétés chimiques ou physiques du matériau encapsulé et de la coque.

Mots-clés : émulsion, énergie interfaciale, viscosité, sans tensioactif, agitateur suspendu, polymère polymérisable aux UV, microcapsules, système de rhéologie optique, pression osmotique, efficacité, encapsulation.

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Chapter 1

Introduction

Aims of the work

The main objective of this thesis is to present a new process for the fabrication of microcapsules, which is based on emulsification of non-miscible fluids, without the use of any surfactant. The only requirements are favorable interfacial energies and a viscosity ratio between the inner phase (phase 1) and the liquid polymer that is used to make the shell (shell, phase 2) that is close to 1, and between this liquid polymer (shell, phase 2) and the outer phase (phase 3) that is also close to 1.

We made two types of microcapsules. We designed capsules with a core made either of an aqueous solution of sodium alginate or of poly alpha olefin 40 oil. The shell is made of a free radical cross linkable aliphatic or epoxy urethane acrylate liquid polymer. These capsules are dispersed in an aqueous solution. We used these capsules for the following goals:

- 1) To determine the physical properties of the fluids used to prepare the microcapsules: density, viscosity and interfacial tensions.
- 2) To trace an emulsification diagram for the first emulsion and for the double emulsions according to the viscosity ratios and to the shear rates and to find the optimum fragmentation conditions.
- 3) To visualize the fragmentation of the double emulsion and to make movies which capture the steps of the fragmentation of the double emulsions for both types of microcapsules.
- 4) To measure the effects of initiator concentration and UV exposure on the polymerization of the shell polymer.
- 5) To evaluate the encapsulation efficiency for both types of microcapsules.
- 6) To compare different methods for triggering the rupture of the capsules and the release of encapsulated material.

Organization of the manuscript

This thesis is organized as follows:

Chapter 1

Introduction: definition of emulsions and microencapsulation.

Chapter 2

Literature review about emulsions and the microencapsulation process.

Chapter 3

Focuses on emulsion preparation. This chapter starts with a characterization of the physical properties of the fluids that are used to prepare the microcapsules. We determine experimentally the fragmentation diagram for single and the double emulsions by varying the viscosity ratio and the shear rate to find the conditions of optimum fragmentation.

Chapter 4

Next we present visualization experiments: images and movies of double Emulsion fragmentation which show the steps of double emulsions fragmentation for the two types of microcapsules.

Chapter 5

Then we study the effects of initiator concentration and UV exposure duration on the polymerization. We characterize the microcapsules by measuring their size distribution via ImageJ for the images obtained through bright field optical microscopy, Fluorescence images of dyes dissolved in the acrylate shell, and Laser beam scattering using a Master Sizer and also through Transmission electron microscopy for both types of capsules. We determined the encapsulation efficiency for these capsules and we present different methods for triggering the rupture of the capsules and the release of their content.

Introduction

1-1-Introduction of Microencapsulation

Microencapsulation is the process of enclosing small solid particles, liquid droplets or gas bubbles with a thin film of coating or shell material. The release of their content can be triggered under specific environmental conditions. In microencapsulation, the material inside the microcapsules is referred to as the core, whereas the coating of this core is sometimes called a shell or wall material. The term microcapsule describes particles with diameters between 1 and 1000 μm . Depending on the morphology of the microcapsules, they can be classified into two basic categories as mono-core type and multiple-nuclear (matrix) type, as shown in Figure 1.1.

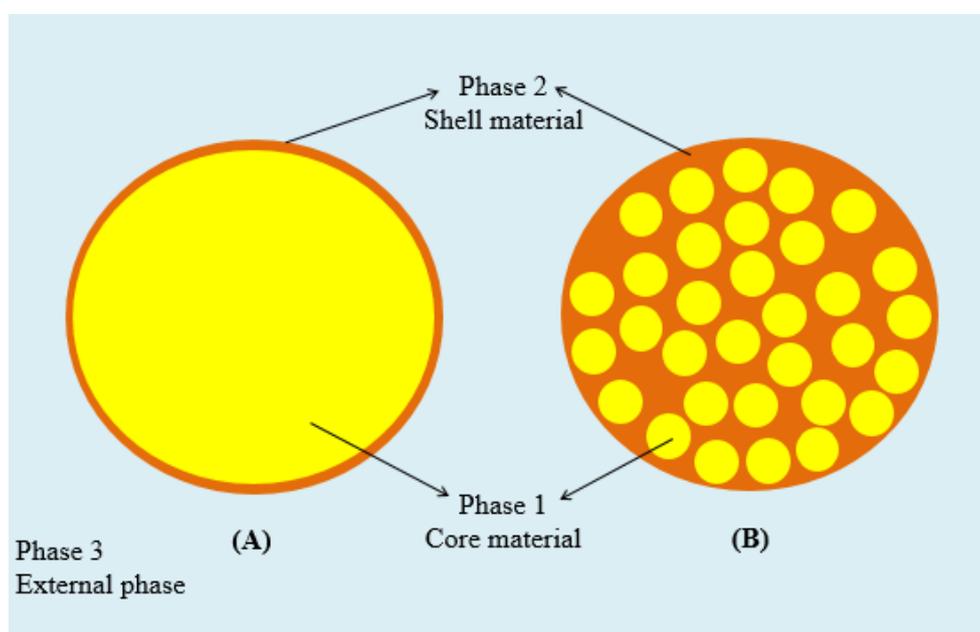


Figure 1. 1
Two structures characteristic of commercial microcapsules: (a) mono-core type (b) multi nuclear (matrix) type.

Microencapsulation technologies have been extensively used in the pharmaceutical and food industries. The main motivations are (1) controlled and/or site-specific release of encapsulated drugs (2) protection of the encapsulated materials against oxidation and external environmental conditions like light or moisture), (3) masking of odour, taste and colour of encapsulated materials, (4) Improving the shelf-life of encapsulated materials, (5) protection of encapsulated materials from undesirable phenomena, and (6) ease of use handling as powder-like encapsulated materials.

1-2-Emulsion classification

Colloid dispersions are systems that consist of small particles with sizes in the range 1-1000 nm [19]. Simple colloidal dispersions are two-phase systems consisting of a dispersed phase and a continuous phase. Table 1.1 shows the different classifications of simple colloidal dispersions [19]. Emulsions are liquid-liquid dispersions comprised of two non-miscible liquids. They are thermodynamically unstable [19]. In emulsions, one of the two liquids forms the continuous phase in which the other is dispersed as spherical droplets. There are two main types of emulsions that can be made: oil-in-water (o/w) or water-in-oil (w/o).

It is difficult to determine the type of emulsion with the naked eye. However, there are five simple tests that can be used: dilution, dye-solubility, filter paper (CoCl_2), fluorescence and conductivity. The dilution technique is based on the solubility of the continuous phase. O/W emulsions can be diluted with water and w/o emulsions can be diluted with oil. The dye-solubility test uses either a water-soluble or oil-soluble dye and then the emulsion is observed with the microscope. If a water-soluble dye is used, then an o/w emulsion will have a dyed continuous phase and a w/o will have a dyed dispersed phase. The filter paper tests involve impregnating filter paper with CoCl_2 . After the paper is dried it should have a blue tint, and when it is dipped in an o/w emulsion the filter paper will change from blue to pink. The fluorescence test operates on the idea that under UV light some oils are fluorescent. Using this test o/w emulsion show spotty patterns, while w/o emulsions are fluorescent. The conductivity test requires a light bulb attached with wires to two electrodes. When the electrodes are dipped in the emulsion a o/w emulsion will cause the bulb to glow due to the good electrical conductivity of water, while a w/o emulsion will not glow due to the low conductivity of oils [20].

Colloidal dispersions are heterogeneous in nature and always consist of at least two phases: the dispersed phase and the dispersion medium. Dispersed Phase: It is the substance consists of particles or droplets of colloidal size (1 to 100 nm). Dispersion Medium: It is the medium in which the colloids particles are dispersed.

For example, in a colloidal dispersion of sulphur in water, sulphur particles constitute the 'dispersed phase' and water is the 'dispersion medium'. Each of the two phases namely, dispersed phase and dispersion medium can be solid, liquid or gas. Thus, different types of colloidal solutions are possible depending upon the physical state of the two phases. Different types of colloidal solutions and their examples are shown in Table 1.1. You should note that gases cannot form a colloidal solution between themselves, because they form homogenous mixtures.

Types of Colloidal Solutions

S.No.	Dispersed Phase	Dispersion Medium	Type of Colloidal Solution	Examples
1.	Solid	Solid	Solid solution	Gemstones,
2.	Solid	Liquid	Sol	Paints, muddy water, gold sol, starch sol, arsenious sulphide sol.
3.	Solid	Gas	Aerosol of solids	Smoke, dust in air
4.	Liquid	Solid	Gel	Jellies, Cheese
5.	Liquid	Liquid	Emulsion	Milk, Cream
6.	Liquid	Gas	Aerosol	Mist, fog, cloud
7.	Gas	Solid	Solid foam	Foam rubber, pumice stone
8.	Gas	Liquid	Foam	Froth, whipped cream

Table 1. 1
Table Types of Colloidal Solutions

Out of the various types of colloids listed above, the most common are sols (solid in liquid type), gels (liquid in solid type) and emulsions (liquid in liquid type). If the dispersion medium is water, then the 'sol' is called a hydrosol; and if the dispersion medium is alcohol then the 'sol' is called an alcosol.

1-3-Formulation

1-3-1-How Emulsions Are Made

To make a metastable emulsion, in addition to oil and water an emulsifier must be present. Due to the immiscibility of oil and water the emulsion is naturally unstable. However, if an emulsifier is added the emulsion can become kinetically stabilized. Emulsifiers improve stability by preventing droplets coalescence. Emulsifiers are structured to have a hydrophilic head that is solvated by the water phase and a hydrophobic or lipophilic tail that is solvated by the oil phase.

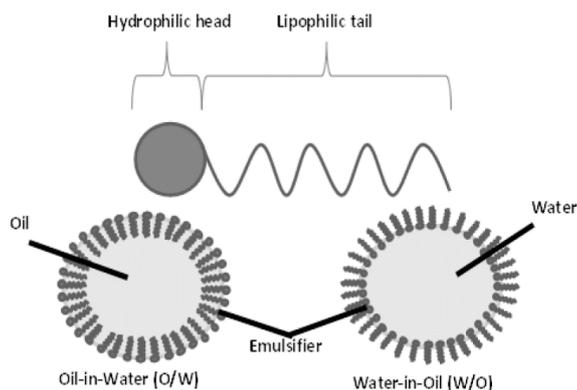


Figure 1. 2
Structure of o/w and w/o emulsions

Pictured at the top of Figure 1.2. Emulsifiers act as a protective layer between the droplet phase and the continuous phase that prevents the droplet from coalescence with other droplets [19]. In emulsion stabilised by surfactants, the type of emulsion (W/O or O/W) is determined by Bancroft's rule: the continuous phase is the one in which the emulsifier is preferentially soluble. For instance, with hydrophilic surfactant such as $C_{12}E_6$, the emulsion may be oil in water even when the oil volume fraction is 95%, conversely it is possible to produce a water in oil emulsion with lipophilic surfactant even when the water volume fraction is 95%. (Aronson and Petko, Lissant) [21].

However, in the present work, we have no surfactant and therefore Bancroft's rule does not apply. We shall see that the emulsion types are then determined mainly the relative volumes of the aqueous phase and of the oily phase. If the two phases have very different volumes, the phase that has the lowest volume is typically the dispersed phase, while the phase with the larger volume is the continuous phase. However, if the phases are roughly equal in volume, then other factors can influence which phase is the continuous and which phase is the dispersed phase [13].

The usual process for making an emulsion involves a Rayleigh instability to break the drops into smaller droplets and the Marangoni effect to prevent the coalescence of these droplets.

In a first stage, mechanical or hydrodynamic shear forces are applied to the emulsion, this causes the droplets to become elongated. Rayleigh has shown that for a given volume of disperse phase, a cylinder has higher surface area than a sphere, consequently a varicose instability will grow when the droplets are sufficiently elongated and it will fragment the original drop into a large number of droplets.

In emulsion made with surfactants, a Marangoni effect stabilizes the new droplets and prevents their coalescence: the surface pressure of the surfactant creates a surface flow toward the new surfaces and this surface flow produces a bulk flow of continuous phase that keeps the droplets away from each other.

However, in the present work, we did not use any surfactants. The mechanism that stabilizes the new droplets is not known, it can be a combination of surface forces and hydrodynamic forces.

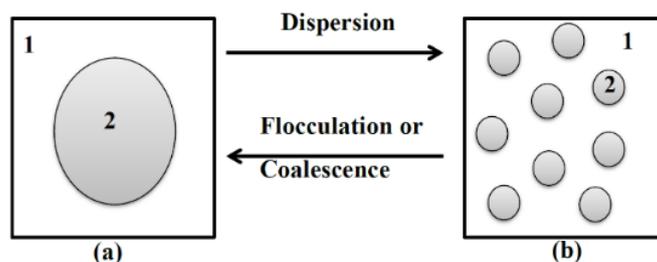


Figure 1. 3

Emulsion formation through breakdown in (b) 1 is the continuous phase and 2 is the dispersed phase [9]

The dispersion process is also influenced by the shear in the system, viscosity of the phases, interfacial energy, the pressure of solid particles, and dissolved substances [9]. Droplet breakup can be determined by the critical Weber number. The critical Weber number for turbulent flow is also dependent on the density and viscosity of the dispersed phase, as well as, the droplet diameter and interfacial tension. The Weber dimension is defined by equation 4, where is τ_{def} the deformation stress, r is the radius of the droplet, and σ

$$We = \frac{\tau_{def} r}{\sigma}$$

Weber number [9]

is the interfacial tension. When the following two conditions are met droplet break up takes place [Isaa92, pg.53]. First, when the Weber number is greater than the critical Weber number. The second condition is that the deformation time must be longer than the critical deformation time. The critical deformation time is shown in equation 5, where η_d is the viscosity of the dispersed phase and is ΔP the Laplace pressure difference [9].

$$\tau_{def,cr} = \frac{\eta_d}{\tau_{def} - \Delta P}$$

Critical deformation time [9]

Emulsions formulation and droplet size are heavily dependent on the method used, the emulsifier concentration, dispersed phase concentration, energy input, and temperature. The influence of these factors will be discussed in more detail in the following section.

1-3-2- Shearing of Coarse Emulsions

It is possible to generate monodisperse emulsions by applying a shear (tangential) force to viscoelastic emulsions with large, polydisperse droplets [6]. A crude polydisperse emulsion is first prepared by progressively incorporating oil into the continuous phase containing a surfactant. In a second step, a high shear rate is applied to the crude emulsion which becomes monodisperse after no more than a few seconds (Figure 2.3). The shear has the effect to reduce both the average droplet diameter and the distribution width [17].

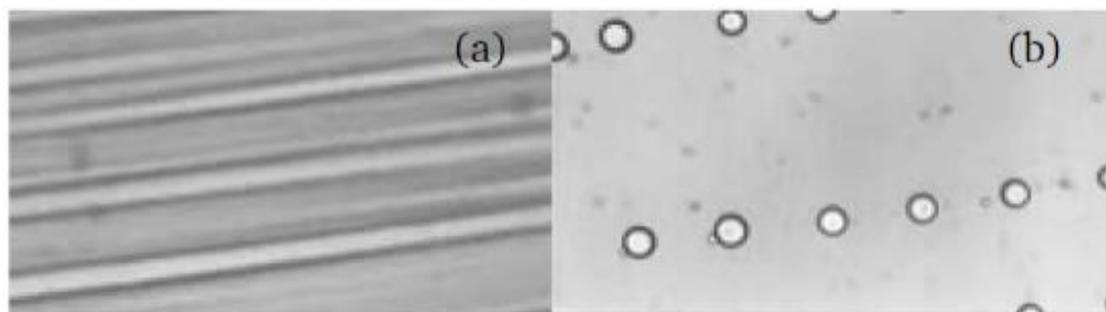


Figure 1. 4
Images of monodisperse emulsion formation by shearing coarse emulsions. (a) The droplets of the precursor emulsion elongate into long cylinders under an applied shear stress, and (b) break up into aligned droplets of similar size. From [17].

The shear stress induces a Rayleigh instability in the droplets by stretching them into long cylinders. Under the driving force of surface tension, the cylinders break up into droplets to minimize their surface area. The final drop size is primarily determined by the rate of growth of the varicose instability, and is slightly affected by the ratio of the dispersed and continuous phase viscosities. This latter parameter influences the distribution width and appears to be relevant to control the final monodispersity. If the viscosity ratio p between the dispersed and continuous phases lies between 0.01 and 2, the shear force applied to the coarse polydisperse emulsion leads to a monodisperse emulsion with a mean diameter directly governed by the stress [17].

The viscosity ratio is defined as

$$p = \frac{\eta_d}{\eta_c}$$

It is necessary that the precursor emulsion (either O/W or W/O) is viscoelastic and the shear rate is well controlled. By tuning these variables, it is possible to produce emulsions with mean droplet diameters between 0.3 and 10 μm with polydispersity as low as 1.06, although typical values are closer to 1.16 [5]. Additional polydispersity may be introduced if the precursor emulsion contains droplets smaller than the mean droplet diameter of the final monodisperse emulsion [7].

1-4- Droplet dynamics

The viscoelastic properties of emulsions are intimately linked to the ability of the suspended droplets to pack and deform [3]. The shape of a droplet is governed by a balance between competing forces: the shear stress applied during a rheological experiment and the interfacial tension [10]. The shear stresses tend to stretch and elongate the droplet in the direction of the flow, while the interfacial tension and viscosity of the droplet oppose the elongation [1].

The influence of these effects is given by the capillary number and viscosity ratio first introduced in chapter 3

$$\text{Ca} \equiv \frac{\eta_c G \dot{\gamma}}{\xi}$$

And

$$p = \frac{\eta_d}{\eta_c}$$

quantified droplet deformation by introducing the deformation parameter

$$D \equiv \frac{L - B}{L + B}$$

where L and B are the lengths of the major and minor axes of the droplet with volume $(4/3) \pi L B^2$, respectively. The deformation parameter is zero for a spherical droplet and tends to 1 as the droplet becomes infinitely slender.

In terms of the capillary number and viscosity ratio, the deformation parameter is:

$$D = Ca \left(\frac{19p + 16}{16(p + 1)} \right)$$

If $p < 1$, low shear rates (typically below 1 s^{-1}) cause the droplet to elongate and assume an elliptical shape with its long axis orientated to the direction of shear as the shear rate increases, the droplet is further elongated and its long axis rotates into the plane of shear. At higher shear rates, the droplet may deform further into long, thin threads until a critical shear rate is reached when the droplet will break.

When $p > 1$ the degree of deformation is modest. At most the droplet will form a prolate ellipsoid with its long axis orientated in the direction of shear and no breakup is observed [10].

The deformable nature of droplets is responsible for the non-Newtonian and viscoelastic effects seen in the majority of emulsion systems, even when both phases are Newtonian liquids.

Summary for the first chapter in french language

Résumé du premier chapitre :

Définition des émulsions et de la microencapsulation et types de colloïdaux solutions.

Pour produire une émulsion métastable, un émulsifiant doit être présent en plus de l'huile et de l'eau. En raison de l'immiscibilité de l'huile et de l'eau, l'émulsion est naturellement instable. Cependant, si un émulsifiant est ajouté, l'émulsion peut être stabilisée cinétiquement.

Cependant, dans le présent travail, nous n'avons utilisé aucun émulsifiant. Le mécanisme qui stabilise les nouvelles gouttelettes n'est pas connu. Il peut s'agir d'une combinaison de forces superficielles et de forces hydrodynamiques.

Il est possible de générer des émulsions monodisperses en appliquant une force de cisaillement (tangentielle) aux émulsions viscoélastiques à grosses gouttelettes polydispersées. La contrainte de cisaillement induit une instabilité de Rayleigh dans les gouttelettes en les étirant dans de longs cylindres. Sous la force motrice de la tension superficielle, les cylindres se décomposent en gouttelettes afin de minimiser leur surface.

L'influence de ces effets est donnée par le nombre de capillaires et le rapport de viscosité introduits au chapitre 3.

Chapter 2

Literature Review

2-1- Droplet rupture under shear flows

A key stage in the creation of an emulsion is the deformation of larger drops and their subsequent break up in shear flows. The interfacial force holding a droplet together must therefore be overcome in order to deform a droplet and this can occur if a large enough viscous shear force is applied to the drop. Taylor in 1934 did the first pioneering work to understand these mechanisms using an experimental setup consisting of a “four roller mill” [2]. The apparatus consisted of four independently controllable rotating cylinders submerged in a continuous phase. A droplet was introduced into the center of the assembly, and by varying the cylinders’ rotation, droplet rupture could be observed under a multitude of different shear flows. The possible flow conditions of the device ranged from elongational flow with no vorticity, to pure shear (Couette flow) consisting of equal parts vorticity and elongation. Taylor’s findings can be crudely summarized as follows, albeit with different terminology:

The ratio between the interfacial tension and the counteracting shear forces can be expressed by using the capillary (Ca) number. Small values of Ca represent dominance of interfacial forces over the applied shear and therefore drops are only slightly deformed. Increasing Ca leads to higher deformations and once a critical value is reached the droplet can no longer exist in an equilibrium state and ruptures into two or more droplets. The capillary numbers for pure shear flow and elongational shear flow are calculated as:

$$Ca_s = \frac{\dot{\gamma}\mu_c r}{\sigma}$$

$$Ca_e = \frac{\dot{\epsilon}\mu_c r}{\sigma}$$

Where the variables are: shear rate ($\dot{\gamma}$), deformation rate ($\dot{\epsilon}$), dynamic viscosity of continuous phase (μ_c), droplet radius (r), and interfacial tension (σ).

Taylor’s predictions for critical capillary numbers, however, were limited as only one viscosity ratio was used in his experiments. In order for a droplet to be ruptured under equilibrium conditions (i.e. neglecting time), it has been found that the critical capillary number is affected by both the type of the shear field and the viscosity ratio (p) of the emulsion.

$$p = \frac{\eta_d}{\eta_c}$$

Where the viscosity ratio (p) is the dispersed phase viscosity (η_d) divided by the continuous phase viscosity (η_c).

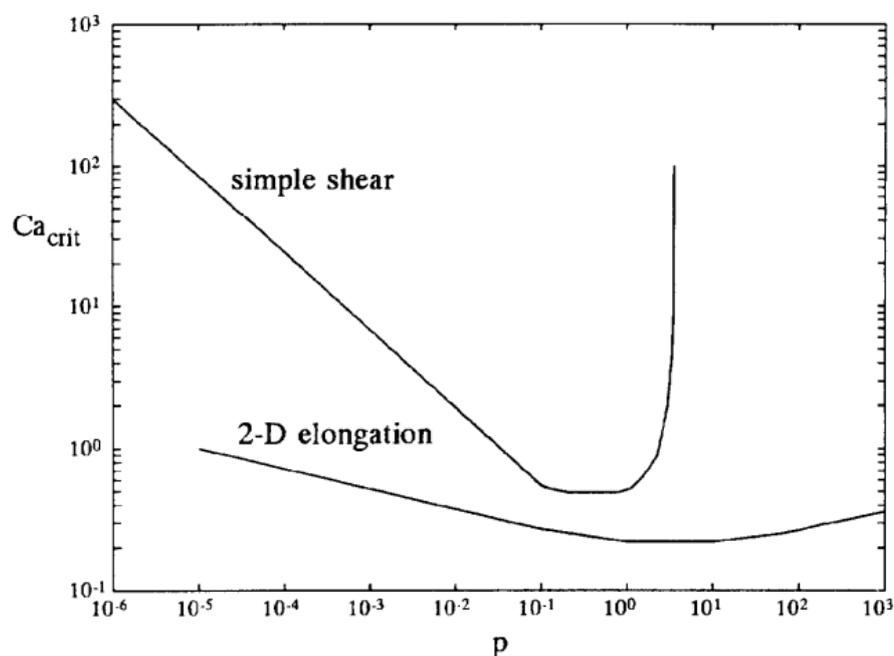


Figure 2. 1
Grace curves - critical capillary number for various viscosity ratios under simple (pure) shear flow and 2-D elongation flow [4].

In 1982 Grace radically improved the theory of droplet rupture by doing many experiments using the same four roller mill apparatus but this time using many different viscosities for the fluids [15]. His results can be seen in Figure 5 and to this day are widely used in emulsifying process design to predict required shear flows for emulsions of desired sizes. It is important to note that droplet rupture is promoted when viscosities of both phases are similar.

However, these predictions were valid for emulsions stabilized by surfactant only.

Since the work by Grace, there have been many more studies of drop rupture under similar conditions, with a focus on drop shape, effects of shear cessation during rupture, and how many drops result during and after break-up.

Comprehensive works such as those by Bentley, Stone, Leal, and Rallison [12] - [18] go to great detail in describing the dynamics of droplet rupture and can be briefly generalised as follows:

$P < 1$. Droplets submitted to capillary numbers just short of the critical value are stretched into stable shapes. The lower the viscosity ratio, the more elongated these steady shapes become. When a critical value is reached they rupture into two or more drops, the more elongated the stable shape, the more drops will result from the rupture. As well as the main drops resulting from the rupture, satellite (much smaller drops) drops are often formed in between the main drops. The lower the viscosity ratio, the higher the likelihood and number of satellite drops are formed.

$P > 1$. Above a viscosity ratio of 3.5, drop rupture cannot occur in pure shear flows (under such conditions droplets rotate instead of changing shape).

2-2- Sub and Super critical capillary rupture

When creating an emulsion, predicting the final droplet size is often the most important factor in the process design. The works described in the section above are crucial in understanding how much shear is required to rupture emulsion drops of known size and properties but are impractical in predicting final droplet size for most emulsifying processes. Critical capillary numbers are calculated theoretically or determined experimentally, by assuming a very slow increase of shear until rupture occurs whereby at all lower shear values the droplet maintains a stable equilibrium shape. This description of gradual shear increase is at odds with the majority of emulsification processes where often drops are subject to a sudden increase in shear far above critical values [4].

Under supercritical capillary number conditions, drops do not have time to form equilibrium shapes and instead are stretched into long thin liquid threads. The less the drop resembles a sphere and the thinner the liquid cylinder becomes, the less force is required to further deform the drop and so the drop keeps stretching [11]. Once a drop deforms into a long and slender continually stretching state, capillary waves begin to appear on the surface. At some point the amplitude of this varicose instability becomes too large and the droplet breaks into many (potentially thousands) drops due to Rayleigh-Plateau instability [15], [14].

Understanding and predicting when a stretching liquid thread will rupture into many drops is a very complicated task and not well understood, which makes final droplet size predictions challenging. It is known that viscosity ratio plays a very important part in this process, increasing viscosity ratio results in increasing the stretch before rupture as the higher the viscosity, the more viscous damping occurs on the forming capillary waves. It has been shown that the most efficient viscosity ratio for forming small drops under shear is not equal to one, as the Grace graph suggests, but to use higher viscosity ratios to maximize droplet stretching (and minimize satellite drops) before rupture [4].

Another important phenomenon worth discussing is the fact that drops can also be ruptured under sub-critical capillary number conditions. As mentioned above, droplets can be stretched into very long liquid threads at super-critical conditions which continue to stretch until rupture occurs, however, if the shear flow is suddenly stopped during this stretching, instead of returning to its original drop shape, the liquid thread often ruptures into many drops (more prominent at low viscosity ratios). When considering a very low viscosity ratio system, stable equilibrium drop shapes at sub-critical conditions can be extremely slender and long, and it has been shown that if the shear flow is stopped suddenly (rather than gradually), this long slender shape will rupture into many drops [15], [14], [18]. Another phenomenon associated with sub-critical rupture is “tip-streaming”, this only occurs in surfactant containing continuous phases and at low viscosity ratios. The droplet will obtain a stable slender shape, but instead of entirely rupturing, very small droplets will be formed and released from the pointed ends of the slender drop. This is due to the forced movement of surfactant molecules at the surface of the drop from the center to the ends, thus creating a distribution of interfacial tensions along the slender drop with much lower interfacial tensions at the points [14].

2-3- Methods used to create monodisperse emulsions

2-3-1- Controlled shearing of emulsions

It has been shown by Mason and Bibette [6]– [17] that monodisperse emulsions can be created by applying uniform shear stress to a polydisperse coarse emulsion. The reasoning behind this is that if every droplet in an emulsion is subjected to a large enough shear stress that is equal for every droplet, then the droplets will all rupture and reduce in size to a value below the critical capillary number.

In order to subject an emulsion to a uniform shear stress a Couette flow is utilized (Figure 2.2). Couette flow is observed when a liquid is placed between two parallel plates where one is stationary and the other is moving. Due to the non-slip condition of the liquid at the plate boundaries, a viscous shear driven flow is induced where the shear stress at every point in the liquid is equal.

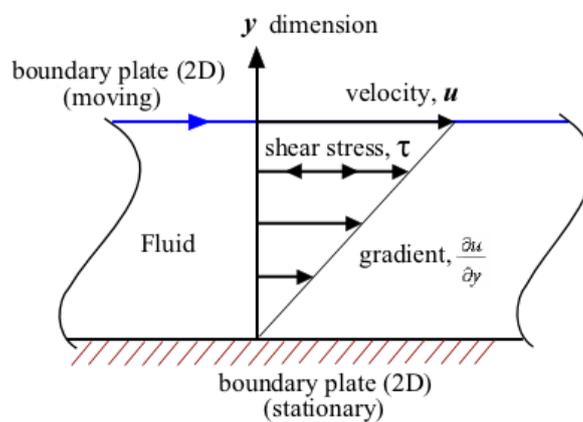


Figure 2. 2
Simple Couette flow

This flow regime can be created using various geometries but the most common is two concentric cylinders where one rotates and the other is stationary (Figure 2.3).

2-3-2- Couette instrument

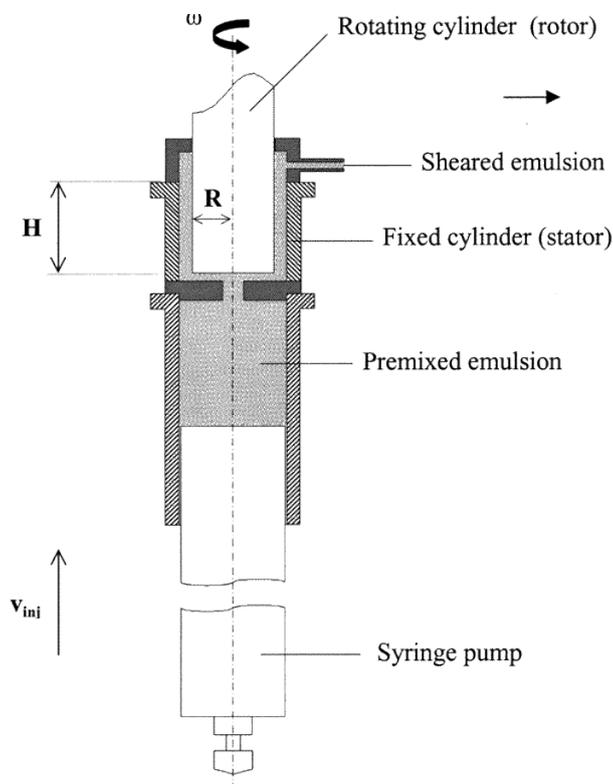


Figure 2. 3
Scheme of a commercialized Couette cell where a coarse emulsion is forced through an area of uniform shear stress to create monodisperse emulsions

It was discovered, however, that monodisperse emulsions are only produced if the initial coarse emulsion is shear thinning [5], whereas shearing Newtonian emulsions yields polydisperse results. The proposed reason for this is the mechanism of droplet rupture. When a polydisperse shear-thinning emulsion is sheared, the diameters of all the liquid threads formed from drop stretching at rupture are very similar (therefore resulting in similar sized drops). However, when a polydisperse Newtonian emulsion is sheared, the diameter of the liquid threads produced at rupture seems to be a function of the initial droplet size and therefore yields polydisperse results [7], [8].

This special case of monodisperse rupture that occurs if the emulsion is shear-thinning may at first seem rather specific in application, as the majority of industrial emulsions do not contain shear thinning materials as their continuous phases. However, when an emulsion's phase ratio is increased to levels above $\approx 50\%$, the increased droplet interactions due to the close packing dramatically changes the rheology of the emulsions increasing its viscosity and exhibiting shear-thinning effects [16]. It is for this reason that this method of creating monodisperse emulsions has great potential in being used for a very wide range of materials.

2-4- Emulsion stability

Once an emulsion is formed there are mechanisms by which an emulsion can be destroyed; one being coalescence, another being Ostwald ripening. Coalescence is the mechanism by which when two droplets come together, the thin film of continuous phase separating the two is ruptured and the droplets merge into one bigger droplet. The rate of coalescence can be reduced by using surfactants to coat the droplets and by reducing the size of the droplets.

Ostwald ripening is the mechanism where dispersed phase in smaller droplets dissolves in the continuous phase and precipitates on to larger droplets causing smaller droplets to shrink and larger droplets to grow [22].

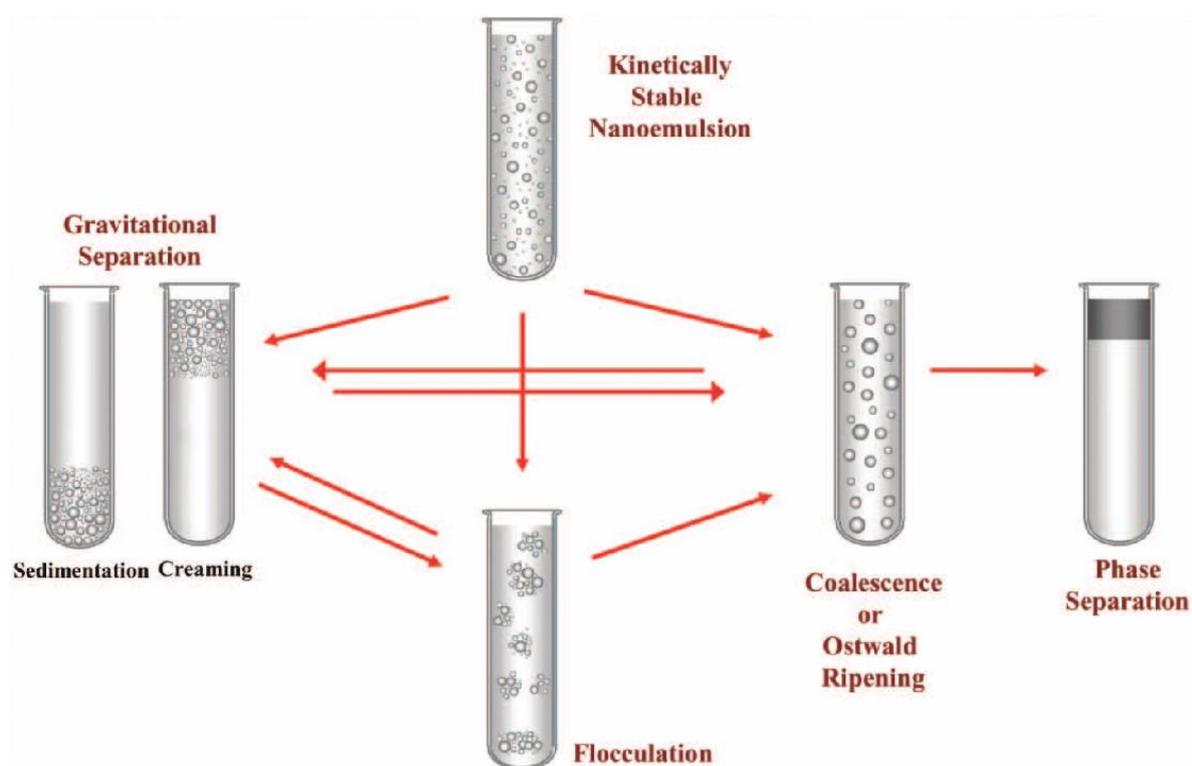


Figure 2. 4
Scheme of different types of instability of emulsions [22]

2-4-1 Coalescence

The coalescence phenomenon of drops in liquid / liquid systems is reviewed with particular focus on its technical relevance and application. Due to the complexity of coalescence, a comprehensive survey of the coalescence process and the numerous influencing factors is given. Subsequently, available experimental techniques with different levels of detail are summarized and compared.

These techniques can be divided in simple settling tests for qualitative coalescence behavior investigations and gravity settler design, single-drop coalescence studies at flat interfaces as well as between droplets, and detailed film drainage analysis.

To model the coalescence rate in liquid/liquid systems on a technical scale, the generic population balance framework is introduced.

Additionally, different coalescence modeling approaches are reviewed with ascending level of detail from empirical correlations to comprehensive film drainage models and detailed computational fluid and particle dynamics [23].

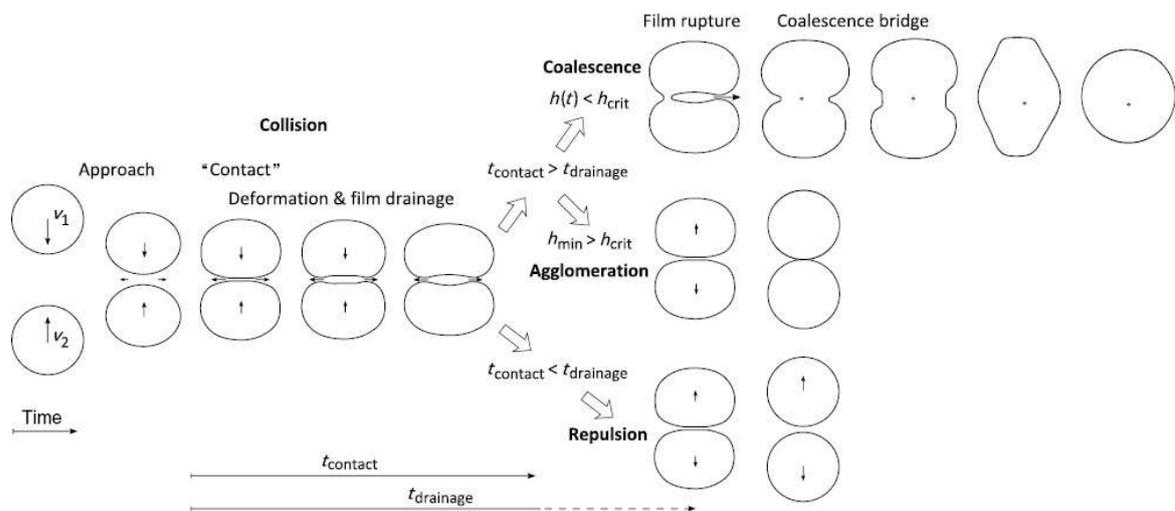


Figure 2. 5
Scheme shows the mechanism of coalescence [23]

Summary for the second chapter in french language

Résumé du deuxième chapitre :

Nous présentons la rupture des gouttelettes sous les écoulements de cisaillement et les courbes de Grace - nombre de capillaires critiques pour divers rapports de viscosité sous un écoulement de cisaillement simple (pur) et un écoulement d'élongation 2D.

Nous présentons de méthodes utilisées pour créer des émulsions monodisperses par cisaillement contrôlé d'émulsions à l'aide de l'instrument Couette.

Chapter 3

Emulsions Preparation

3-1- Physical Properties of the Fluids

3-1-A- Density

We have measured the density of all the fluids in this study. These values are required in the calculation of the interfacial tension, the density different also control the creaming velocity of the droplets and capsules.

1- Density values for the system made of Aqueous core / Aliphatic Urethane Acrylate Shell / Aqueous External phase

The aqueous phase was either water or an aqueous solution of sodium alginate of concentration 7%, 10% and 15%, the shell was a cross-linkable aliphatic urethane acrylate liquid polymer.

No:	Material name	Density in g/cm ³ at 25°C
1	water	0.994
2	Aqueous solution of 7 % sodium alginate	1.029
3	Aqueous solution of 10 % sodium alginate	1.043
4	Aqueous solution of 15 % sodium alginate	1.051
5	Aliphatic urethane acrylate CN991 liquid polymer	1.239

Table 3-1-A. 1

Density values of fluids used in the aqueous phase / acrylate shell / aqueous phase system

The results show that there are no large density differences. This makes it easier to control the sedimentation or creaming of the droplets and capsules.

2- Density values for the system made of Oil PAO40 core/ Epoxy Urethane Acrylate Shell / Glycerol external phase

The oil phase is poly alpha olivine40, the shell is Epoxy Urethane Acrylate liquid polymer and the external phase is Glycerol.

No:	Material name	Density in g/cm ³ at 25°C
1	Poly alpha olivine 40	0.841
2	Glycerol	1.2536
3	Epoxy urethane acrylate liquid polymer	1.236
4	Epoxy urethane acrylate polymer with 10% of HDDA	1.1447

Table 3-1-A. 2

Density value of fluids used for oil / acrylate shell / aqueous phase system

The results show that there are significant differences between the density values. This suggests that the droplets of poly alpha olefin can cream in the liquid epoxy urethane acrylate polymer and the capsules can cream in glycerol.

According to the sedimentation equation of the droplets of the oil poly alpha olefin with size 15 μm.

Sedimentation velocity of a particle is given by Stokes' law:

$$V = \frac{2(d_p - d_f) g r^2}{9\eta f}$$

where V is the sedimentation rate terminal, fall or settling velocity, d is the density (p and f respectively indicate particle and fluid), g is the acceleration due to gravity, r is the radius of the particle and ηf is the dynamic viscosity of the fluid.

Aqueous core phase capsules

Creaming of droplets of aqueous solution of 10% sodium alginate in aliphatic urethane acrylate liquid polymer

No:	Droplets Size in μm	60	40	20	10
1	Creaming speed in mm/h	-1.632793388	-0.72568595	-0.181421488	-0.045355372
2	Comment	fast creaming	slow creaming	slow creaming	slow creaming

Table 3-1-A. 3

From the results it is negative values because the droplets have lower density than the outer phase, so it will cream by the time.

Creaming speed of droplets of solution of sodium alginate 10% have size 60μm is -1.632 mm/h and the one that have size of 10μm is -0.0453 mm/h. from that the speed of creaming decreased with decrease the size of the droplets.

Sedimentation capsules of aqueous solution of 10% sodium alginate shell of aliphatic urethane acrylate polymer in external phase aqueous solution of 10% sodium alginate

No:	Capsules Size in μm	60	40	20	10
1	Sedimentation speed in mm/h	0.465802129	0.207023169	0.051755792	0.012938948
2	Comment	fast creaming	fast creaming	slow creaming	slow creaming

Table 3-1-A. 4

From the results it is positive values because the capsules have higher density than the outer phase the aqueous solution of 10% sodium alginate, so it will sediment by the time.

sedimentation speed of capsules that have aqueous solution of sodium alginate 10% and shell of aliphatic urethane acrylate have size 60μm is 0.4658 mm/h and the one that have size of 10μm is 0.0129mm/h. from that the speed of sedimentation decreased with decrease the size of the capsules.

Oil core phase capsules

Creaming of droplets of PAO40 in Epoxy urethane acrylate liquid polymer

No:	Droplets Size in μm	20	10	5	3
1	Creaming speed in mm/h	-0.281110744	-0.070277686	-0.017569421	-0.006324992
2	Comment	Fast creaming	Slow creaming	Slow creaming	Slow creaming

Table 3-1-A. 5

The results it is negative values because the oil droplets of PAO40 have lower density than the outer phase epoxy urethane acrylate polymer, so it will cream by the time.

Creaming speed of oil droplets of PAO40 in epoxy urethane acrylate as external phase have size 20 μm is -0.2811 mm/h and the one that have size of 3 μm is -0.0063 mm/h. from that the speed of creaming decreased with decrease the size of the droplets.

Creaming of droplets of PAO40 in Glycerol

No:	Droplets Size in μm	20	10	5	3
1	Creaming speed in mm/h	-0.352372985	-0.088093246	-0.022023312	-0.007928392
2	Comment	Fast creaming	Slow creaming	Slow creaming	Slow creaming

Table 3-1-A. 6

The results it is negative values because the oil droplets of PAO40 have lower density than the outer phase Glycerol, so it will cream by the time.

Creaming speed of oil droplets of PAO40 in Glycerol as external phase have size 20 μm is -0.3523 mm/h and the one that have size of 3 μm is -0.0079 mm/h. from that the speed of creaming decreased with decrease the size of the droplets.

Creaming capsules of PAO40 shell of epoxy urethane acrylate polymer in external phase Glycerol

No:	Capsules Size in μm	20	10	5	3
1	Creaming speed in mm/h	-0.272177913	-0.068044478	-0.01701112	-0.006124003
2	Comment	Fast creaming	Slow creaming	Slow creaming	Slow creaming

Table 3-1-A. 7

From the results it is negative values because the capsules have lower density than the outer phase, so it will cream by the time.

Creaming speed of capsules that have PAO40 oil as core and shell of epoxy urethane acrylate in Glycerol as external phase that have size 20 μm is -0.2721 mm/h and the one that have size of 3 μm is -0.00612 mm/h. from that the speed of creaming decreased with decrease the size of the capsules.

3-1-B- Rheology

The aim of measuring the fluids viscosity was to find the concentration that yields the optimum viscosity ratio for the fragmentation of droplets. The other benefit is to find out whether the polymer solution is a dilute Newtonian fluid or a semi-dilute non-Newtonian fluid.

3-1-B.1 Viscosity of Aqueous phase / Aliphatic Urethane Acrylate Shell / Aqueous phase System as function of shear rate

The aqueous phase was prepared from water with different concentrations of sodium alginate 0%, 7%, 10% and 15%, and the acrylate shell was made of the aliphatic urethane acrylate liquid polymer.

The viscosity was measured at shear rates ranging from 1 to 2000 sec^{-1}

No:	Description	Viscosity pas at 1sec ⁻¹	Viscosity pa.s at 10sec ⁻¹	Viscosity pa.s at 100sec ⁻¹	Viscosity pa.s at 500sec ⁻¹	Viscosity pa.s at 1000sec ⁻¹	Viscosity pa.s at 2000sec ⁻¹
1	Aliphatic urethane acrylate CN991 liquid polymer	10.3602	10.0579	9.76346	--	--	--
2	water	0.037658	0.00287538	0.00150547	0.00158087	0.00203399	0.00269181
3	Aqueous solution of sodium alginate 5%	0.579143	0.549588	---	---	---	---
4	Aqueous solution of sodium alginate 7%	2.6850	2.11424	1.30088	0.78988	0.615121	0.094742
5	Aqueous solution of sodium alginate 10%	14.9934	8.28345	3.65076	1.83509	0.352791	0.020604
6	Aqueous solution of sodium alginate 15%	291.513	55.0585	15.1648	0.765473	0.120133	0.029286

Table 3-1-B. 1

Viscosity of the fluids in the aqueous phase / acrylate shell / aqueous phase system plotted as a function of shear rate

The aliphatic urethane acrylate polymer is a Newtonian fluid since it has almost constant viscosity at all shear rates.

On the other hand, the aqueous solution of sodium alginate at concentrations higher than 5% is strongly shear-thinning. This indicates that the polymer solution is semi-dilute, that is the macromolecules are overlapped.

Another important consequence of this non-Newtonian behavior of concentrated sodium alginate solutions is that, they transmit a much smaller stress than Newtonian fluids at the same shear rate. This is important for the emulsification process.

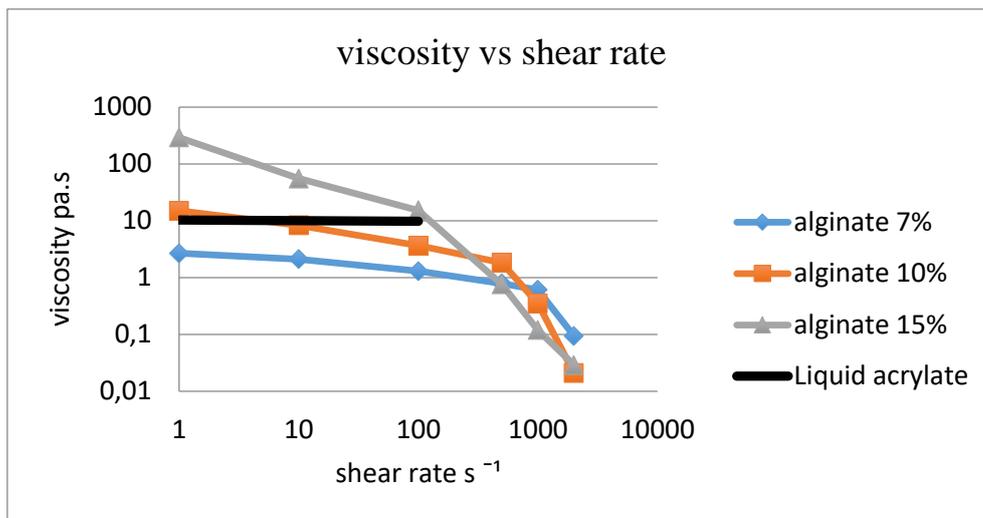


Figure 3-1-B. 1

Graph of the viscosity of fluids plotted against shear rate for aqueous phase / acrylate shell / aqueous phase system

From the graph we see that at low shear rate the aliphatic urethane acrylate polymer has almost the same viscosity as the 10% aqueous solution of sodium alginate.

Since the aliphatic urethane acrylate liquid polymer is Newtonian but the solution of sodium alginate is shear-thinning the viscosity ratio will not have the same values at different shear rates. This is an important difference compared to the case where all the fluids are Newtonian.

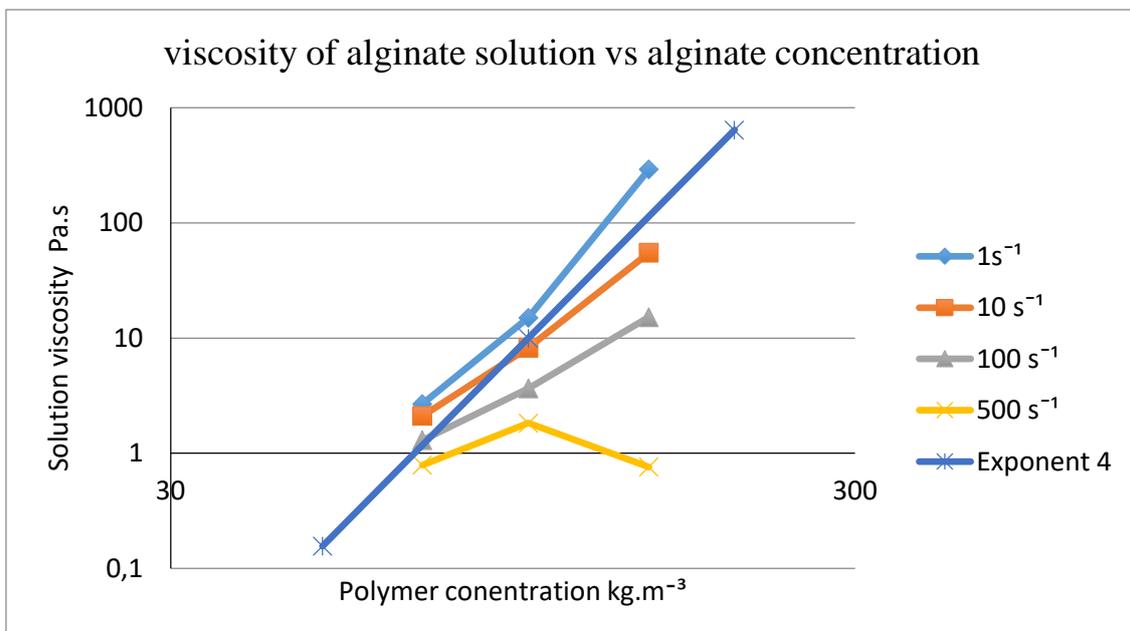


Figure 3-1-B. 2

The variation of solution viscosity with alginate concentration shows, a concentration of 10% of sodium alginate, the alginate macromolecules are strongly overlapped

3-1-B.2 Viscosity of Oil phase / Epoxy Urethane Acrylate Shell / Aqueous System VS Shear rate

The internal phase oil is poly alpha olivine40, the acrylate shell is Epoxy Urethane Acrylate liquid polymer and the external aqueous phase is Glycerol.

No :	Description	Viscosity pa. s at 1sec ⁻¹	Viscosity pa. s at 10sec ⁻¹	Viscosity pa. s at 100sec ⁻¹	Viscosity pa. s at 500sec ⁻¹	Viscosity pa. s at 1000sec ⁻¹	Viscosity pa. s at 2000sec ⁻¹
2	75% CN109 with 25% HDDA	0.845093	0.847270	---	---	---	---
3	100% Glycerol	0.969308	0.918148	0.922537	0.914022	0.862442	0.765855
1	PAO 40	0.922470	0.900229	0.879400	0.875925	0.864336	0.780864

Table 3-1-B. 2

Viscosity of poly alpha olefin oil (core), polymer shell Epoxy urethane acrylate polymer and Glycerol vs shear rate.

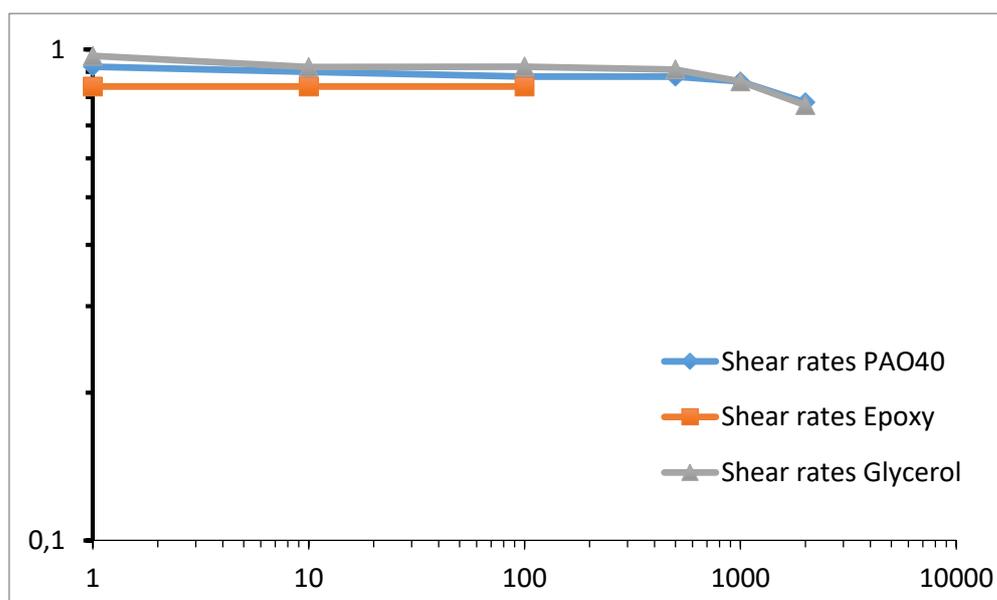


Figure 3-1-B. 3

Graph of the viscosity values of fluids plotted vs shear rate for oil / Epoxy urethane acrylate shell / aqueous phase system.

Since all these fluids Glycerol, PAO40 Oil, and Epoxy urethane acrylate polymer have almost constant viscosity values regardless of shear rate, we conclude that are Newtonian fluids.

3-1-C Interfacial Tension

The aim of these experiments was to find out if the effect of wetting can stabilise the topology of the droplets and the capsules, we measured interfacial tensions through the pendant droplet (PD) method.

This optical method uses the shape of a drop of a liquid in another non-miscible liquid in a cuvette.

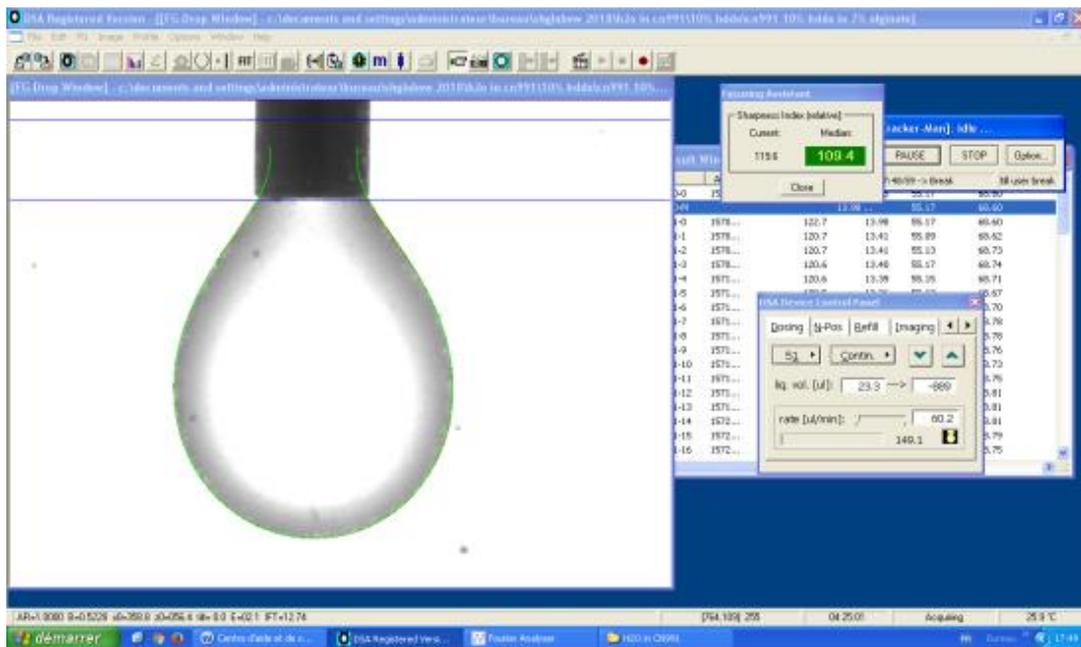


Figure 3-1-C. 1

Screenshot of the analysis software of the KRÜSS DSA30 interfacial tension device

3-1-C.1 Interfacial Tension of Aqueous phase / Aliphatic Urethane Acrylate Shell / Aqueous phase System

The aqueous phase was prepared from water with different concentration of sodium alginate 0%, 3%, 7% and 10% and the acrylate shell from the Aliphatic Urethane Acrylate liquid polymer.

No:	Pendent drop fluid	Continues phase	Interfacial tension mN/m
1	Aliphatic urethane acrylate CN991	Water with 0% Sodium alginate	13,7
2	Aliphatic urethane acrylate CN991	Water with 3% Sodium alginate	13,1
3	Aliphatic urethane acrylate CN991	Water with 7% Sodium alginate	12,9
4	Aliphatic urethane acrylate CN991	Water with 10% Sodium alginate	13,4

Table 3-1-C. 1

Since fluids 1 and 3 are chemically identical, the relevant interfacial tensions are between fluids 1 and 2 and also between 2 and 3.

Aqueous Phase / Acrylate Shell / Aqueous phase Model

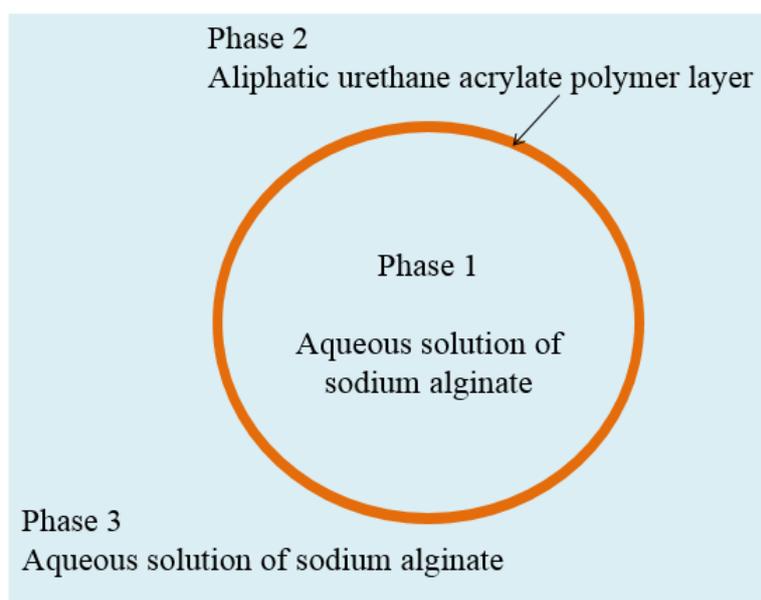


Figure 3-1-C. 2

Capsule structure of aqueous phase / acrylate shell / aqueous phase with the labeling of the three phases

To simplify the equation, we used the following symbols:

Interfacial tension between phase 1 and 2 = A

Interfacial tension between phase 2 and 3 = B

Interfacial tension between phase 1 and 3 = C

In a double emulsion the general equation for stable wetting is

$$C > A + B$$

But in our case the $C = 0 \text{ mN/m}$, there for we do not have the stability provided by wetting.

$$0 \text{ mN/m} < 13.4 \text{ mN/m} + 13.4 \text{ mN/m}$$

$$0 \text{ mN/m} < 26.8$$

There is no stability originating from the interfacial tension between the fluids. This would make us believe that the possibility to produce these capsules is low.

3-1-C.2 Interfacial Tension of Oil Phase / Acrylate shell / Aqueous Phase System

The oil phase is poly alpha olivine 40, the acrylate shell is Epoxy Urethane Acrylate liquid polymer and the aqueous phase is Glycerol.

No:	Description	Interfacial tension mN/m	Temperature °C
1	Glycerol in oil	22.41	25.0
2	Epoxy urethane acrylate in oil	5.24	25.0
3	Glycerol in epoxy acrylate	11.81	25.0

Table 3-1-C. 2

Interfacial tension between the fluids of oil / acrylate shell / aqueous phase system

Oil / acrylate shell / Aqueous Phase Model

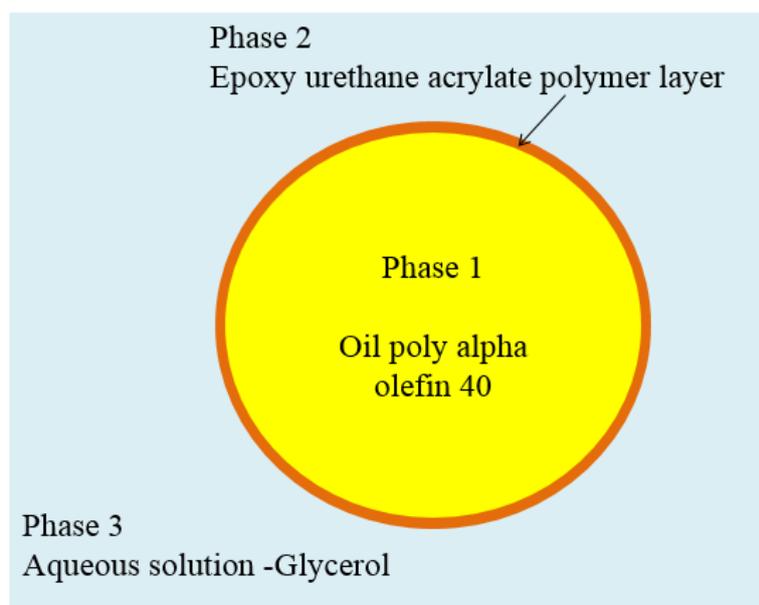


Figure 3-1-C. 3

Capsule structure with labeling the three phase

To simplify the equation, we used the following symbols:

Interfacial tension between phase 1 and 2 = A

Interfacial tension between phase 2 and 3 = B

Interfacial tension between phase 1 and 3 = C

In a double emulsion the general equation for stable wetting is

$$C > A + B$$

$$22,41 \text{ mN/m} > 5,24 \text{ MN/m} + 6,57 \text{ mN/m}$$

$$22,41 \text{ mN/m} > 11,81$$

There is stability originating from the interfacial tension between the fluids. This would make us believe that the possibility to produce these capsules is very high.

3-2 Fragmentation Diagram

3-2-A Shear Rate Applied by the Overhead Mixer

The aim of this section is to evaluate the shear rate where the emulsification take place. The shear rate is highest in the gap between the Anchor stirrer and the internal wall of the beaker, and this is the region where the droplets will be broken by hydrodynamic forces.

We used a R 1330 Anchor stirrer with a diameter \varnothing : 4.5 cm, Shaft \varnothing : 8 mm, Shaft length: 350 mm and a VWR213-1171 Borosilicate glass beaker with an internal diameter $\varnothing = 5.0$ cm and the volume 150ml. Therefor the gap was 0.25 cm.



Figure 3-2-A. 1

Emulsification equipment: overhead mixer, anchor stirrer and glass beaker

Approximate shear rate in the beaker

The shear rate in the gap is calculated from the ratio of the linear velocity of the blade tip to the gap with:

$$\text{Shear rate in Sec}^{-1} = \frac{\text{Linear velocity in m/s}}{\text{Gap in m}}$$

The linear velocity V is calculated from the angular velocity W :

$$V = r \times W$$

Where V is the linear velocity in m/s, r is the radius in m, and W is the angular velocity in rad/s

$$V = r \times \text{RPM} \times 0.10472$$

Hence for rotational speed of 200 rpm:

$$V = 0.045 \times 200 \times 0.10472 = 0.9424 \text{ m/s}$$

Therefore, the shear rate is: $\frac{0.9424 \text{ m/s}}{0.0025 \text{ m}} = 376 \text{ Sec}^{-1}$

No:	Rotational speed in rpm	Radius of mixer in m	Gap in cm	Gap in μm	Gap in m	linear Velocity m/s	shear rate sec^{-1}
1	200	0.045	0.25	2500	0.0025	0.94248	376.992
2	500	0.045	0.25	2500	0.0025	2.3562	942.48
3	1000	0.045	0.25	2500	0.0025	4.7124	1884.96
4	2000	0.045	0.25	2500	0.0025	9.4248	3769.92

Table 3-2-A. 1

Approximated shear rate applied by overhead mixer

We will see that the choice of the shear rate is extremely important: firstly, if the shear rate is too low, one may obtain multicore capsules with excessively large polydisperse diameters. secondly if the shear rate is too high it will break the capsules and we may obtain polymer spheres instead of capsules particularly if the interfacial tension is not in the right sequence.

3-2-B Fragmentation Diagram for the First Emulsion

3-2-B.1 First Emulsion: Aqueous Phase in Aliphatic Urethane Acrylate Liquid Polymer

- Materials and Equipment:

Deionized water with zero concentration of salt, Sodium Alginate: this is an ionizable polysaccharide extracted from algae. It has a molar mass in the range 20000 to 42000 g/mol

Aliphatic urethane diacrylate CN991 this is a liquid polymer with difunctional. It can be cross linked by exposure to UV light and particularly to free radicals.

Initiator for UV polymerization (2-hydroxy 2-methylpropiophenone)

Scale, Plastic beaker, Overhead mixer, UV oven, Glass slides and covers slip, Small plastic pipette, Optical microscope.

- Preparation of aqueous solutions and liquid polymers:

1- Aliphatic acrylate shell liquid polymer

Place 19.5g of aliphatic urethane diacrylate polymer CN991 in a 50 ml beaker, add to it 0.5g of 2-hydroxy 2-methylpropiophenone and mix them using the overhead mixer for 2 minutes at 2000rpm.

2- Sodium alginate solution:

Place the appropriate amount of sodium alginate (1% to 15%) in a 100 ml beaker and add to it the appropriate amount of deionized water to avoid losing the powder from the top surface of the beaker then mix them using the overhead mixer for 5 minutes at 1000 rpm and transfer it to a closed small bottle, used it the next day.

- Emulsification

Place 4 g of aliphatic urethane acrylate liquid polymer in a 50ml plastic beaker and add to it 4 g of the aqueous solution of 1% sodium alginate.

Attach it on the overhead mixer and use a rotational velocity 200 rpm for a duration of 1 minute

Take a small droplet from the emulsion, using a small plastic pipette and place it on a glass slide, then add a cover slip and put it in the UV oven for 1 minute in order to maintain the same structure during the emulsification then examine it on the optical microscope using the objective lens 100X.

Repeat the experiment with fresh solution of acrylate liquid polymer and water with using angular velocity 500, 1000 and 2000 rpm for duration 1 minute.

Repeat the experiment with using the second aqueous solution of 3%, 5%, 7%, 10% and 15% sodium alginate with starting with the different rotational velocity 200, 500, 1000 and 2000 rpm.

Note:

All the images show emulsions after polymerization of the acrylate liquid polymer by UV radiation, because the emulsion is not stable in contact with glass surfaces. Indeed, the acrylate liquid polymer wets the glass slide and the cover slip, causing droplet coalescence and destruction of the emulsions.

Imaging the results of emulsification through optical microscopy

The flowing bright field images show the state of the first emulsion after emulsification of aqueous solution with different concentrations of sodium alginate in aliphatic urethane acrylate liquid polymer CN991. The objective lens was 100x and the scale bar was 20 micrometres.

- 1- 50%: 50% of aqueous solution of 1% sodium alginate in aliphatic urethane acrylate liquid polymer. Viscosity Ratio = 0.0017, Rotational speed 2000 rpm

Visual observation during the emulsification shows the following:

- 1- At the bottom of the beaker we can see layer of aliphatic urethane liquid polymer containing a small drop of water.
- 2- At the top of the beaker we see a water layer with occasional small droplets of acrylate urethane liquid polymer.

If we stop the shear all the big droplets will coalesce and float on the top of the acrylate phase, but the very small drop of water will remain instable droplets for half hour but it will coalesce with the other drops and move to the top by the effect of the density and finally after one day will form two phases.

This image was taken from the middle of the beaker after the shear was interrupted. It shows nearly complete phase separation with a large domain of aqueous phase separating two large domains of liquid acrylate polymer (darker colour because of the higher refractive index).

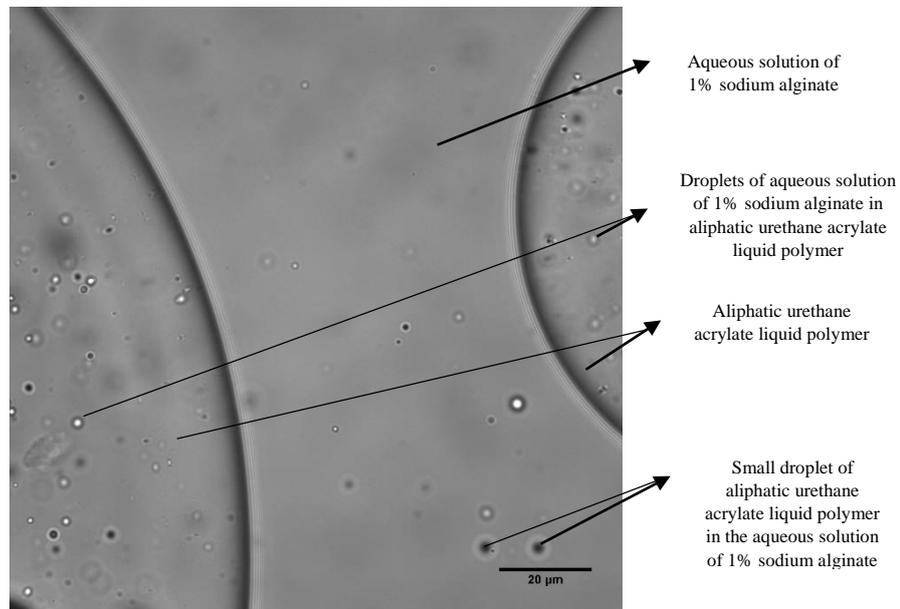


Figure 3-2-B. 1

These observations are consistent with a fast coalescence of the large drops of aqueous phase and production of much smaller droplets by tip streaming as in low viscosity ratio emulsification. We observed very poor fragmentation tip streaming and phase separation even under high shear rate.

2- 50%: 50% of aqueous solution of 3% sodium alginate in aliphatic urethane acrylate liquid polymer. Viscosity Ratio = 0.012 Rotational speed 2000 rpm

Visual observation during the emulsification shows the following:

During the shear, the content of the beaker is homogeneous: it contains a turbid mixture of large aqueous droplets in a continuous phase made of aliphatic urethane acrylate liquid polymer.

If we stop the shear the droplets evolve through fast coalescence events.

This image was taken from the beaker after the shear was interrupted. It shows nearly complete phase separation. It shows in the law left corner a large domain of aqueous phase containing a few bright drops of liquid acrylate polymer and in the upper part of the image a large domain of acrylate urethane liquid polymer containing many drops of the aqueous solution of sodium alginate.

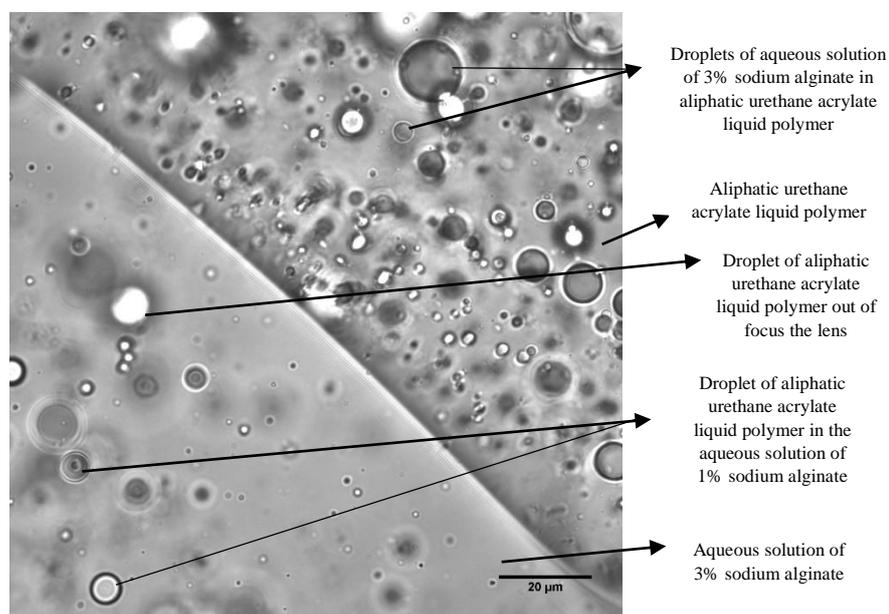


Figure 3-2-B. 2

These observations are consistent with a fast coalescence of the large drops of aqueous phase and it yields phase separation immediately after stopping the shear.

We observed very poor fragmentation tip streaming and phase separation even under high shear rate.

- 3- 50%: 50% of aqueous solution of 5% sodium alginate in aliphatic urethane acrylate liquid polymer. Viscosity Ratio = 0.055 Rotational speed 2000 rpm

Visual observation during the emulsification shows the following:

During the shear, the content of the beaker is homogeneous: it contains a turbid mixture.

If we stop the shear the droplets evolve through fast coalescence events.

This image was taken from the beaker after the shear was interrupted. It shows some features of a multiple emulsion: in a continuous phase of the aqueous solution of sodium alginate we can see drops of acrylate urethane liquid polymer which contain many small droplets of the aqueous sodium alginate solution.

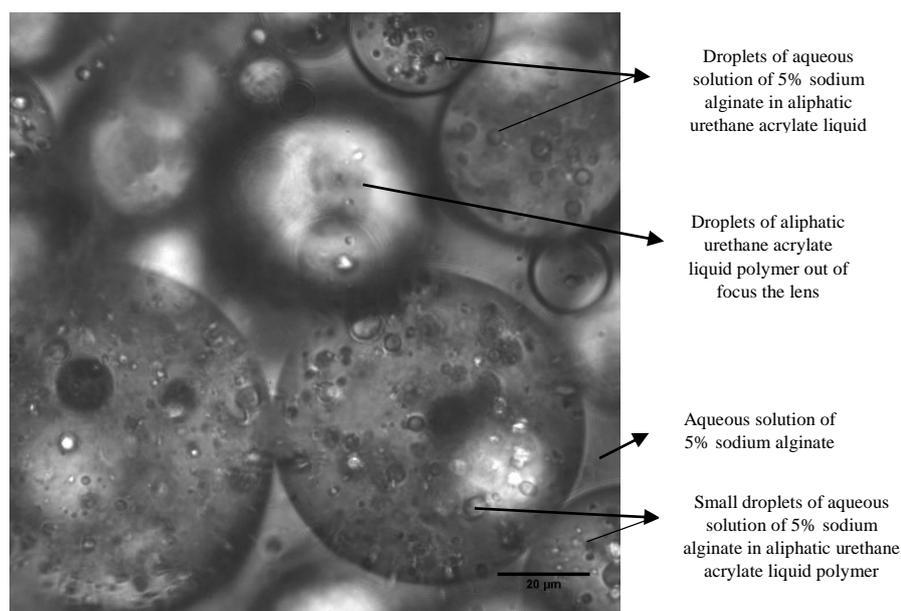


Figure 3-2-B. 3

These observations are consistent with a multiple emulsion of drops of acrylate urethane liquid polymer contain many small droplets of aqueous solution of alginate, these drops are dispersed in a continuous phase of aqueous solution of sodium alginate.

This emulsion does not show the structure that we want to obtain, which is a single emulsion of aqueous solution of sodium alginate in continues phase of aliphatic urethane acrylate liquid polymer.

- 4- 50%: 50% of aqueous solution of 7% sodium alginate in aliphatic urethane acrylate liquid polymer. Viscosity Ratio = 0.210, Rotational speed 2000 rpm

Visual observation during the emulsification shows the following:

During the shear, the content of the beaker is homogeneous: it contains a turbid mixture.

If we stop the shear the droplets evolve through fast coalescence events.

This image was taken from the beaker after the shear was interrupted. It shows some features of a multiple emulsion: smaller drops of acrylate urethane liquid polymer contain many small droplets of aqueous solution of alginate, these drops are dispersed in a continuous phase aqueous of sodium alginate.

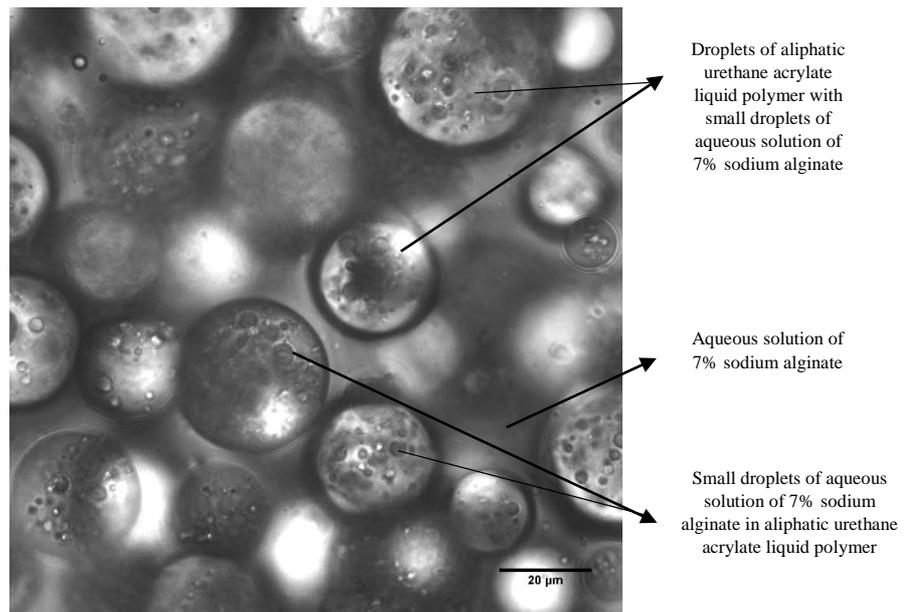


Figure 3-2-B. 4

This emulsion does not show the structure that we want to obtain, which is a single emulsion of aqueous solution of sodium alginate in continuous phase of aliphatic urethane acrylate liquid polymer.

- 5- 50%: 50% of aqueous solution of 10% sodium alginate in aliphatic urethane acrylate liquid polymer. Viscosity Ratio = 0.823 Rotational speed 2000 rpm

Visual observation during the emulsification shows the following:

During the shear, the content of the beaker is homogeneous: it contains a turbid mixture.

If we stop the shear the droplets remain stable with a low rate of coalescence. The beginning of phase separation takes place after 15 minutes.

This image was taken from the beaker after the shear was interrupted. It shows the acrylate urethane liquid polymer as continuous phase contain many small droplets of aqueous solution of alginate with average of size 15 μ m.

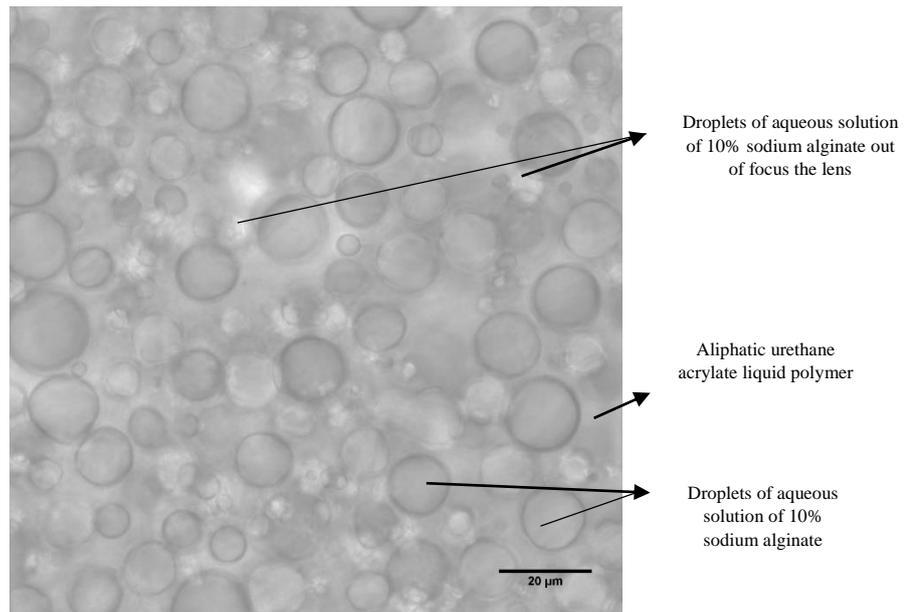


Figure 3-2-B. 5

These observations are consistent with a large number of small droplets of aqueous solution of alginate with average of size 15 μ m dispersed in a continuous phase of acrylate urethane liquid polymer. This is the emulsion structure that we wanted to prepare. It is remarkable that we obtained this structure with a viscosity ratio close to 1. The viscosity ratio at the shear rate of the experiment (100 sec^{-1}) was = 0.8.

This phenomenon of fragmentation and the good stability of the emulsions are not due to:

- 1- Density of the aqueous solution

The fragmentations and the stability of emulsion are not related to the relative densities of the two phases since they have nearly same values as before:

Water density = 0.994 g/cm^3 and aqueous phase of 10% sodium alginate = 1.04 g/cm^3 .

- 2- The fragmentations and the stability of emulsion are not related to the interfacial tensions because they are almost the same:

The interfacial tension between the water and the aliphatic acrylate polymer is 14.1 mN/m. The interfacial tensions between the aqueous solution of 10% sodium alginate and the aliphatic acrylate polymer is 13.1 mN/m.

- 6- 50%: 50% of aqueous solution of 15% sodium alginate in aliphatic urethane acrylate liquid polymer. Viscosity Ratio = 5.477 Rotational speed 2000 rpm

Visual observation during the emulsification shows the following:

During the shear, the content of the beaker is homogeneous: it contains a turbid mixture.

If we stop the shear the droplets remain stable with a low rate of coalescence. The beginning of phase separation takes place after 15 minutes.

This image was taken from the beaker after the shear was interrupted. It shows the acrylate urethane liquid polymer as continuous phase containing polydisperse droplets of aqueous solution of sodium alginate. Some of the droplets are non-spherical.

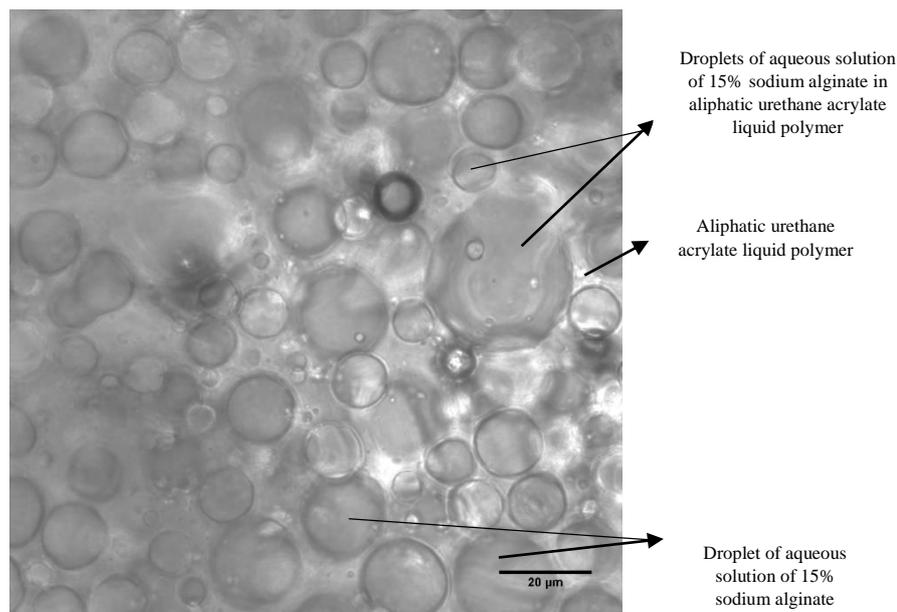


Figure 3-2-B. 6

These observations are consistent with a poor fragmentation with polydisperse droplets of aqueous solution of sodium alginate dispersed in acrylate urethane liquid polymer as continuous phase. The droplets sizes range from 5 to 40 μm .

This emulsion has the structure that we want to prepare but the droplets are not monodisperse in sizes. This is because the dispersed phase of the aqueous solution of sodium alginate has a higher viscosity than the continuous phase the aliphatic urethane acrylate. Indeed, the viscosity ratio is 5.5. It is well known that fragmentation is difficult when the internal phase has higher viscosity than the external phase, because of that the droplets have the possibility to rotate without fragmentation.

We can summarise all the results of the emulsification of aqueous solutions of sodium alginate in aliphatic urethane acrylate liquid polymer by a graph with three different zones (Figure 3-2-B.7).

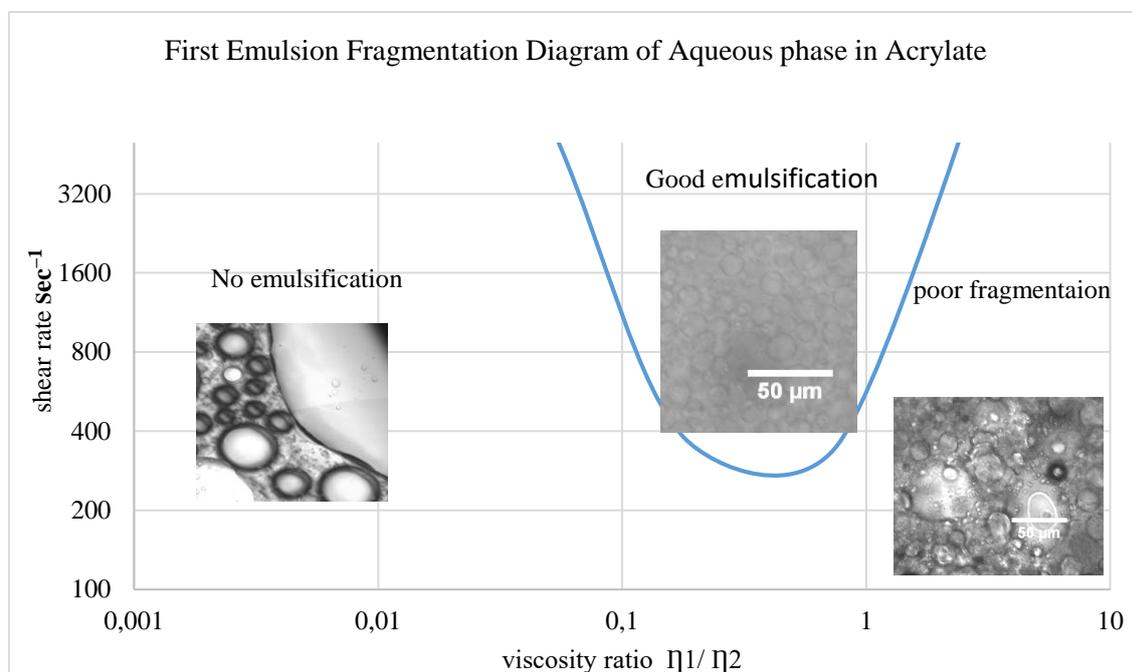


Figure 3-2-B. 7

Fragmentation diagram of single emulsion aqueous phase in aliphatic urethane acrylate polymer

We can distinguish three different zones in this diagram:

- 1- Low viscosity between $\eta_1/\eta_2 = 0.001$
We observed poor fragmentation with high rate of coalescence and almost completely phase separation.
- 2- Optimum viscosity ratio $\eta_1/\eta_2 = 0.8$ which is close to 1
We observed good fragmentation with nearly monodisperse droplets of aqueous solution of sodium alginate dispersed in aliphatic urethane acrylate as external phase.
- 3- High viscosity ratio $\eta_1/\eta_2 = 5.5$
We observed poor fragmentation with polydisperse and non-spherical droplets of aqueous solution of sodium alginate dispersed in aliphatic urethane acrylate liquid polymer as external phase.

Effect of the viscosity ratio on the fragmentation of the aqueous solutions of sodium alginate in aliphatic urethane acrylate liquid polymer.

No:	Description	Phase 1 viscosity pa.s at 10 sec ⁻¹	Phase 2 viscosity pa.s at 10 sec ⁻¹	Viscosity ratio	Degree of the fragmentation
1	Water in CN991	0.0017	10.058	0.00017	Very poor (phase separation)
2	3% alginate in CN991	0.122579	10.058	0.01218	Very poor (phase separation)
3	5% alginate in CN991	0.549588	10.058	0.05464	poor
4	7% alginate in CN991	2.11424	10.058	0.21020	poor
5	10% alginate in CN991	8.28345	10.058	0.82356	Very good
6	15% alginate in CN991	55.0585	10.058	5.47410	poor

Table 3-2-B. 1

Viscosity ratio effect on the stability for the first emulsion aqueous phase in acrylate polymer

Conclusion:

From these results we conclude that in order to have nearly monodisperse droplets and good emulsification of aqueous solutions of sodium alginate in aliphatic urethane liquid polymer, we need to use two fluids that have almost the same viscosity. The viscosity ratio at the shear rate of the experiment (100 sec⁻¹) was = 0.8 which is close to 1.

In comparison with the classical emulsification diagram of (0), the optimum is the same but the range of good viscosity ratios is much narrower. The differences are that we did not use any surfactant and also that one fluid is Newtonian but the other is non-Newtonian.

3-2-B.2 First Emulsion: Oil phase in Epoxy Urethane Acrylate Liquid Polymer

- Materials and the Equipment:

Low viscosity silicon oil with viscosity 10mpa.s, Medium viscosity silicon oil with viscosity 0.5 Pa.s (PDMS), High viscosity silicon oil with viscosity 5 Pa.s (PDMS), Epoxy urethane acrylate liquid polymer CN109, 1.6 Hexanediol diacrylate, Initiator for UV polymerization (2-hydroxy 2-methylpropiophenone), Balance, Plastic beaker, Overhead mixer, UV oven, Glass slides and covers slip, Small plastic pipette.

- Preparation of oil phase and liquid polymers:

- Polymer shell preparation from epoxy urethane acrylate liquid polymer CN109

Place 14.5g of aliphatic urethane acrylate polymer CN991 in 50 ml beaker and add to it 5.0g of 1.6 Hexanediol diacrylate and 0.5g of 2-hydroxy 2-methylpropiophenone and mix them by overhead mixer for 2 minutes at 2000rpm.

- Oil phase preparation

- low viscosity oil

It is used as received from sigma

- Medium viscosity oil

It was prepared by mixing 40% of silicon oil (10 mPa.s) with 60% of silicon oil RTV 615 A, code name (PDMS)

- High viscosity oil

It is used as received, code name RTV 615 A (PDMS)

- The emulsification

- 1- Place 4 g of Epoxy urethane acrylate liquid polymer in a 50ml plastic beaker and add to it 4 g of silicon oil that has low viscosity value 10 mPa.s.
- 2- Fix it on the overhead mixer and stir it at a rotational speed of 200 rpm for duration 1 minute.
- 3- Take a small droplet from the emulsion using the small plastic pipette and put it on the glass slide, then put the cover slip and place it in the UV oven for 1 minute to maintain without coalescence the structure created by emulsification then test it on the optical microscope using the objective lens 100X.
- 4- Repeat the experiment with fresh solution of the Epoxy acrylate liquid polymer and silicon oil with using rotational speed 500, 1000 and 2000 rpm for duration 1 minute
- 5- Repeat the experiment using the medium viscosity and then the high viscosity silicon oil (PDMS) using different rotational speeds 200, 500, 1000 and 2000 rpm.

Note:

All the images show emulsions after polymerization of the epoxy urethane acrylate liquid polymer by UV radiation, because the emulsion is not stable in contact with glass surfaces. Indeed, the acrylate liquid polymer wets the glass slide and the cover slip, causing droplet coalescence and destruction of the emulsions.

Imaging the results of emulsification through optical microscopy

The following bright field images show the state of the first emulsion after emulsification of oils with different viscosities in epoxy urethane acrylate liquid polymer CN109. The objective lens was 20x for the low viscosity emulsion, because it was necessary to scan a large area on the slides and 100x for the highest viscosity ratio emulsion. The scale bar was 20 micrometres.

A- Low viscosity ratio = 0.022

- 1- Rotation speed 200 rpm, 50%: 50% of silicon oil 10 mPa.s emulsified in epoxy urethane acrylate liquid polymer. Low viscosity ratio $\eta_1/\eta_2 = 0.022$

Visual observation during the emulsification shows the following:

- 1- At the bottom of the beaker we can see turbid layer of epoxy urethane acrylate liquid polymer containing a small droplets of silicon oil.
- 2- At the top of the beaker we see a layer of silicon oil which rotates on top of the epoxy urethane acrylate polymer with no fragmentation.

This image was taken from the middle of the beaker after the shear was interrupted. It shows nearly complete phase separation with a very large domain of epoxy urethane acrylate liquid polymer.

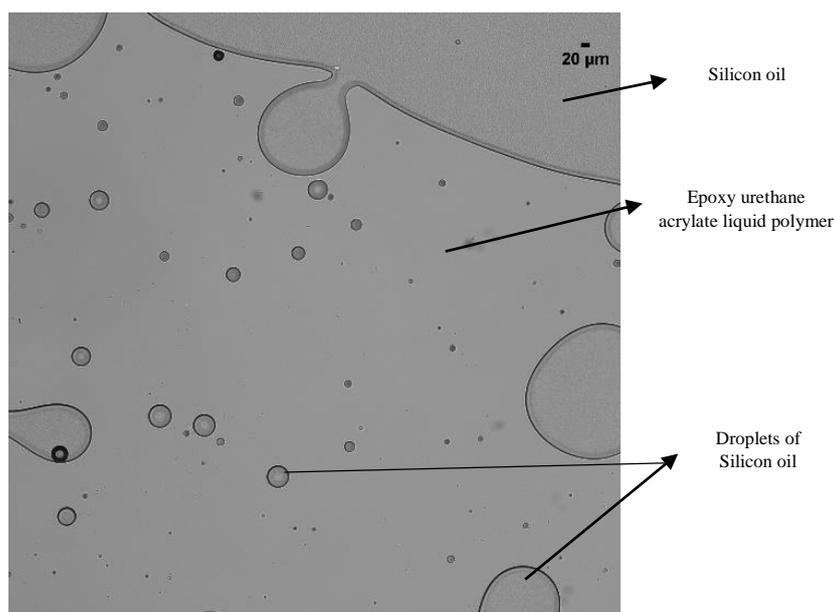


Figure 3-2-B. 8

These observations are consistent with a very poor fragmentation, fast coalescence of the large drops of silicon oil and production of much smaller droplets by tip streaming. This is expected since we are at low viscosity ratio = 0.022 even with having low interfacial tension = 4.13 mN/m.

- 2- Rotational speed 500 rpm, 50%: 50% of silicon oil 10 mPa.s in Epoxy urethane acrylate liquid polymer with low viscosity ratio $\eta_1/\eta_2 = 0.022$

Visual observation during the emulsification shows the following:

Even though we increased the rotational speed to 500 rpm, we observed no improvement in the fragmentation and the mixture separated in two phases.

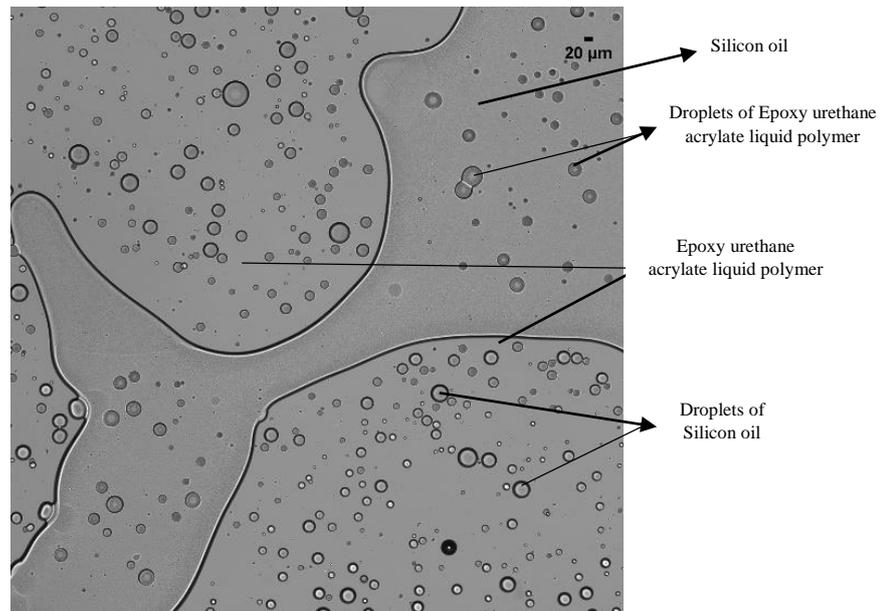


Figure 3-2-B. 9

These observations of emulsification at a low viscosity ratio = 0.022 are consistent with a poor fragmentation, production of very small droplets by tip streaming, even with increased rotational speed to 500 rpm, and fast coalescence of the large drops of silicon oil.

- 3- Rotational speed 1000 rpm, 50%: 50% of silicon oil 10 mPa.s in epoxy urethane acrylate liquid polymer. Low viscosity ratio $\eta_1/\eta_2 = 0.022$

Visual observation during the emulsification shows the following:

With increasing the rotational speed to 1000 rpm, we observe a slight improvement in the fragmentation but the mixture still goes to phase separation.

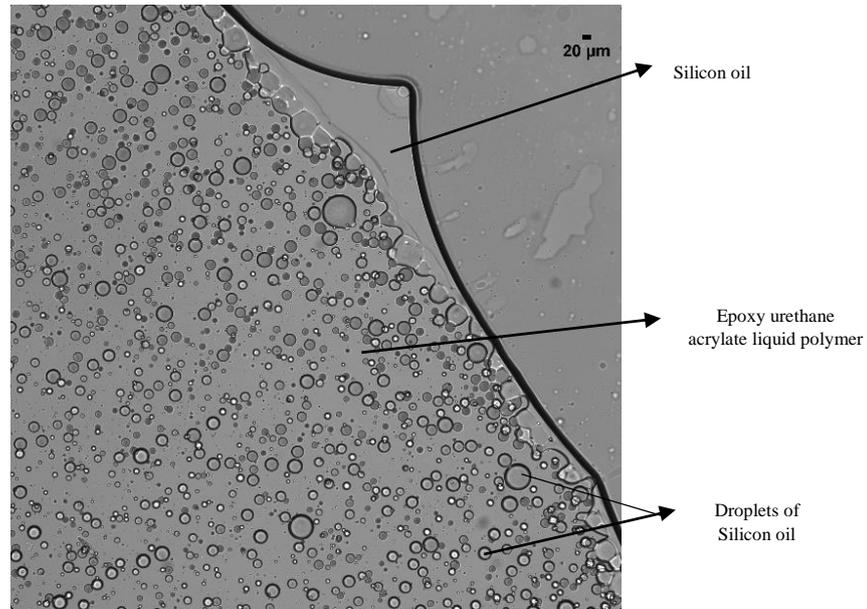


Figure 3-2-B. 10

These observations at a low viscosity ratio = 0.022 are consistent with a poor fragmentation which produce numerous very small droplets and it finishes with phase separation because of fast coalescence of large droplets, even at a rotational speed increased to 1000 rpm.

- 4- Rotational speed 2000 rpm, 50%: 50% of silicon oil 10 mPa.s in epoxy urethane acrylate liquid polymer. Low viscosity ratio $\eta_1/\eta_2 = 0.022$.

Visual observation during the emulsification shows the following:

With increasing the rotational speed to 2000 rpm, we observe a slightly improvement in the fragmentation but we still have phase separation.

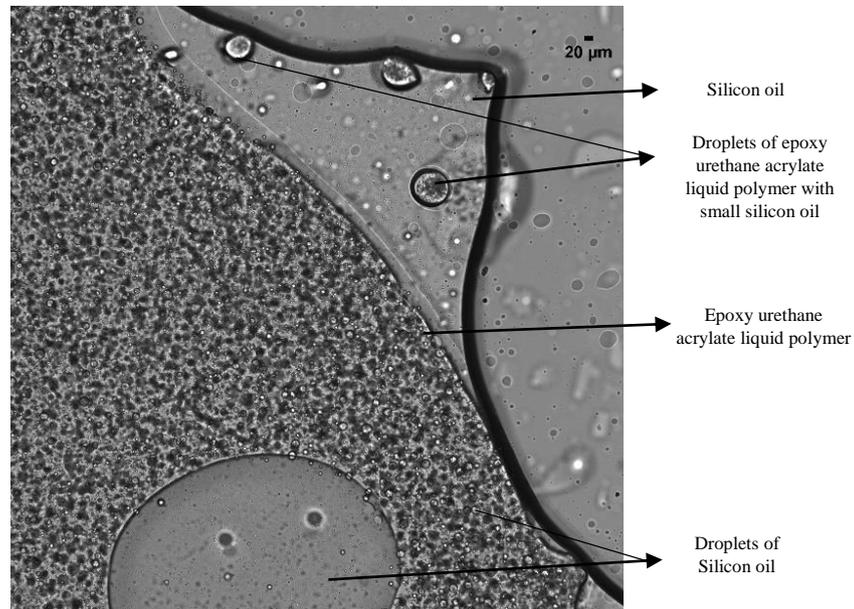


Figure 3-2-B. 11

These observations at low viscosity ratio emulsification 0.022 are consistent with a very poor fragmentation even with increasing the rotational speed to 2000 rpm, fast coalescence of the large drops of silicon oil and production of much smaller droplets. We still have phase separation.

If we stop the shear all the droplets of oil coalesce and will finish with phase separation after a half hour.

General conclusion for the emulsification at low viscosity ratio

Applying high rotation speeds to better shear the mixture we have better fragmentation but the emulsion still has a high rate of coalescence and goes to phase separation.

B- Optimum viscosity ratio = 1.08

- 1- Rotational speed 200 rpm, 50%: 50% of oil phase (60% PDMS with 40% silicon oil) in Epoxy urethane acrylate liquid polymer. Medium viscosity ratio $\eta_1/\eta_2 = 1.08$

Visual observation during the emulsification shows the following:

In the beaker we can see a turbid mixture containing the medium viscosity silicon oil in epoxy urethane acrylate liquid polymer with no large scale phase separation.

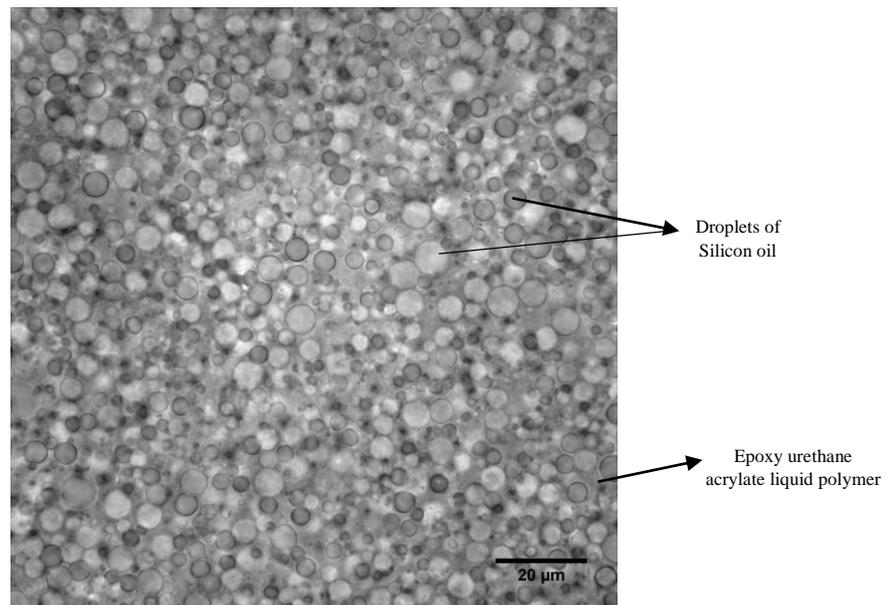


Figure 3-2-B. 12

These observations at the optimum viscosity ratio emulsification = 1.08 are consistent with a very good fragmentation even at a low rotational speed = 200 rpm, and a very low rate of coalescence of the droplets of medium viscosity silicon oil. The average droplets size is around 5 μm .

If we stop the shear the droplets of the medium viscosity silicon oil remain stable even after two weeks, with no large scale phase separation. We think that this is due to the low interfacial tension = 5.04 mN/m and to the optimum viscosity ratio which close to 1.

- 2- Rotational speed 500 rpm 50%: 50%, oil phase (60% PDMS with 40% silicon oil) in Epoxy urethane acrylate liquid polymer. Medium viscosity ratio $\eta_1/\eta_2 = 1.08$

Visual observation during the emulsification shows the following:

With increased rotational speed to 500 rpm, we can see turbidity in the whole beaker, with no large scale phase separation.

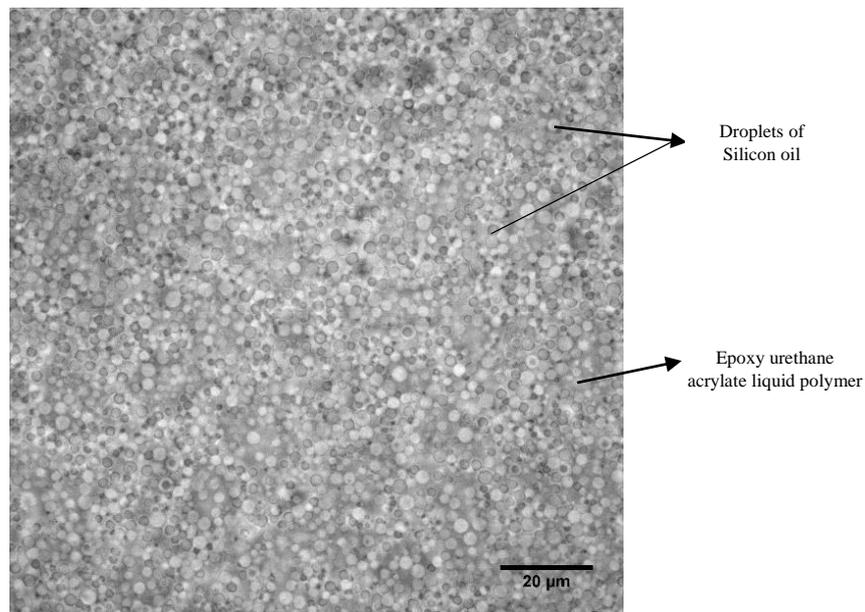


Figure 3-2-B. 13

These observations at the optimum viscosity ratio emulsification = 1.08 are consistent with a very good fragmentation at a rotational speed 500 rpm, and a very low rate of coalescence of the droplets of medium viscosity silicon oil that have an average size around 3 μm.

If we stop the shear the droplets of the medium viscosity silicon oil remain stable even after two weeks with no large scale phase separation.

- 3- Rotational speed 1000 rpm 50%: 50%, oil phase (60% PDMS with 40% silicon oil) in Epoxy urethane acrylate liquid polymer. Medium viscosity ratio $\eta_1/\eta_2 = 1.08$

Visual observation during the emulsification shows the following:

With increased rotational speed to 1000 rpm, we can see turbidity in the whole beaker, with no large scale phase separation.

There is an apparent aggregation in the emulsion and we can see clearly segregation with a pseudo period of 20 micrometer

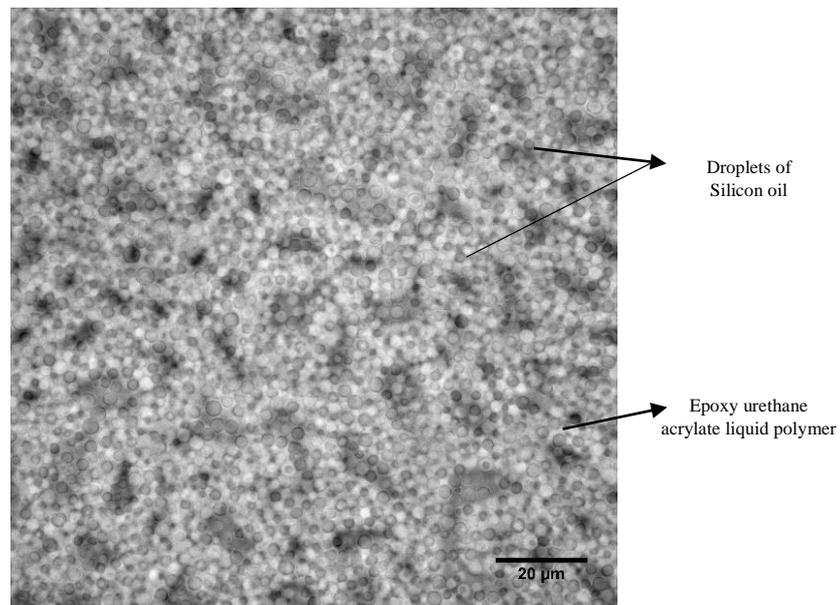


Figure 3-2-B. 14

These observations at the optimum viscosity ratio emulsification = 1.08 are consistent with a very good fragmentation at the rotational speed 1000 rpm, and a very low rate coalescence of droplets of medium viscosity silicon oil that have sizes around 3 μm .

If we stop the shear the droplets of the medium viscosity silicon oil remain stable even after two weeks with no large scale phase separation.

There is an apparent aggregation in the emulsion and we can see clearly segregation with a pseudo period of 20 micrometer.

- 4- Rotational speed 2000 rpm 50%: 50%, oil phase (60% PDMS with 40% silicon oil) in Epoxy urethane acrylate liquid polymer, Medium viscosity ratio $\eta_1/\eta_2 = 1.08$

Visual observation during the emulsification shows the following:

With increased rotational speed to 2000 rpm, we can see turbidity in the whole beaker, with no large scale phase separation.

There is an apparent aggregation in the emulsion and we can see clearly segregation with a pseudo period of 20 micrometers.

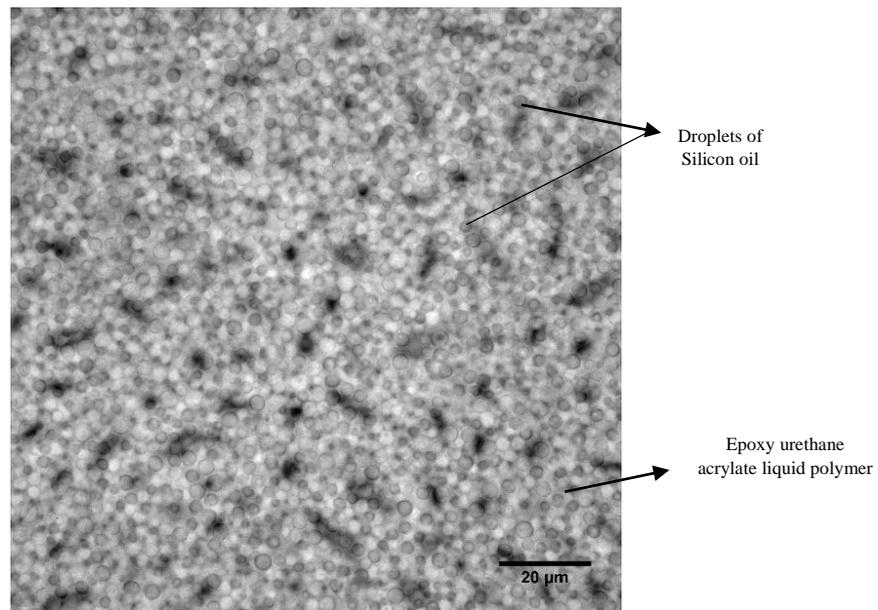


Figure 3-2-B. 15

These observations in optimum viscosity ratio emulsification = 1.08 are consistent with a very good fragmentation with rotational speed 2000 rpm, very low rate of coalescence of medium viscosity silicon oil that have average sizes around 3 μm .

If we stop the shear the droplets of the viscos silicon oil will remain stable even after two weeks with no phase separation.

There is an apparent aggregation in the emulsion and we can see clearly segregation with a pseudo period of 20 micrometers.

Conclusion:

General conclusion for the fragmentation in Optimum viscosity ratio emulsion close to 1

Even with applying low rotation speed of 200 rpm to shear the mixture, the products show a good fragmentation, a small rate of coalescence up to two weeks and no large scale phase separation.

C- High viscosity ratio = 8.6

- 1- Rotational speed 200 rpm 50%: 50%, oil phase (PDMS RTV615A) in Epoxy urethane acrylate liquid polymer under. High viscosity ratio $\eta_1/\eta_2 = 8.6$

Visual observation during the emulsification shows the following:

At the lower rotational speed = 200 rpm, we can see in the whole beaker a turbid mixture of the high viscosity silicon oil and epoxy urethane acrylate liquid polymer with no phase separation.

We can see very many tiny droplets with an average size about 1 μm .

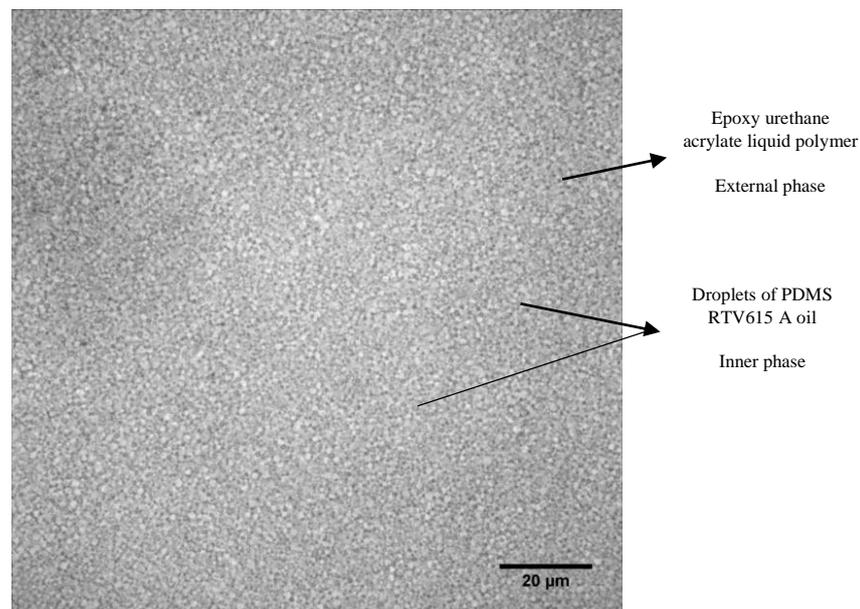


Figure 3-2-B. 16

These observations of Newtonian fluids at high viscosity ratio = 8.6 are consistent with a very good fragmentation even with rotational speed 200 rpm, and a very low rate coalescence of the high viscosity silicon oil which have an average size around 1 μm .

If we stop the shear the droplets of the high viscosity silicon oil remain stable even after two months with no phase separation.

We think that this is due to the low interfacial tension = 3.83 mN/m and to the optimum viscosity ratio which close to 1.

- 2- Rotational speed 500 rpm 50%: 50%, oil phase (PDMS RTV615A) in Epoxy urethane acrylate liquid polymer. High viscosity ratio $\eta_1/\eta_2 = 8.6$

Visual observation during the emulsification shows the following:

With increasing the rotational speed = 500 rpm, we can see in the whole beaker a turbid mixture of the high viscosity silicon oil and epoxy urethane acrylate liquid polymer with no phase separation.

We can see very many tiny droplets with an average size about 1 μm .

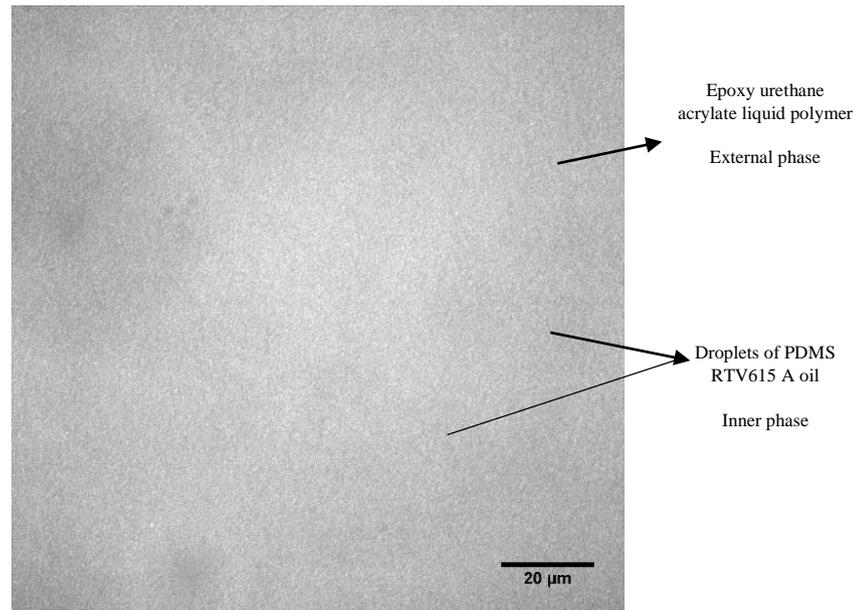


Figure 3-2-B. 17

These observations of Newtonian fluids at high viscosity ratio = 8.6 are consistent with a very good fragmentation even with rotational speed 500 rpm, and a very low rate coalescence of the high viscosity silicon oil which have an average size less than 1 μm .

If we stop the shear the droplets of the high viscosity silicon oil remain stable even after two months with no phase separation.

We think that this is due to the low interfacial tension = 3.83 mN/m and to the optimum viscosity ratio which close to 1.

Also it is remarkable that with using silicon oil that have higher viscosity (RTV 615 A) we obtain much smaller droplets of silicon oil in epoxy urethane acrylate liquid polymer.

- 3- Rotational speed 1000 rpm, 50%: 50% of oil phase (PDMS RTV615A) in Epoxy urethane acrylate liquid polymer. High viscosity ratio $\eta_1/\eta_2 = 8.6$

Visual observation during the emulsification shows the following:

With increasing the rotational speed = 1000 rpm, we can see in the whole beaker a turbid mixture of the high viscosity silicon oil and epoxy urethane acrylate liquid polymer with no phase separation.

We can see very many tiny droplets with an average size about 1 μm .

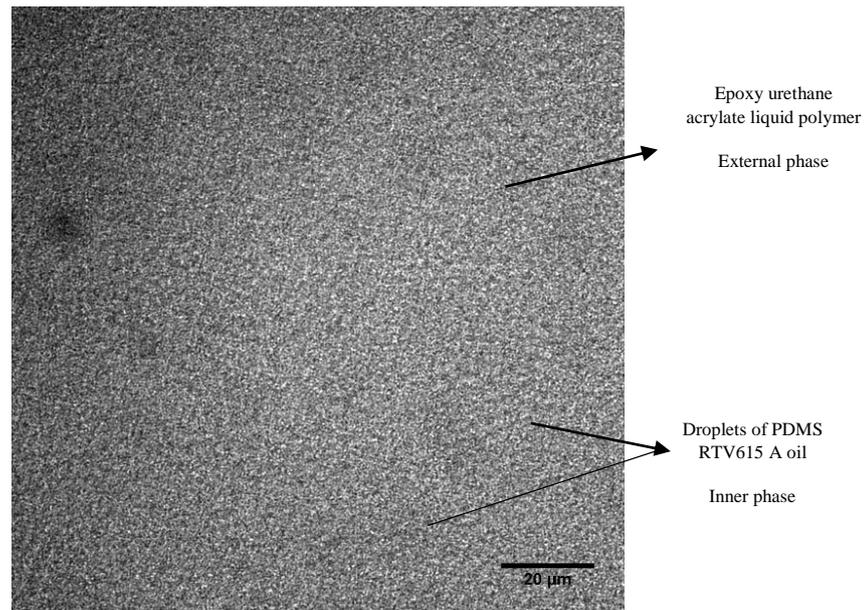


Figure 3-2-B. 18

These observations of Newtonian fluids at high viscosity ratio = 8.6 are consistent with a very good fragmentation even with rotational speed 1000 rpm, and a very low rate coalescence of the high viscosity silicon oil which have an average size less than 1 μm .

If we stop the shear the droplets of the high viscosity silicon oil remain stable even after two months with no phase separation.

We think that this is due to the low interfacial tension = 3.83 mN/m and to the optimum viscosity ratio which close to 1.

Also it is remarkable that with using silicon oil that have higher viscosity (RTV 615 A) we obtain much smaller droplets of silicon oil in epoxy urethane acrylate liquid polymer.

- 4- Rotational speed 2000 rpm, 50%: 50% of oil phase (PDMS RTV615A) in Epoxy urethane acrylate liquid polymer. High viscosity ratio $\eta_1/\eta_2 = 8.6$

Visual observation during the emulsification shows the following:

With increasing the rotational speed = 2000 rpm, we can see in the whole beaker a turbid mixture of the high viscosity silicon oil and epoxy urethane acrylate liquid polymer with no phase separation. We can see very many tiny droplets with an average size about 1 μm .

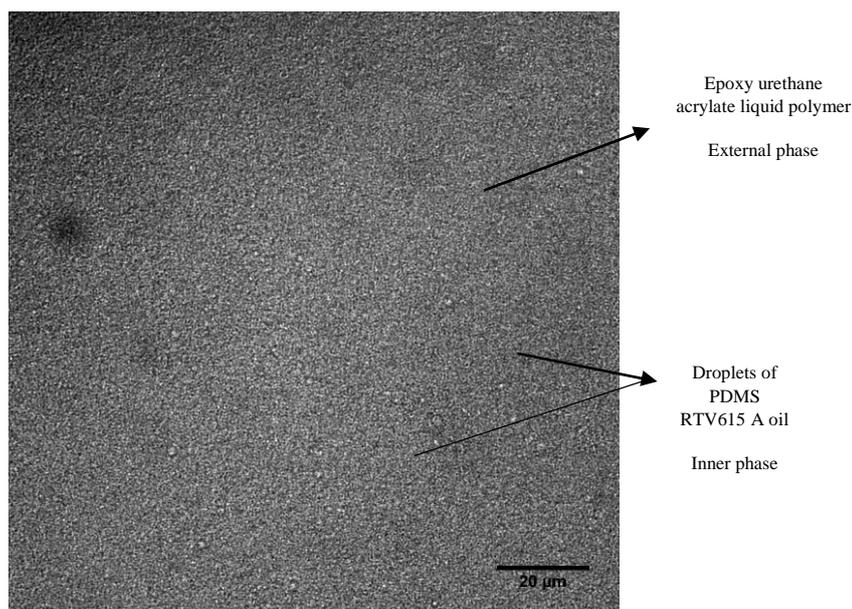


Figure 3-2-B. 19

These observations of Newtonian fluids at high viscosity ratio = 8.6 are consistent with a very good fragmentation even with rotational speed 2000 rpm, and a very low rate coalescence of the high viscosity silicon oil which have an average size less than 1 μm .

If we stop the shear the droplets of the high viscosity silicon oil remain stable even after two months with no phase separation.

We think that this is due to the low interfacial tension = 3.83 mN/m and to the optimum viscosity ratio which close to 1.

Also it is remarkable that with using silicon oil that have higher viscosity (RTV 615 A) we obtain much smaller droplets of silicon oil in epoxy urethane acrylate liquid polymer.

General conclusion for the fragmentation in high viscosity ratio = 8.6

Even with applying low rotation speed of 200 rpm for 2 minutes to shear the emulsion, it produces good fragmentation with oil droplets that have an average size less than 1 μm , and small rate of coalescence up to two months and no large scale phase separation.

We summarise the results of the fragmentation of silicon oil in epoxy urethane acrylate liquid polymer in an emulsification diagram similar to the classical diagram proposed by Grace. This diagram defines three different zones according to the viscosity ratio and the shear rate. It is approximate, because we haven't examined systems with intermediate values of the viscosity ratio between the three regions with low, medium and high viscosity ratio.

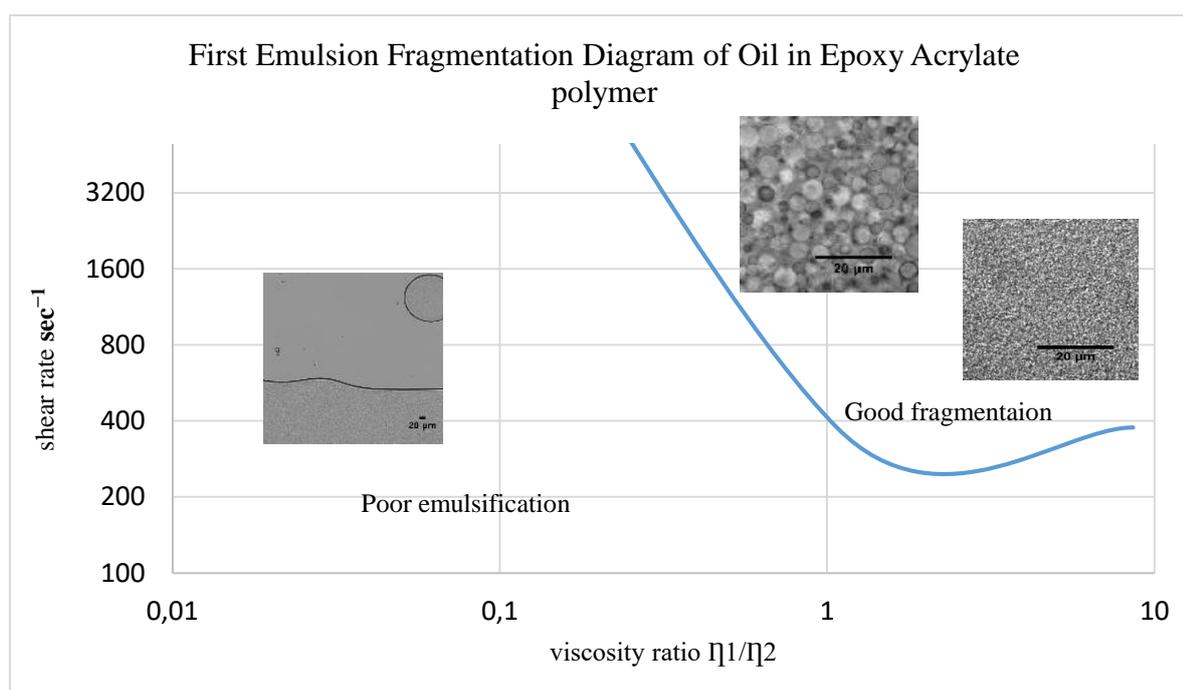


Figure 3-2-B. 20

Approximate fragmentation diagram for first emulsion oil in epoxy urethane acrylate polymer i

According to this diagram we identify three different regions:

1- Low viscosity ratio between $\eta_1/\eta_2 = 0.022$

We observed poor fragmentation with high rate of coalescence and almost complete phase separation even though the interfacial between the two fluids was low = 4.13 mN/m.

2- Optimum viscosity ratio $\eta_1/\eta_2 = 1.08$ which close to 1

We observed good fragmentation with nearly monodisperse droplets of silicon oil medium viscosity dispersed in epoxy urethane acrylate as external phase.

This emulsion remains stable even after two weeks with no phase separation, the interfacial tension is low but not zero has the similar value = 5.04 mN/m.

3- High viscosity ratio $\eta_1/\eta_2 = 8.6$

We observed very good fragmentation with monodisperse droplets of high viscosity silicon oil (RTV615 A) with size average size less than $1\mu\text{m}$ dispersed in epoxy urethane acrylate as external phase.

This emulsion remains stable even after two months with no phase separation and the interfacial between the two fluids = 3.83 mN/m .

This behaviour is totally different from that observed by Grace, who had emulsification failure at high values of the viscosity ratio.

Effect of viscosity ratio on the fragmentation of first emulsion: oil in epoxy urethane acrylate liquid polymer

No:	Description	Phase 1 viscosity pa.s at 10 sec^{-1}	Phase 2 viscosity pa.s at 10 sec^{-1}	Viscosity ratio	Evaluation the emulsification
1	Silicon oil 10mpa.s in CN109 30% HDDA	0.0102469	0.468282	0.02188	Phase separation
2	40% silicon oil 60% of RTV 615 A in CN109 30% HDDA	0.508906	0.468282	1.08	Good fragmentation
3	100% RTV 615 A in CN109 30% HDDA	4.00963	0.468282	8.56242	Good fragmentation

Table 3-2-B. 2

Effect of the viscosity ratio on the stability for the first emulsion of oil in Epoxy urethane acrylate liquid polymer

Discussion and conclusion:

The results of emulsifying silicon oil phase in epoxy urethane acrylate liquid polymer depend on the viscosity ratio between the two phases as follows:

Low viscosity ratio $\eta_1/\eta_2 = 0.02$

The inner phase (silicon oil 10mpa.s) has a much lower viscosity than the epoxy acrylate liquid polymer phase (47mpa.s).

The results were poor fragmentation because of two phenomena: tip streaming which yields many small droplets, and coalescence of the large oil drops. During emulsification these phenomena lead to phase separation even at high shear rate. When we stop the shear all the big droplets of oil coalesce and float on the top of the epoxy acrylate liquid polymer phase. The very small droplets of oil remain stable for a half hour, but in the end they will coalesce with the other droplets, move to the top under the effect of their density, and finally after one day they will form two phases.

Optimum viscosity ratio $\eta_1/\eta_2 = 1$

We have good fragmentation and good stability time for the first emulsion using a silicon oil phase that has almost the same viscosity of the epoxy urethane acrylate liquid polymer, so that the viscosity ratio $\eta_1/\eta_2 = 1.08$. We argue :

- 1- The stability of the emulsion doesn't result from the density values because silicon oil (10mpa.s) has a density = 0.93 g/cm³ and high viscosity silicon oil (PDMS) has almost the same density = 0.97 g/cm³ and yet they behave very differently.
- 2- The stability of the emulsion doesn't result from the interfacial tensions because silicon oil (10mpa.s) has an interfacial tension = 4.13 mN/m with epoxy urethane liquid polymer, and the high viscosity silicon oil (PDMS) has almost the same interfacial tension with epoxy urethane liquid polymer = 3.83 mN/m, and yet they behave very differently.

In the case of optimum viscosity ratio, the medium viscosity silicon oil droplets remain stable up to two weeks with no phase separation.

High viscosity ratio $\eta_1/\eta_2 = 8.6$

The result of dispersing oil that has higher viscosity value than the Epoxy urethane acrylate liquid polymer is also good emulsification, even though the viscosity ratio is large. This behaviour is totally different from that observed by Grace, who had emulsification failure at high values of the viscosity ratio. The good fragmentation may be due to the following features (not exclusively):

Both fluids are Newtonian, and they have a low interfacial tension, which makes it easy to produce small droplets that remain stable even after two months with no phase separation.

3-2-C Maximum Mass Fraction of the First Emulsion

3-2-C.1 Maximum mass fraction for the First Emulsion of aqueous phase in Aliphatic Urethane Acrylate Polymer liquid polymer

We chose to use the aqueous solution of 10% of sodium alginate with viscosity which is close to the viscosity of the aliphatic urethane acrylate liquid polymer (optimum viscosity ratio η_1/η_2 close to 1), because it gives us good fragmentation.

We dispersed the aqueous solution of sodium alginate 10% in aliphatic urethane acrylate liquid polymer. We varied the mass fraction of this phase from 10% until 90%, and we kept the rotational speed at 2000 rpm.

Mass fraction of inner phase 10%, mass fraction of outer phase 90%, rotational speed 2000 rpm, time two minutes.

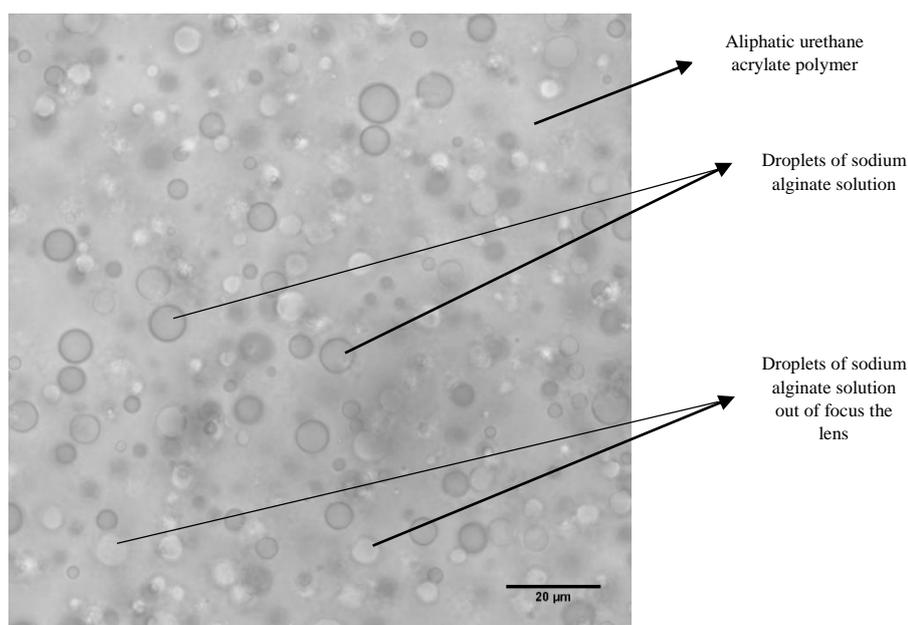


Figure 3-2-C. 1

Mass fraction of inner phase 10%

This emulsification with an inner phase which is the 10% sodium alginate aqueous solution and its mass fraction is 10% of the mixture gives good fragmentation of small droplets of sodium alginate solution, with a range of droplet sizes about 10μm.

Note that the droplets have a different appearance depending on their position with respect the plane of focalisation: droplets that are in focus appear grey with a dark circular boundary, while droplets that out of focus may appear white.

Mass fraction of inner phase 20%, mass fraction of outer phase 80%, rotational speed 2000 rpm, time two minutes.

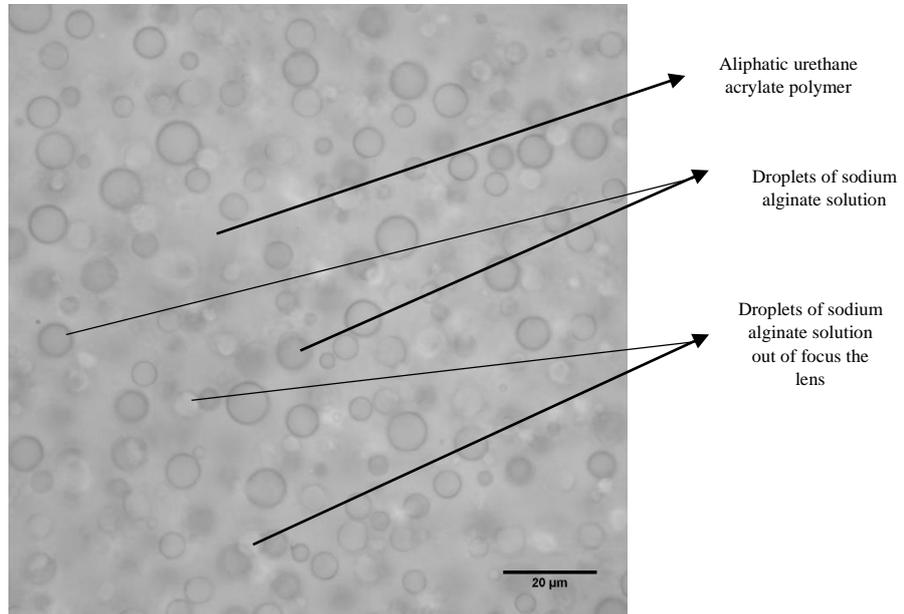


Figure 3-2-C. 2

Mass fraction of inner phase 20%

This emulsification with an inner phase which is the 10% sodium alginate aqueous solution and its mass fraction is 20% of the mixture gives good fragmentation of small droplets of sodium alginate solution, with a range of droplet sizes about 10μm.

Mass fraction of inner phase 30%, mass fraction of outer phase 70%, rotational speed 2000 rpm, time two minutes.

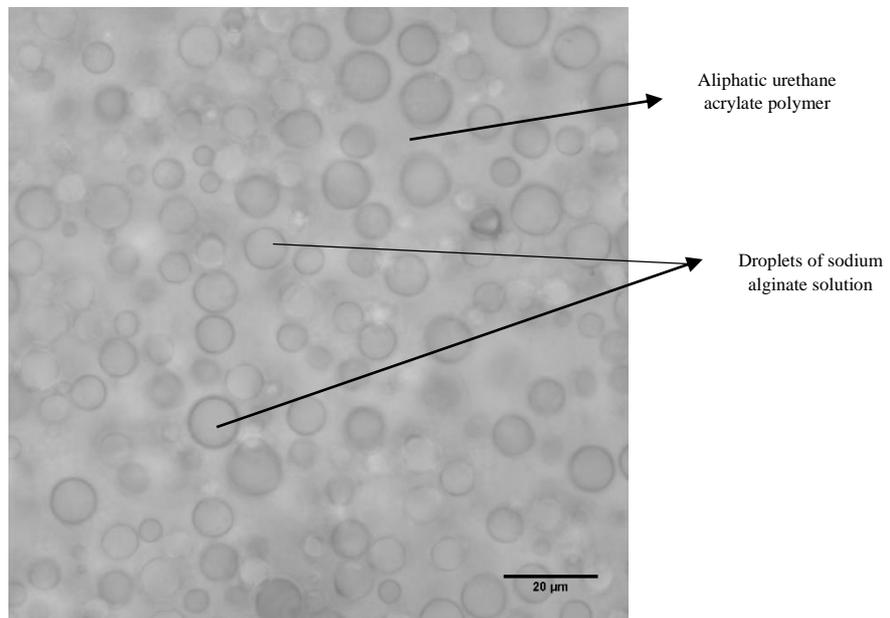


Figure 3-2-C. 3

Mass fraction of inner phase 30%

This emulsification with an inner phase which is the 10% sodium alginate aqueous solution and its mass fraction is 30% of the mixture gives good fragmentation of small droplets of sodium alginate solution, with a range of droplet sizes about 15 μ m.

Mass fraction of inner phase 40%, mass fraction of outer phase 60%, rotational speed 2000 rpm, time two minutes.

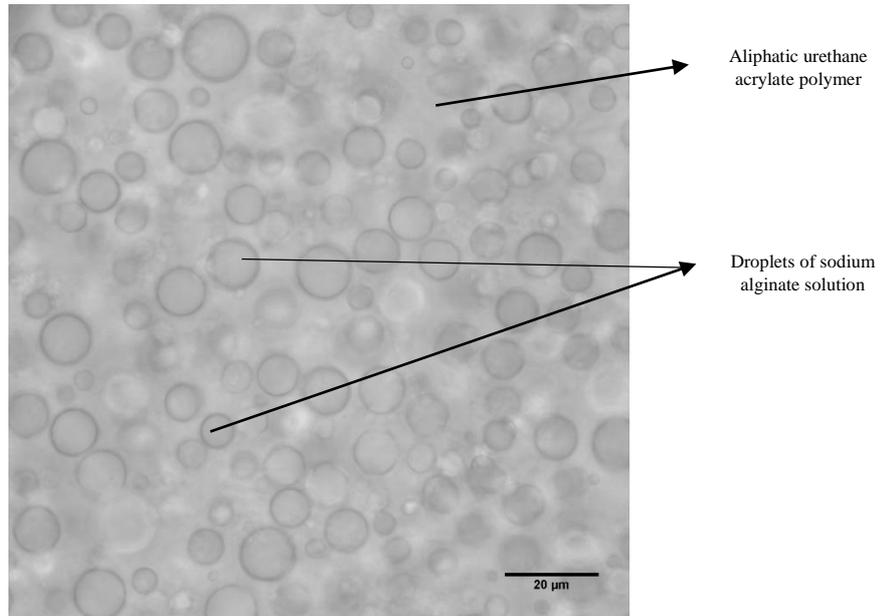


Figure 3-2-C. 4

Mass fraction of inner phase 40%

This emulsification with an inner phase which is the 10% sodium alginate aqueous solution and its mass fraction is 40% of the mixture gives good fragmentation of small droplets of sodium alginate solution, with a range of droplet sizes about 15μm.

Mass fraction of inner phase 50%, mass fraction of outer phase 50%, rotational speed 2000 rpm, time two minutes.

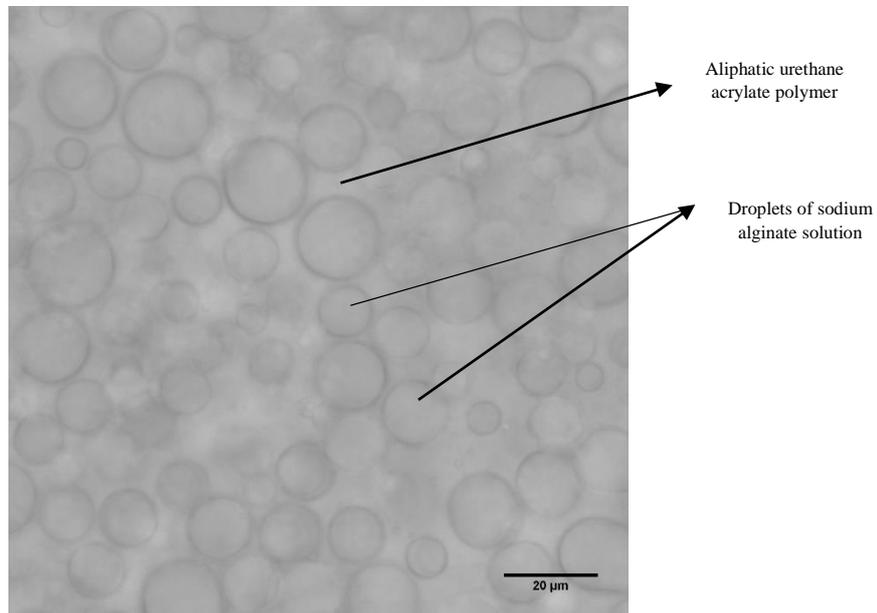


Figure 3-2-C. 5

Mass fraction of inner phase 50%

This emulsification with an inner phase which is the 10% sodium alginate aqueous solution and its mass fraction is 50% of the mixture gives good fragmentation of small droplets of sodium alginate solution, with a range of droplet sizes about 17 μ m.

There is a good match of the numbers and the sizes of the droplets in this image with those of the image 3-2-B.5 which was presented above.

Mass fraction of inner phase 60%, mass fraction of outer phase 40%, rotational speed 2000 rpm, time two minutes.

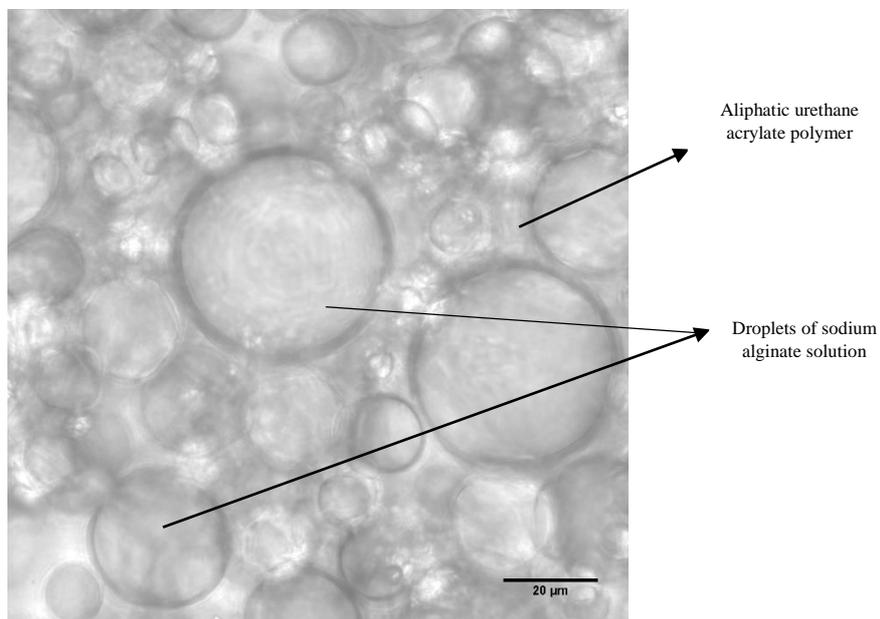


Figure 3-2-C. 6

Mass fraction of inner phase 60%

This emulsification using 60% as mass fraction of the inner phase aqueous solution of 10% sodium alginate gives large polydisperse droplets. The range of droplet sizes is about 40μm.

Mass fraction of inner phase 70%, mass fraction of outer phase 30%, rotational speed 2000 rpm, time two minutes.

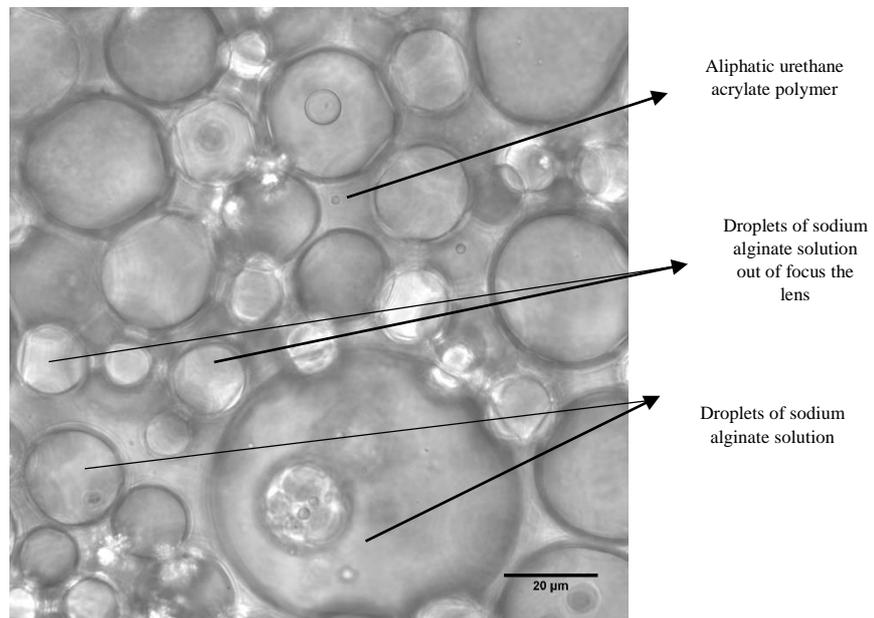


Figure 3-2-C. 7

Mass fraction of inner phase 70%

This emulsification using 60% as mass fraction of the inner phase aqueous solution of 10% sodium alginate gives large polydisperse droplets. The range of droplet sizes is about 60µm. Occasionally there were multiple emulsion droplets.

Mass fraction of inner phase 80%, mass fraction of outer phase 20%, rotational speed 2000 rpm, time two minutes.

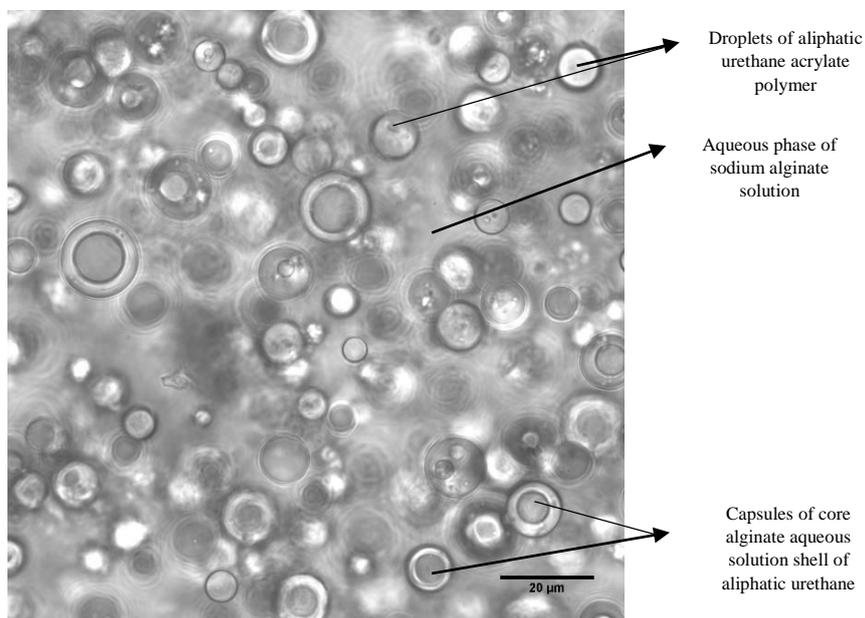


Figure 3-2-C. 8

Mass fraction 80% of aqueous solution

This emulsification using 80% as mass fraction of aqueous solution of 10% sodium alginate yields a reverse emulsion which droplets of aliphatic urethane acrylate in an aqueous solution of 10% sodium alginate which is the external phase. There are also a fair number of capsules which have an inner phase solution of sodium alginate and a shell of aliphatic urethane acrylate liquid polymer and which are dispersed in the aqueous solution of 10% sodium alginate as external phase.

Mass fraction of inner phase 90%, mass fraction of outer phase 10%, rotational speed 2000 rpm, time two minutes.

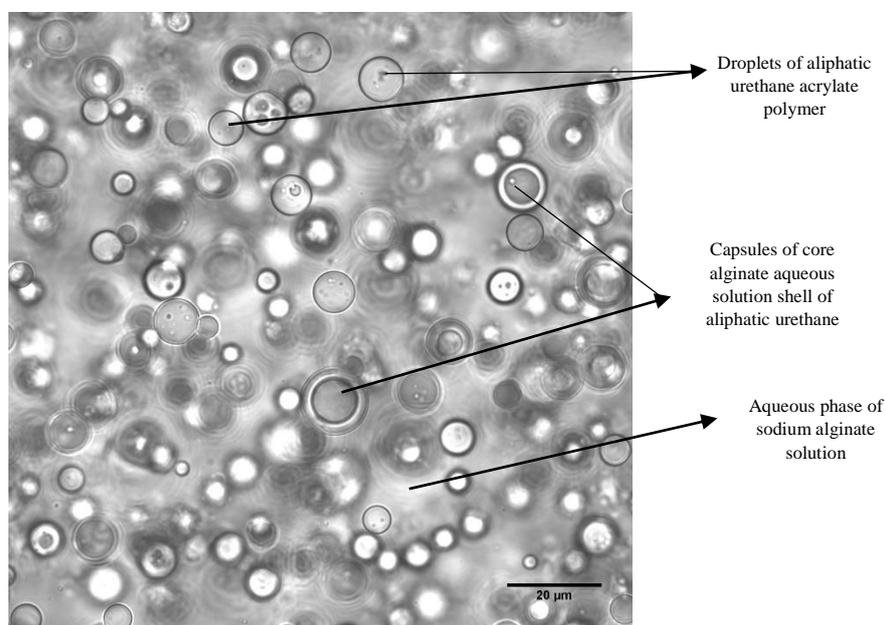


Figure 3-2-C. 9

Mass fraction 90% of aqueous solution

This emulsification using 80% as mass fraction of aqueous solution of 10% sodium alginate yields a reverse emulsion which droplets of aliphatic urethane acrylate in an aqueous solution of 10% sodium alginate which is the external phase. There are also a fair number of capsules which have an inner phase solution of sodium alginate and a shell of aliphatic urethane acrylate liquid polymer and which are dispersed in the aqueous solution of 10% sodium alginate as external phase.

Conclusion

The maximum mass fraction that we can use to prepare the first emulsion of aqueous solution of 10% sodium alginate like inner phase is not more than 70% in aliphatic urethane acrylate liquid polymer. At higher inner phase ratio, we obtain a reverse emulsion which has the aqueous solution of sodium alginate as the external phase and the aliphatic urethane acrylate liquid polymer as internal phase, with a number of co-existing capsules which have wrong morphology.

In order to stay on the safe side, and in view of the preparation of the double emulsion, we prefer to start with a first emulsion that has 50% of the aqueous solution of 10% sodium alginate in aliphatic urethane acrylate liquid polymer.

We also remark that the inversion of the emulsion takes place at an inner phase mass fraction which significantly higher than 50%:50%, yet the viscosity ratio is close to 1.

3-2-C.2 Maximum mass fraction for the First Emulsion of Oil phase / Epoxy Acrylate Polymer liquid polymer

We chose to use the oil poly alpha olefin PAO 40 that has the optimum viscosity value, close to the viscosity of the epoxy urethane acrylate liquid polymer. The viscosity ratio is $\eta_1/\eta_2 = 1.08$ close to 1 and the rotational speed was 2000 rpm.

Mass fraction of inner phase 10%, mass fraction of outer phase 90%, rotational speed 2000 rpm, time two minutes.

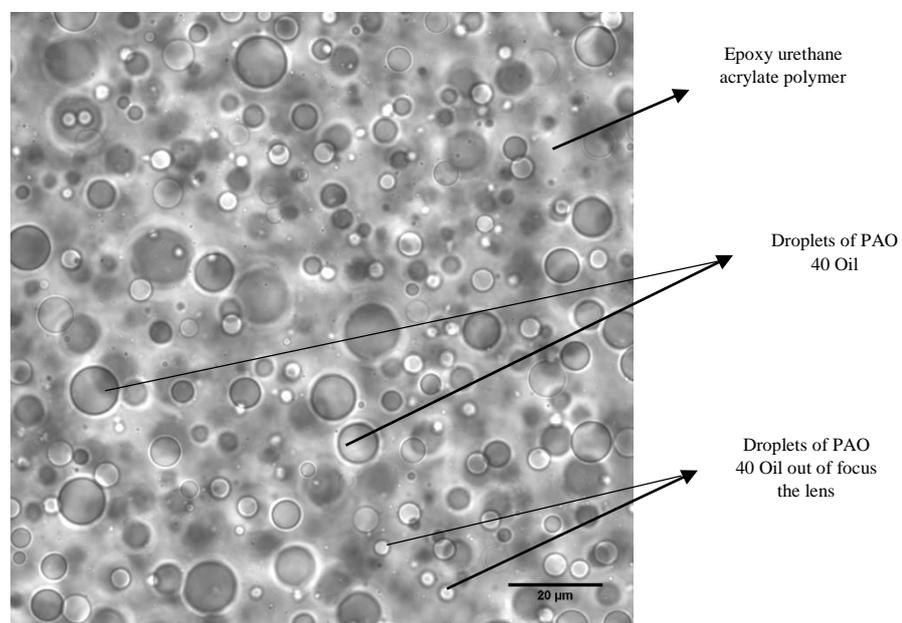


Figure 3-2-C. 10

Mass fraction of oil phase 10%

This emulsification of an inner phase of oil PAO40 poly alpha olefin 40 at a mass fraction equal to 10% of the total emulsion gives good fragmentation. The small droplets of oil are dispersed in epoxy urethane acrylate liquid polymer and have a range of droplet sizes about 10μm.

Mass fraction of inner phase 20%, mass fraction of outer phase 80%, rotational speed 2000 rpm, time two minutes.

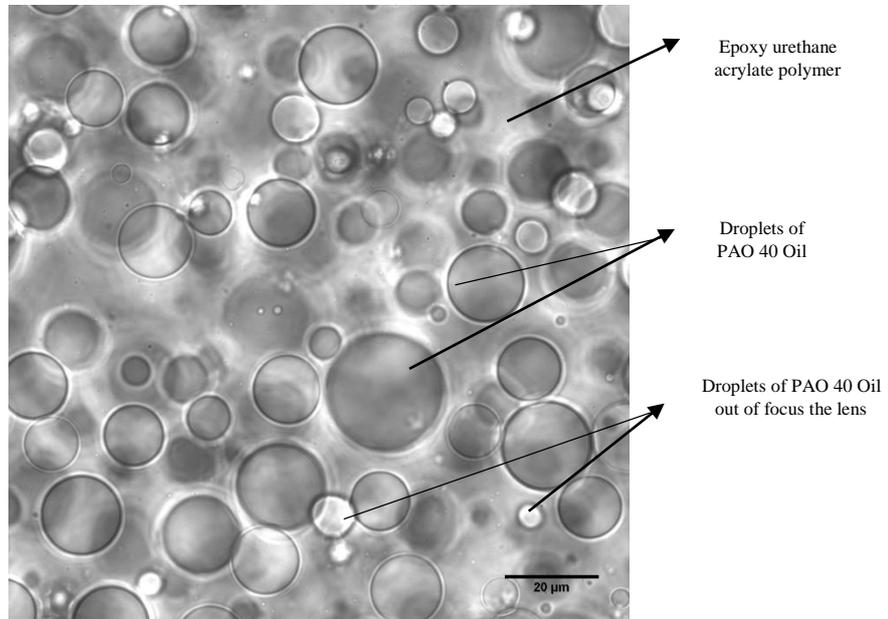


Figure 3-2-C. 11

Mass fraction of oil phase 20%

This emulsification of an inner phase of oil PAO40 poly alpha olefin 40 at a mass fraction equal to 20% of the total emulsion gives good fragmentation. The small droplets of oil are dispersed in epoxy urethane acrylate liquid polymer and have a range of droplet sizes about 20µm.

Mass fraction of inner phase 30%, mass fraction of outer phase 70%, rotational speed 2000 rpm, time two minutes.

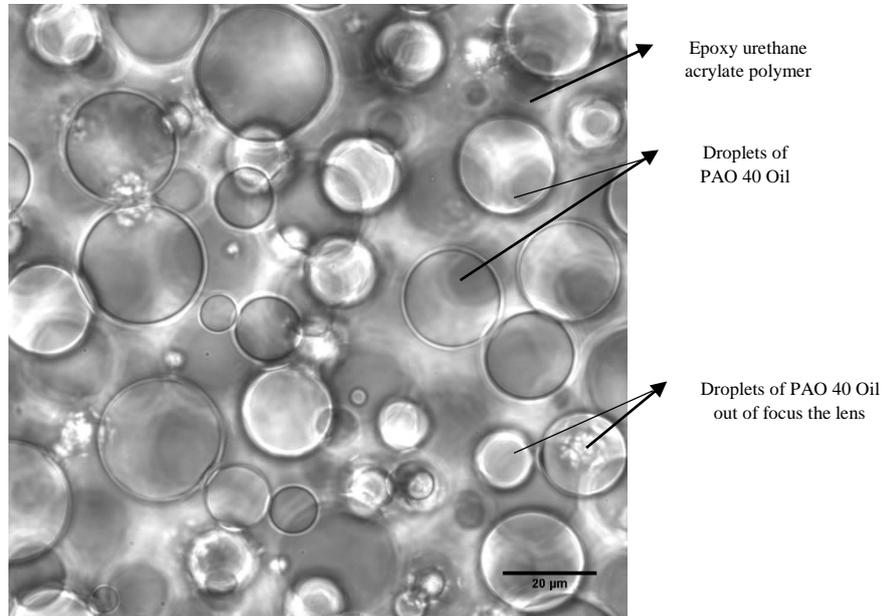


Figure 3-2-C. 12

Mass fraction of oil phase 30%

This emulsification of an inner phase of oil PAO40 poly alpha olefin 40 at a mass fraction equal to 30% of the total emulsion gives fragmentation. The small droplets of oil are dispersed in epoxy urethane acrylate liquid polymer and have a range of droplet sizes about 22µm.

Mass fraction of inner phase 40%, mass fraction of outer phase 60%, rotational speed 2000 rpm, time two minutes.

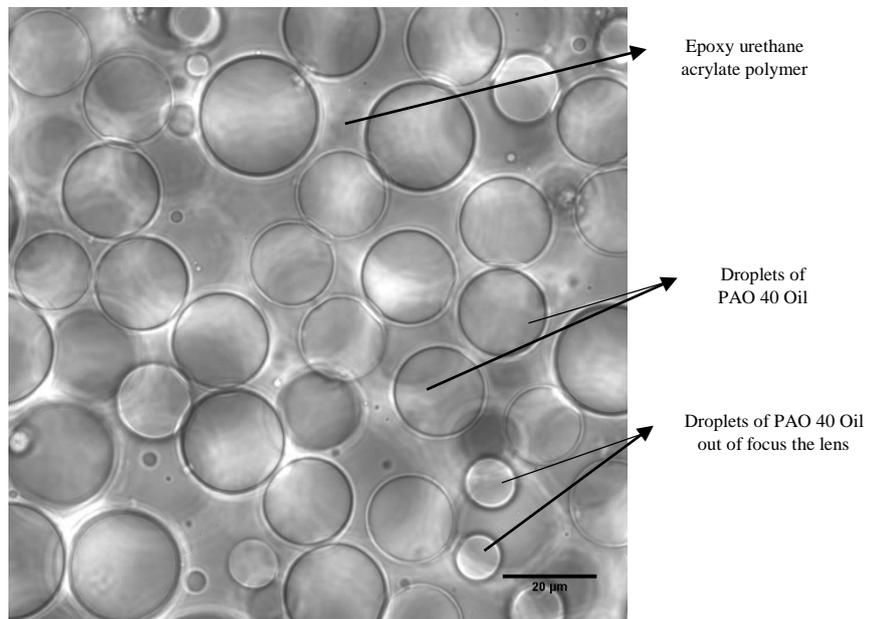


Figure 3-2-C. 13

Mass fraction of oil phase 40%

This emulsification of an inner phase of oil PAO40 poly alpha olefin 40 at a mass fraction equal to 40% of the total emulsion gives good fragmentation. The small droplets of oil are dispersed in epoxy urethane acrylate liquid polymer and have a range of droplet sizes about 22μm.

Mass fraction of inner phase 50%, mass fraction of outer phase 50%, rotational speed 2000 rpm, time two minutes.

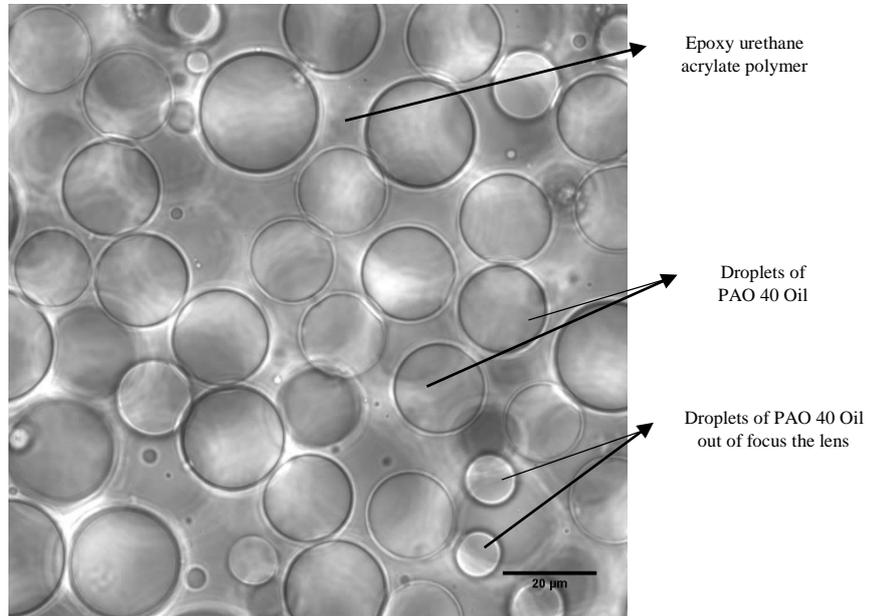


Figure 3-2-C. 14

Mass fraction of oil phase 50%

This emulsification of an inner phase of oil PAO40 poly alpha olefin 40 at a mass fraction equal to 50% of the total emulsion gives good fragmentation. The small droplets of oil are dispersed in epoxy urethane acrylate liquid polymer and have a range of droplet sizes about 22μm.

Mass fraction of inner phase 60%, mass fraction of outer phase 40%, rotational speed 2000 rpm, time two minutes.

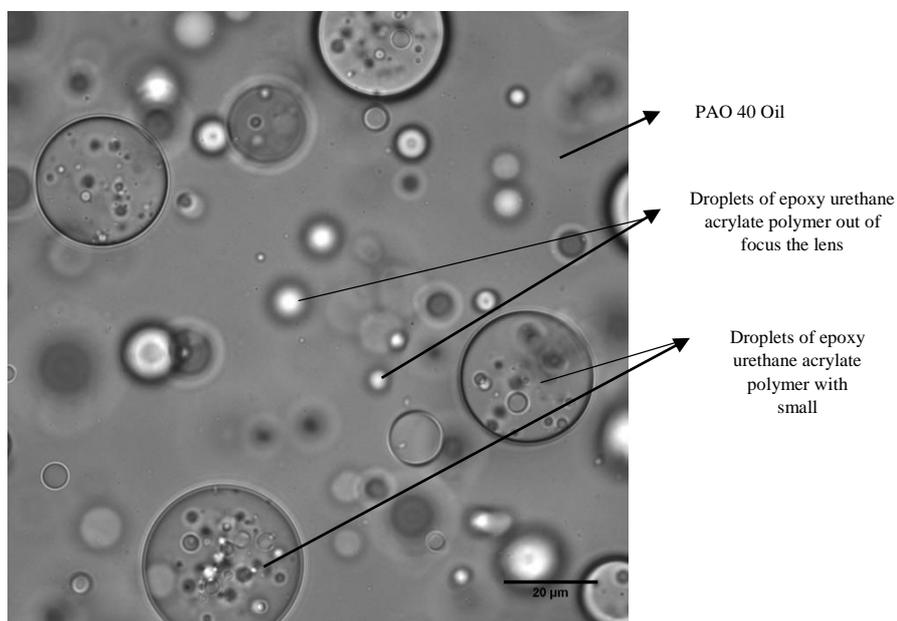


Figure 3-2-C. 15

Mass fraction of oil phase 60%

This emulsification with using 60% as mass fraction of oil poly alpha olefin 40, gives an inverse emulsion with an external phase of poly alpha olefin 40 in which large droplets of epoxy urethane acrylate are dispersed. These large droplets of the epoxy urethane acrylate polymer contain multiple small droplets of poly alpha olefin 40 oil that have sizes less than 3μm.

Mass fraction of inner phase 70%, mass fraction of outer phase 30%, rotational speed 2000 rpm, time two minutes.

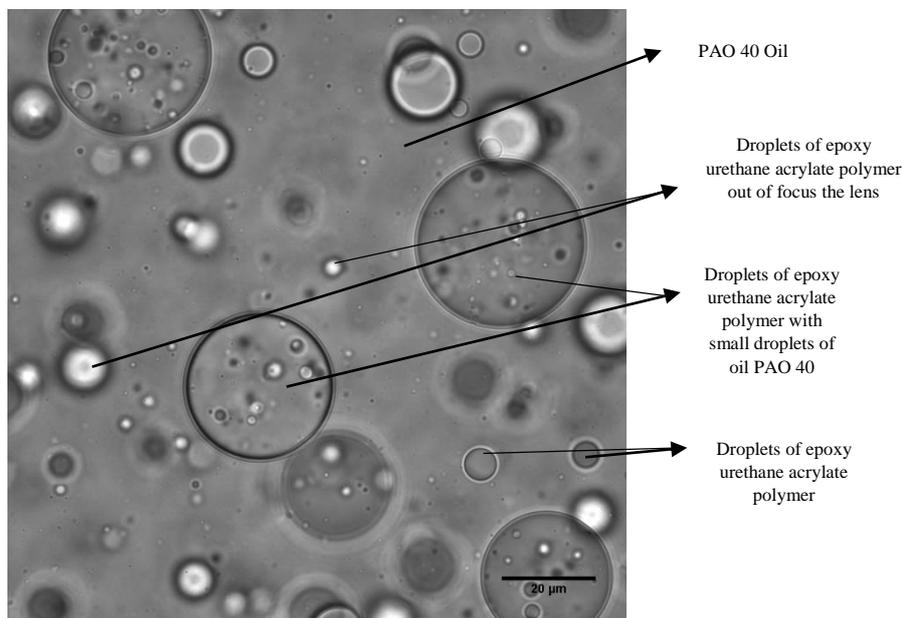


Figure 3-2-C. 16

Mass fraction of oil phase 70%

This emulsification with using 70% as mass fraction of oil poly alpha olefin 40, gives an inverse emulsion with an external phase of poly alpha olefin 40 in which large droplets of epoxy urethane acrylate are dispersed. These large droplets of the epoxy urethane acrylate polymer contain multiple small droplets of poly alpha olefin 40 oil that have sizes less than 3μm.

Mass fraction of inner phase 80%, mass fraction of outer phase 20%, rotational speed 2000 rpm, time two minutes.

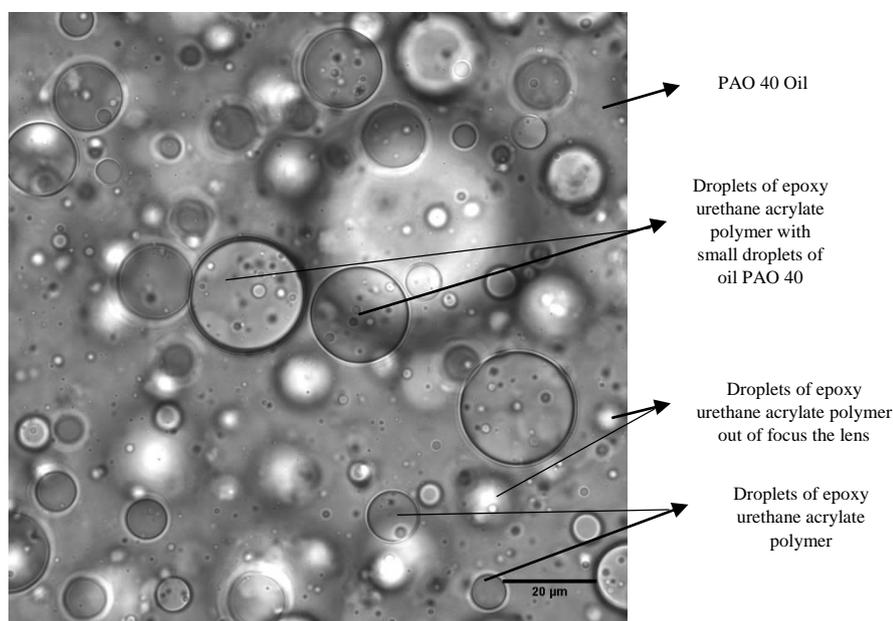


Figure 3-2-C. 17

Mass fraction of oil phase 80%

This emulsification with using 80% as mass fraction of oil poly alpha olefin 40, gives an inverse emulsion with an external phase of poly alpha olefin 40 in which large droplets of epoxy urethane acrylate are dispersed. These large droplets of the epoxy urethane acrylate polymer contain multiple small droplets of poly alpha olefin 40 oil that have sizes less than 3μm.

Conclusion:

In practice, we conclude that the maximum mass fraction that we can use in the first emulsion of oil in epoxy urethane acrylate liquid polymer is not more than 50% of the total emulsion.

It is quite remarkable that with mass fraction of inner phase equal to 50% we obtain an emulsion made exclusively of poly alpha olefin 40 oil droplets in the epoxy urethane acrylate liquid polymer.

This nice asymmetry is observed only with 50% of oil in epoxy urethane acrylate polymer.

If we increase the mass fraction of the inner phase to 60%, we get an inversed emulsion of epoxy urethane acrylate liquid polymer droplets in the poly alpha olefin 40 oil.

3-2-D Double Emulsion Fragmentation Diagram

3-2-D.1 Fragmentation diagram of Double Emulsion: Aqueous phase / Aliphatic Urethane Acrylate polymer / Aqueous Phase

All the double emulsions were formulated to maintain a constant viscosity ration $\eta_1/\eta_2 = 0.8$ between the cores of the capsules (aqueous phase with 10% of sodium alginate) and the liquid polymer shell aliphatic urethane acrylate CN991, this is based on the results presented previously in the first emulsification diagram.

Consequently, the only variable was the viscosity of the external phase, which was the aqueous solution of sodium alginate. For this solution we chose different concentrations in order to have different viscosity ratios η_2/η_3 between the acrylate polymer shell phase 2 and the aqueous external phase 3.

- Materials and the Equipment:

Deionized water, Sodium Alginate, Aliphatic urethane acrylate liquid polymer CN991, Initiator for UV polymerization (2-hydroxy 2-methylpropiophenone), Balance, Plastic beaker of 50 ml, Glass beaker of 150 ml, Overhead mixer, UV oven, Glass slides and covers slip, Small plastic pipette

Double emulsion preparation

- 1- After the evaluation of the fragmentation of the first emulsion, we had concluded that the ideal viscosity ratio between the aqueous phase (aqueous solution of sodium alginate 10%) and the aliphatic urethane acrylate liquid polymer was close to = 1, actually = 0.8.
- 2- First emulsification mix 4 g of aliphatic urethane acrylate liquid polymer with 2.5% of UV initiator based on the total mass of the aliphatic polymer, and add to it 4g of the aqueous solution of sodium alginate 10%). Mix them at rotation speed 2000 rpm by using the overhead mixer with a 4-bladed propeller stirrer for 1 minute. This yields the first emulsion which we keep under constant stirring.
- 3- Second emulsification with high viscosity ratio $\eta_2/\eta_3 = 18.3$ between phase 2 (shell) and phase 3 (External phase). Place 20 g of sodium alginate 5% solution (External phase) in a 150 ml glass beaker and attach it under the overhead mixer. Stir using the Anchor stirrer at a rotation speed 200 rpm. Take 3.0 ml from the first emulsion (still stirred) in a syringe and drop it in the beaker of the external phase (alginate 5%). Continue stirring this mixture at rotation speed 200 rpm for 20 seconds. This produces the double emulsion.
- 4- Pour out the double emulsion in Petri dish to allow homogenous polymerisation by UV in the UV oven for 5.0 minutes.
- 5- Remove the double emulsion from the UV oven, take a small droplet from it with a small plastic pipette, and put it on the glass slide, put a cover slip and observe it on the optical microscope with the objective lens 100X. Take images that show the structure of this double emulsion.
- 6- Repeat the same experiment with a rotation speed increased to 500,1000 and 2000 rpm

- 7- Use another viscosity ratio = 4.76, 3.12, 1.89 and 1.21 between phase 2 and phase 3, while keeping the viscosity ratio between phase 1 and 2 = 0.8 and use different rotation speeds 200, 500, 1000 and 2000 rpm.
- 8- The rest of the procedure is as above.

- 1- Bright field images of double emulsion of aqueous phase / Aliphatic urethane acrylate / aqueous phase with very high viscosity ratio $\eta_2/\eta_3 = 18.3$:

The emulsion was then sheared at a rotation speed of 200 rpm for 20 second and was subsequently washed with water in order to improve transparency and reduce concentration.

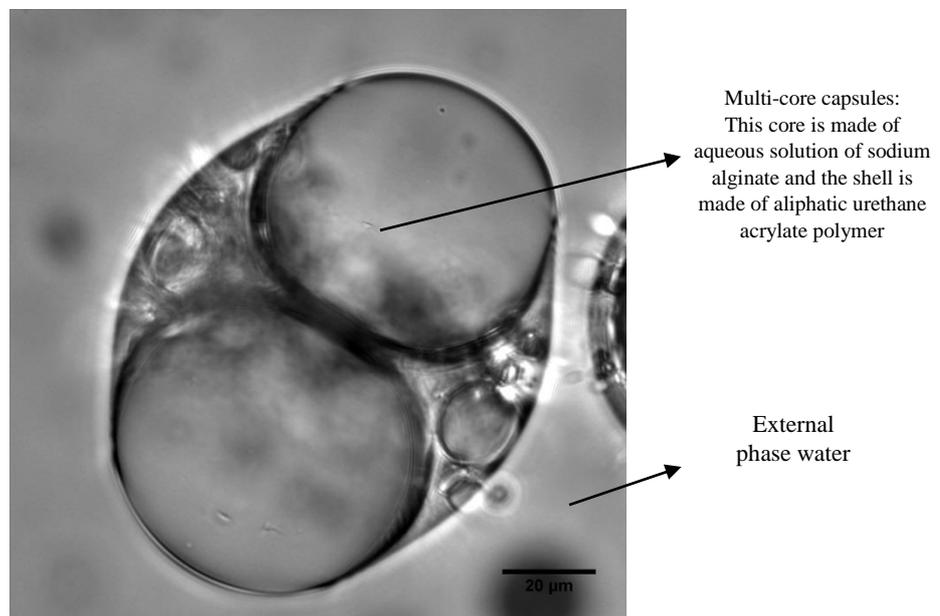


Figure 3-2-D. 1

In this double emulsion we see non-homogenised multi-core droplets of aqueous solution of sodium alginate contained by a shell of aliphatic urethane acrylate polymer. This capsule had a size larger than 40μm, this was the result of a viscosity ratio that was too high and a shear rate that was too low.

The next emulsion was then sheared at a higher rotational speed of 500 rpm for 20 second

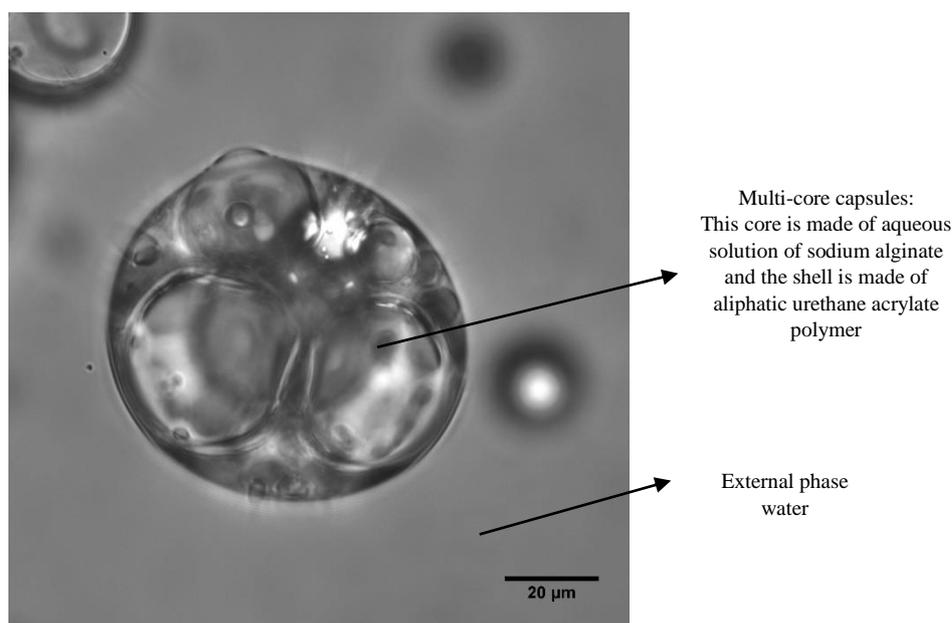


Figure 3-2-D. 2

In this double emulsion we see non-homogenised multi-core droplets of aqueous solution of sodium alginate contained by a shell of aliphatic urethane acrylate polymer. This capsule had a size larger than 40μm, this was the result of a viscosity ratio that was too high and a shear rate that was too low.

The next emulsion was then sheared at a higher rotation speed of 1000 rpm for 20 second

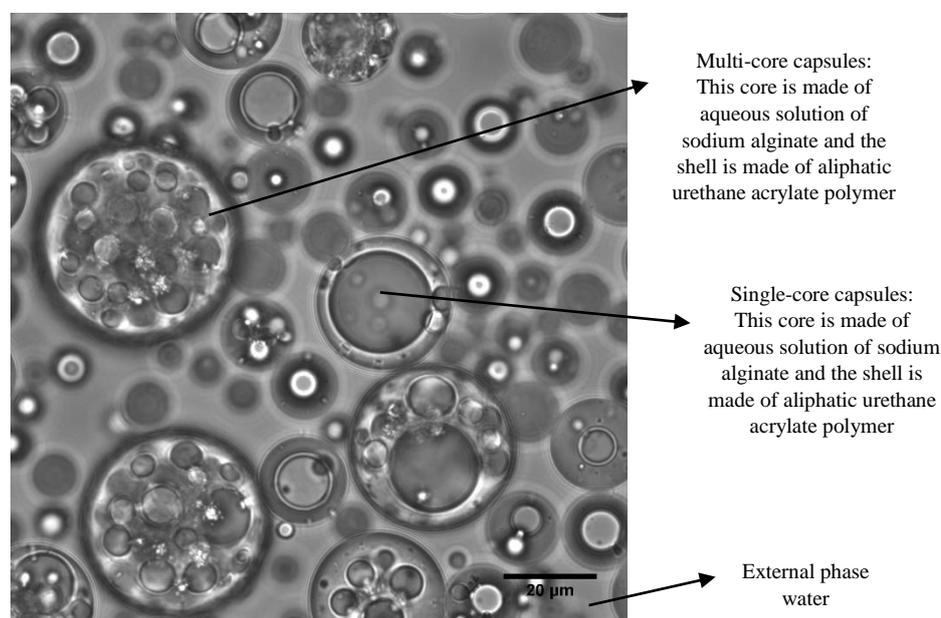


Figure 3-2-D. 3

This double emulsion contained heterogeneous multi core droplets of aqueous solution of sodium alginate within a shell of aliphatic urethane acrylate polymer, these capsules have sizes up to 40μm. Also, there were some capsules that had a single core made of the aqueous solution of sodium alginate and a shell made of aliphatic urethane acrylate polymer.

This emulsion was finally sheared at the highest rotation speed of 2000 rpm for 20 second

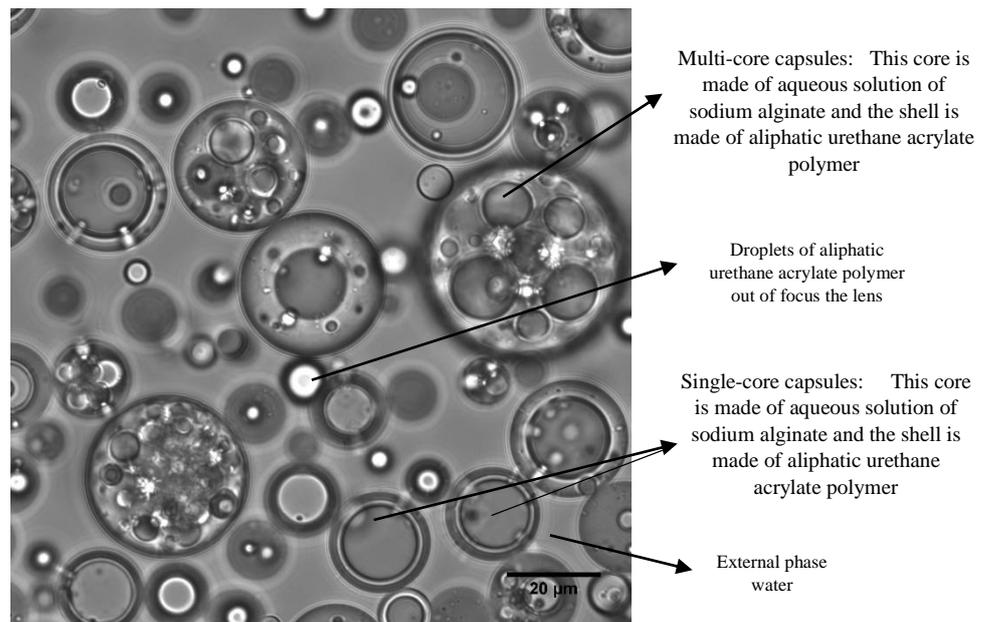


Figure 3-2-D. 4

This double emulsion contained heterogeneous multi core droplets of aqueous solution of sodium alginate within a shell of aliphatic urethane acrylate polymer, these capsules have sizes up to 40μm Also, there were some capsules that had a single homogenous core made of the aqueous solution of sodium alginate and a shell made of aliphatic urethane acrylate polymer.

Now we present the results of experiments in which we reduced in stages the viscosity ratio

- 2- Bright field images of double emulsion of aqueous phase / Aliphatic urethane acrylate/ aqueous phase with viscosity ratio $\eta_2/\eta_3 = 4.76$.

At first the emulsion was sheared at a rotational speed of 200 rpm

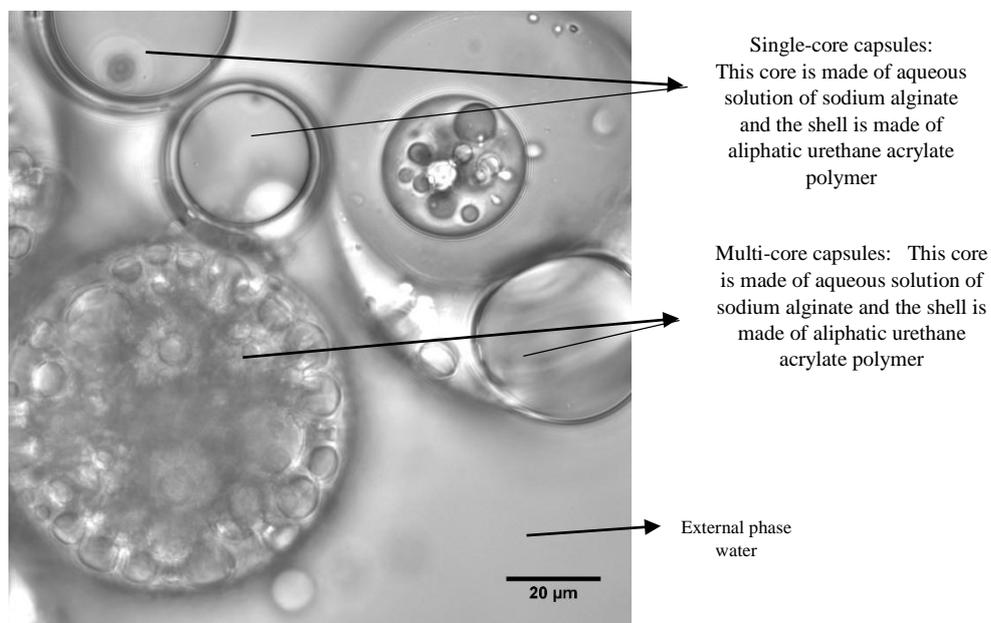


Figure 3-2-D. 5

This double emulsion contained heterogeneous multi core droplets of aqueous solution of sodium alginate within a shell of aliphatic urethane acrylate polymer, these capsules have sizes up to 40μm Also, there were some capsules that had a single core made of the aqueous solution of sodium alginate and a shell made of aliphatic urethane acrylate polymer.

The next emulsion was then sheared at a higher rotational speed of 500 rpm for 20 second rpm

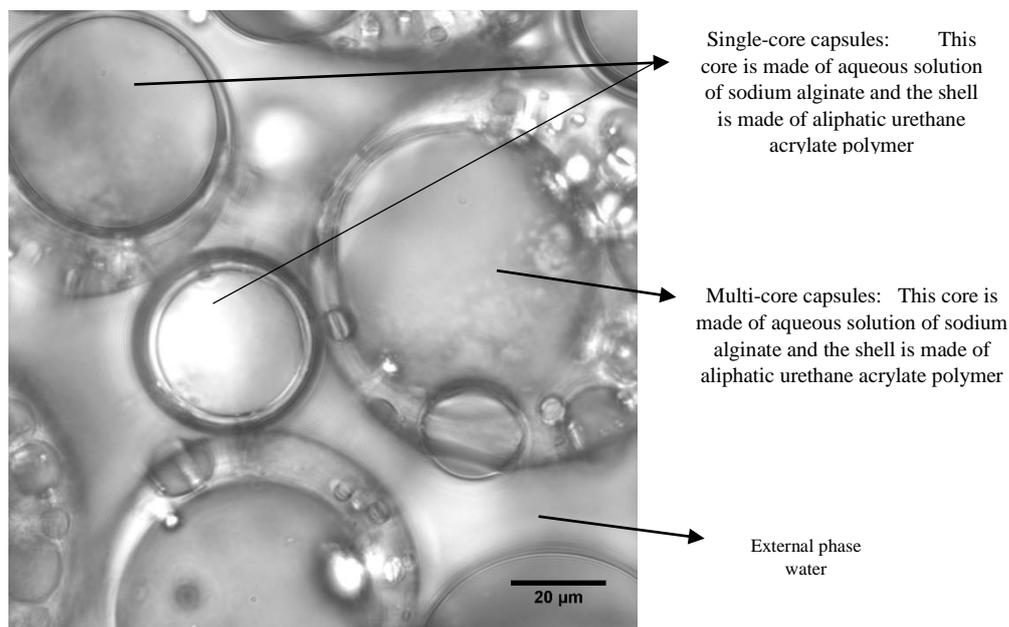


Figure 3-2-D. 6

This double emulsion had more single core capsules and less multi-core capsules. We argue that this change is related to the lower value of the viscosity ratio. All these capsules were polydisperse with sizes up to 60μm

The next emulsion was then sheared at a higher rotational speed of 1000 rpm for 20 second

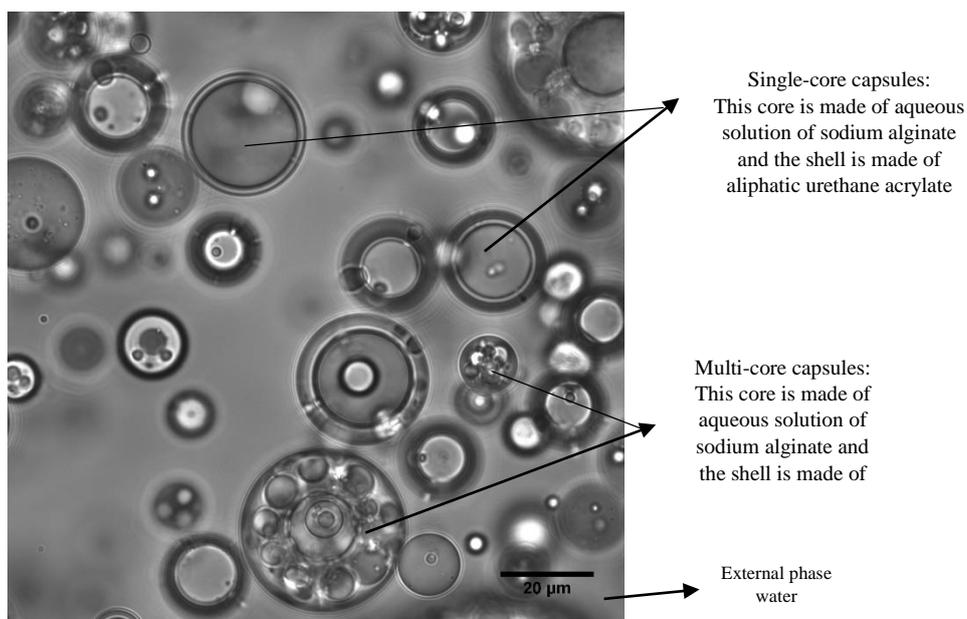


Figure 3-2-D. 7

This double emulsion had a few single core capsules with some multi-core capsules and some empty droplets of aliphatic urethane acrylate polymer. We argue that this change is related to the increase of

the shear rate that produces some empty capsules. All these capsules were polydisperse with sizes up to 40 μm .

The next emulsion was then sheared at the highest rotational of speed 2000 rpm for 20 second

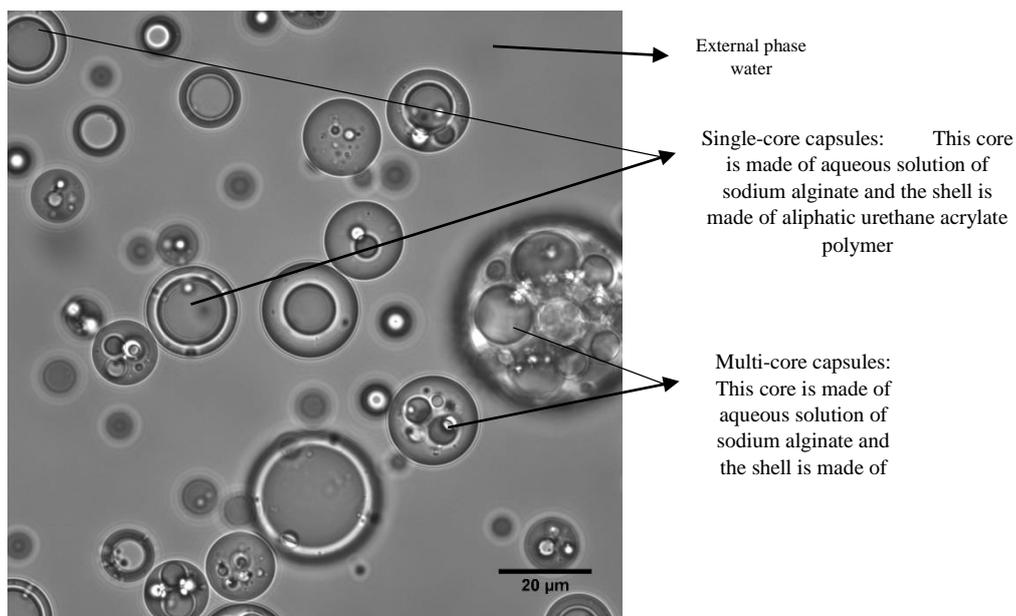


Figure 3-2-D. 8

This double emulsion had 3 types of objects: single homogenous core capsules, heterogeneous multi-core capsules and some empty droplets of aliphatic urethane acrylate polymer. We argue that this change is related to the increase of the shear rate that produces some empty capsules. All these capsules were polydisperse with sizes up to 40 μm

Now we present the results of experiments in which we reduced further the viscosity ratio

- 3- Bright field images of double emulsion of aqueous phase / Aliphatic urethane acrylate/ aqueous phase with high viscosity ratio $\eta_2/\eta_3 = 3.12$.

The emulsion was then sheared at a rotational speed of 200 rpm for 20 second

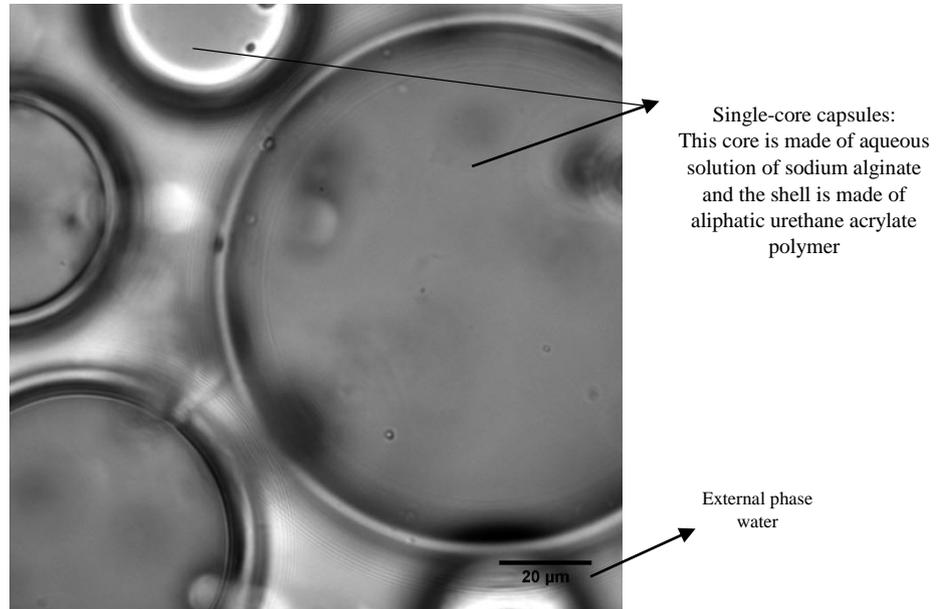


Figure 3-2-D. 9

The double emulsion had a very large and polydisperse capsules with cores made of aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer, some of these capsules had sizes larger than 80μm.

We notice that the emulsions no longer contain the heterogonous multi-core capsules that were easily visible at the viscosity ratios higher than 3.

The next emulsion was then sheared at a higher rotational speed of 500 rpm for 20 second

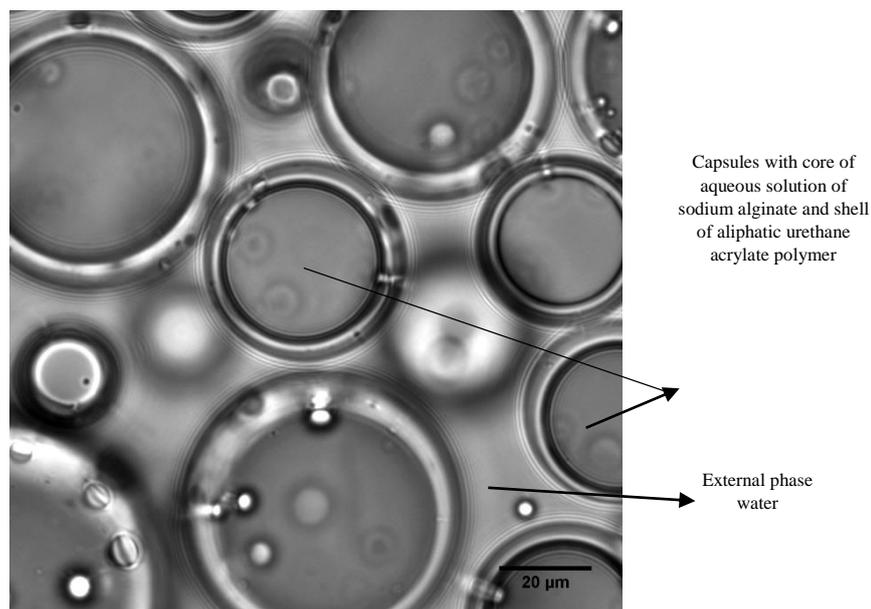


Figure 3-2-D. 10

The double emulsion had large polydisperse capsules with cores made of the aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. Some of these capsules had sizes larger than 40μm.

We notice that the emulsions no longer contain the heterogenous multi-core capsules that were easily visible at the viscosity ratios higher than 3.

The next emulsion was then sheared at a higher rotational speed of 1000 rpm for 20 second

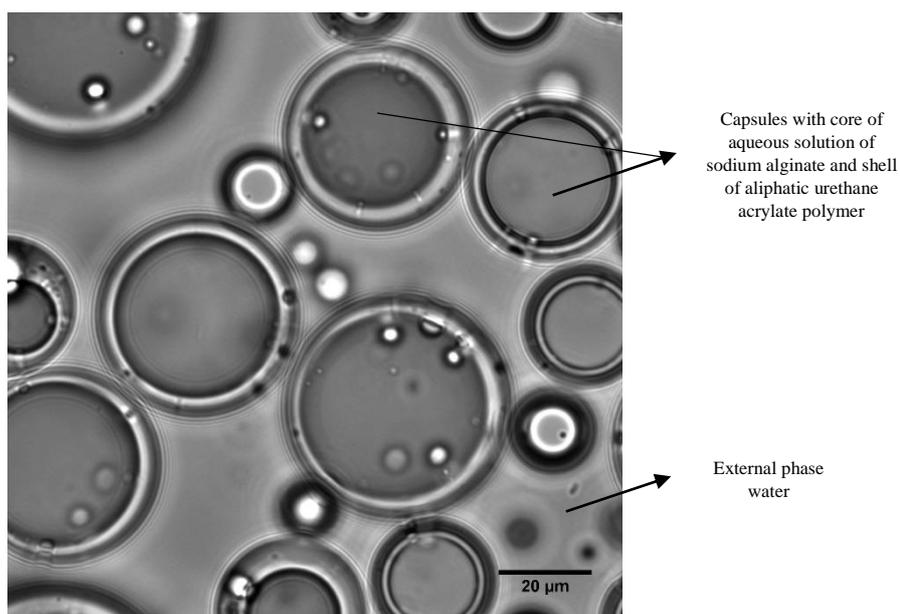


Figure 3-2-D. 11

The double emulsion had large and polydisperse capsules with cores made of the aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. Some of these capsules had size larger than 30 μ m.

We notice that the emulsions no longer contain the heterogenous multi-core capsules that were easily visible at the viscosity ratios higher than 3.

The next emulsion was then sheared at the highest rotational speed of 2000 rpm for 20 second

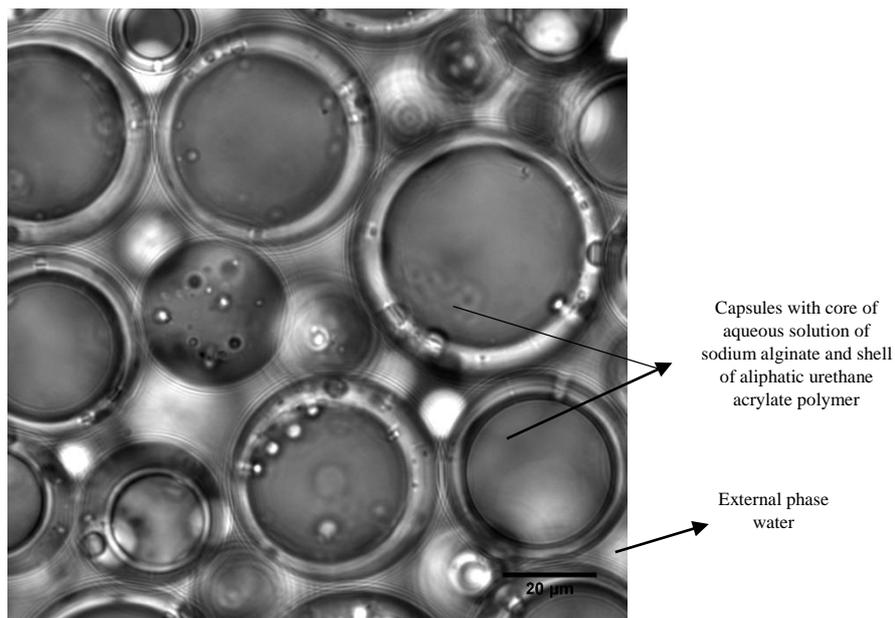


Figure 3-2-D. 12

The double emulsion had large and polydisperse capsules with cores made of the aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. Some of these capsules had size larger than 30 μ m.

We notice that the emulsions no longer contain the heterogenous multi-core capsules that were easily visible at the viscosity ratios higher than 3.

Now we present the results of experiments in which we reduced further the viscosity ratio

- 4- Bright field images of double emulsion of aqueous phase / Aliphatic urethane acrylate/ aqueous phase with good viscosity ratio $\eta_2/\eta_3 = 1.89$

The first emulsion was then sheared at rotational speed of 200 rpm for 20 second

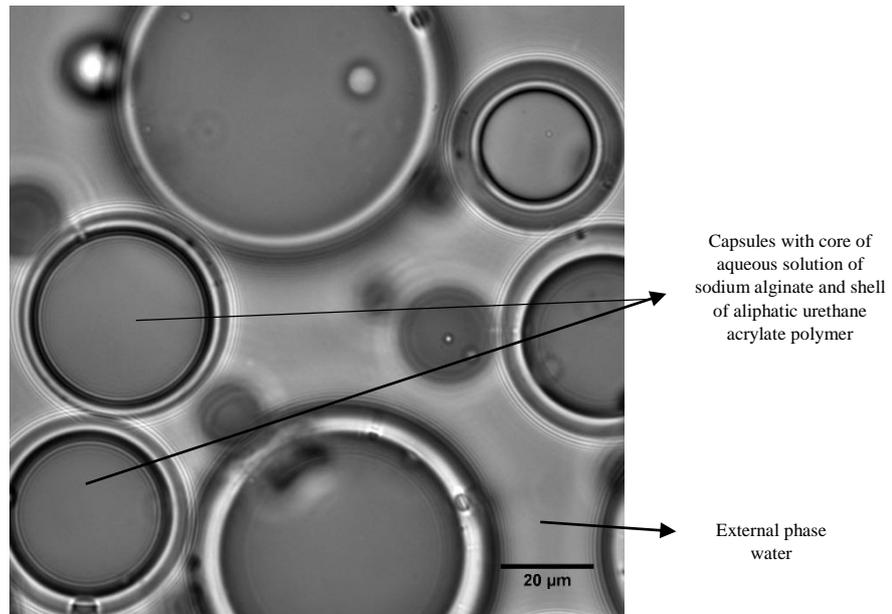


Figure 3-2-D. 13

The double emulsion had large and polydisperse capsules with cores made of the aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. Some of these capsules had size larger than 30μm.

We notice that the emulsions no longer contain the heterogonous multi-core capsules that were easily visible at the viscosity ratios higher than 3.

The next emulsion was then sheared at a higher rotational speed of 500 rpm for 20 second

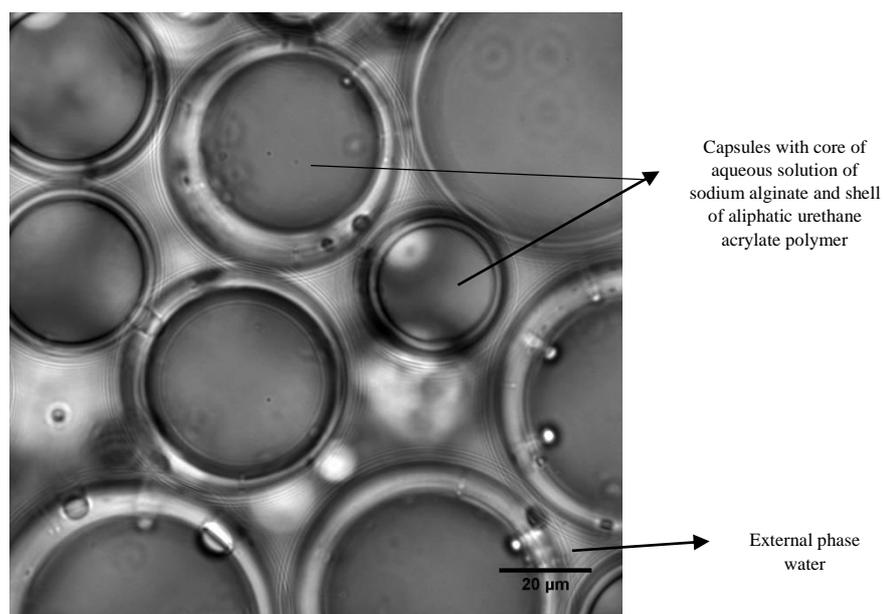


Figure 3-2-D. 14

The double emulsion had large and polydisperse capsules with cores made of the aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. Some of these capsules had size larger than 30μm.

We notice that the emulsions no longer contain the heterogenous multi-core capsules that were easily visible at the viscosity ratios higher than 3.

The next emulsion was then sheared at a higher rotational speed of 1000 rpm for 20 second

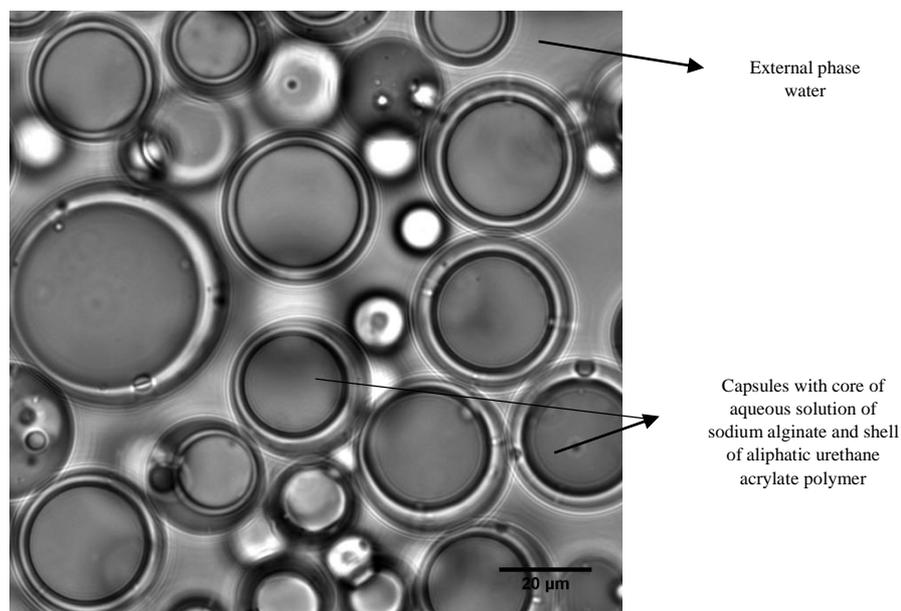


Figure 3-2-D. 15

The double emulsion had large and polydisperse capsules with cores made of the aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. Some of these capsules had size larger than 30μm.

We notice that the emulsions no longer contain the heterogenous multi-core capsules that were easily visible at the viscosity ratios higher than 3.

The emulsions contain mostly homogenous single core capsules with sizes that decreased with increasing shear rates.

The next emulsion was then sheared at the highest rotational speed of 2000 rpm for 20 second

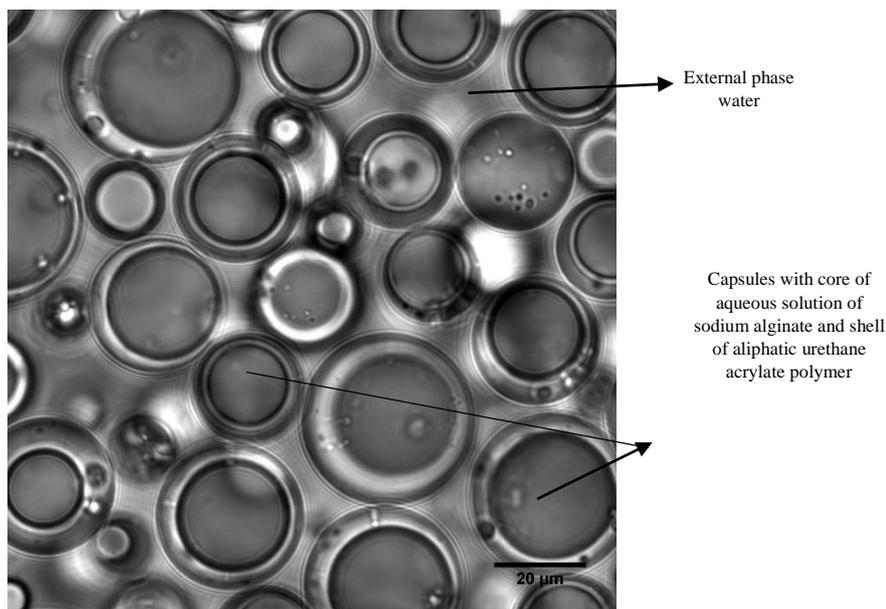


Figure 3-2-D. 16

The double emulsion had large and polydisperse capsules with cores made of the aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. Some of these capsules had size larger than 30μm.

We notice that the emulsions no longer contain the heterogenous multi-core capsules that were easily visible at the viscosity ratios higher than 3.

The emulsions contain mostly homogenous single core capsules with sizes that decreased with increasing shear rates.

Now we present the results of experiments in which we reduced further the viscosity ratio

- 5- Bright field images of double emulsion of aqueous phase / Aliphatic urethane acrylate/ aqueous phase with optimum viscosity ratio $\eta_2/\eta_3 = 1.21$

The emulsion was then sheared at a rotational speed of 200 rpm for 20 second

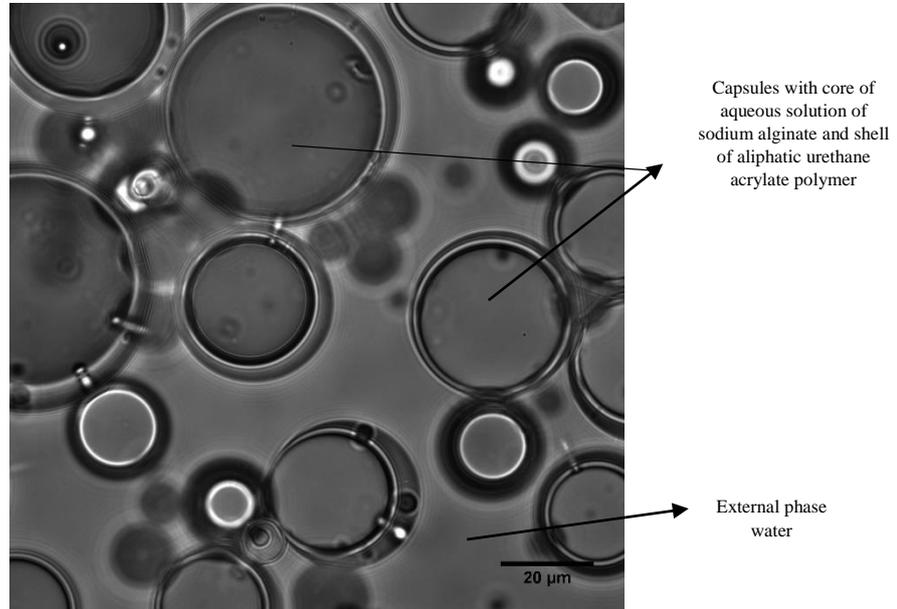


Figure 3-2-D. 17

The double emulsion had very polydisperse capsules with cores made of aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. In addition, there were many very small droplets of urethane acrylate polymer with no aqueous cores.

The next emulsion was then sheared at a higher rotational speed of 500 rpm for 20 second

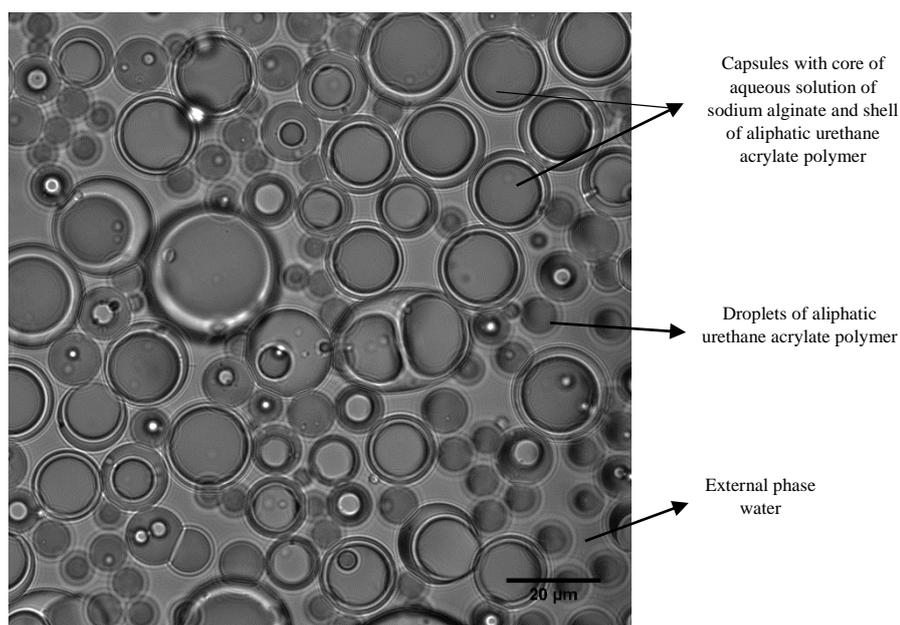


Figure 3-2-D. 18

The double emulsion had very polydisperse capsules with cores made of aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. In addition, there were many very small droplets of urethane acrylate polymer with no aqueous cores

The next emulsion was then sheared at a higher rotational speed of 1000 rpm for 20 second

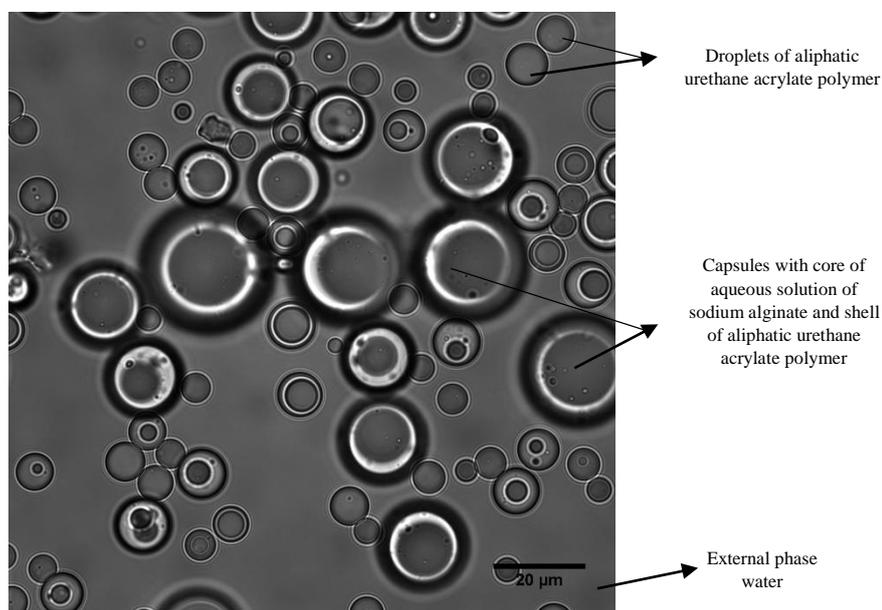


Figure 3-2-D. 19

The double emulsion had some polydisperse capsules with cores made of aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. In addition, there were too many very small droplets of urethane acrylate polymer with no aqueous cores.

The next emulsion was then sheared at the highest rotational speed of 2000 rpm for 20 second

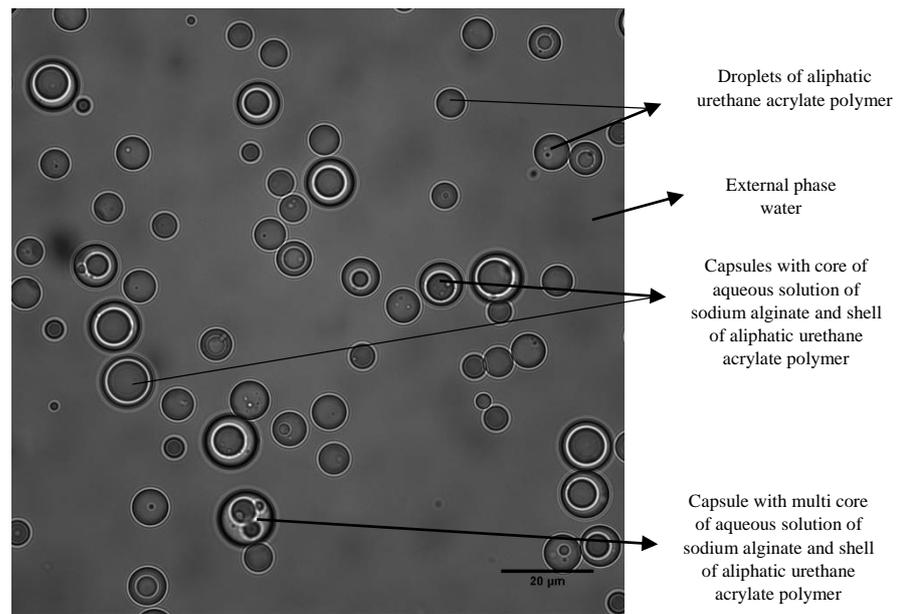


Figure 3-2-D. 20

The double emulsion had a low number of polydisperse capsules with cores made of aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer.

In addition, there were too many very small droplets of urethane acrylate polymer with no aqueous cores.

This encapsulation failure indicates that the high shear forces broke the capsules and that the internal phase 1 was released in to the outer phase 3.

Now we present the results of experiments in which we reduced further the viscosity ratio

- 6- Bright field images of double emulsion of aqueous phase / Aliphatic urethane acrylate/ aqueous phase with low viscosity ratio $\eta_2/\eta_3 = 0.18$

The emulsion was then sheared at a rotational speed of 200 rpm for 20 second

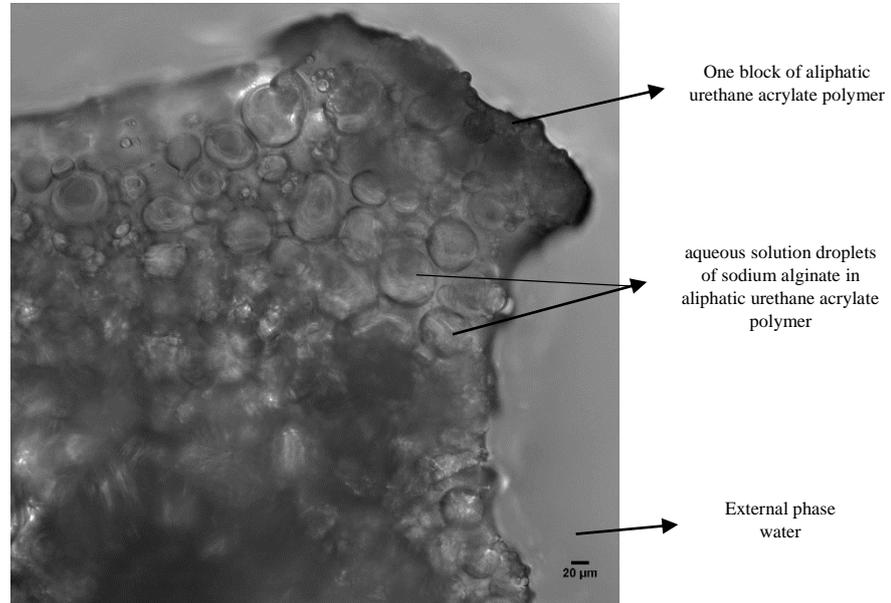


Figure 3-2-D. 21

Here we observed dramatic changes compared to the behaviour at high viscosity ratio:

We observe that the first emulsion was not dispersed in the external phase of aqueous of sodium alginate 15%, resulting in failure of the emulsification.

Instead, we obtained a soft cellular gel made of aqueous droplets of sodium alginate glued by walls of aliphatic urethane polymer.

The next emulsion was then sheared at a higher rotational speed of 500 rpm for 20 second

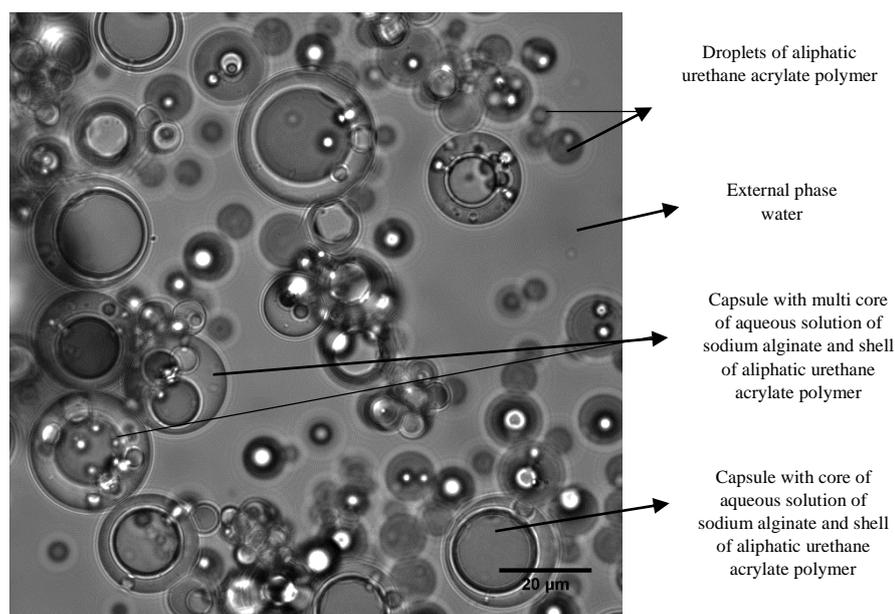


Figure 3-2-D. 22

The double emulsion had some polydisperse capsules with cores made of aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer. In addition, there were too many very small droplets of aliphatic urethane acrylate polymer with no aqueous cores.

The next double emulsion was then sheared at a higher rotational speed of 1000 rpm for 20 second

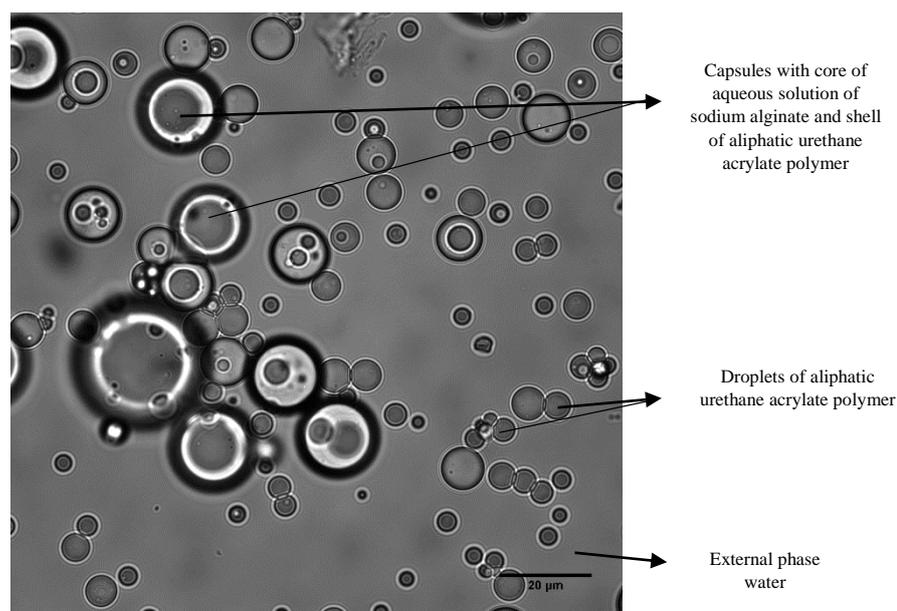


Figure 3-2-D. 23

The double emulsion had some polydisperse capsules with cores made of aqueous solution of sodium

alginate and shells made of aliphatic urethane acrylate polymer.

In addition, there were too many very small droplets of urethane acrylate polymer with no aqueous cores.

The next double emulsion was then sheared at a higher rotational speed of 2000 rpm for 20 second

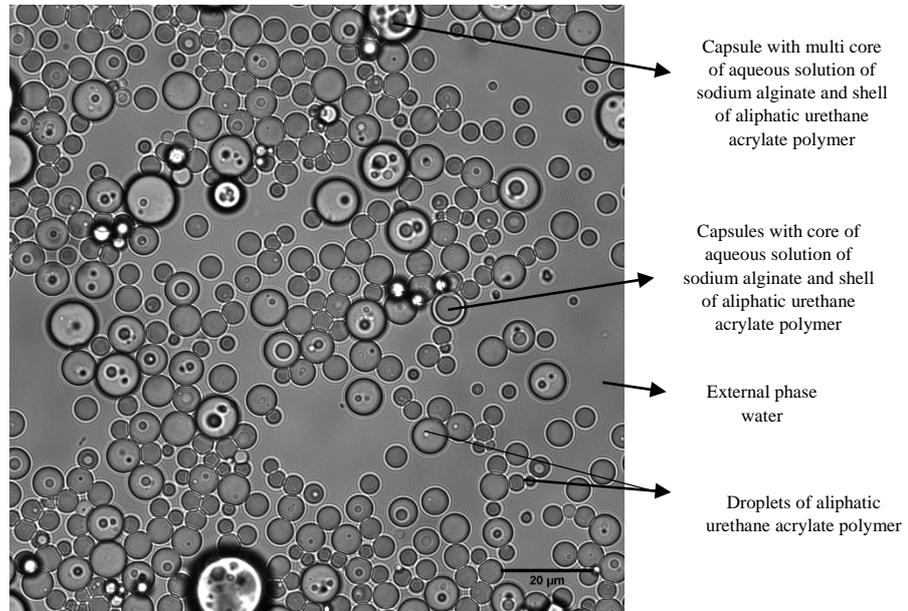


Figure 3-2-D. 24

The double emulsion had a very low number of polydisperse capsules with cores made of aqueous solution of sodium alginate and shells made of aliphatic urethane acrylate polymer.

In addition, there were too many very small droplets of urethane acrylate polymer with no aqueous cores.

This encapsulation failure indicates that the high shear forces broke the capsules and that the internal phase 1 was released in to the outer phase 3.

Interestingly the average volume of a particle matches approximately the average volume of a shell of the same polymer in a capsule.

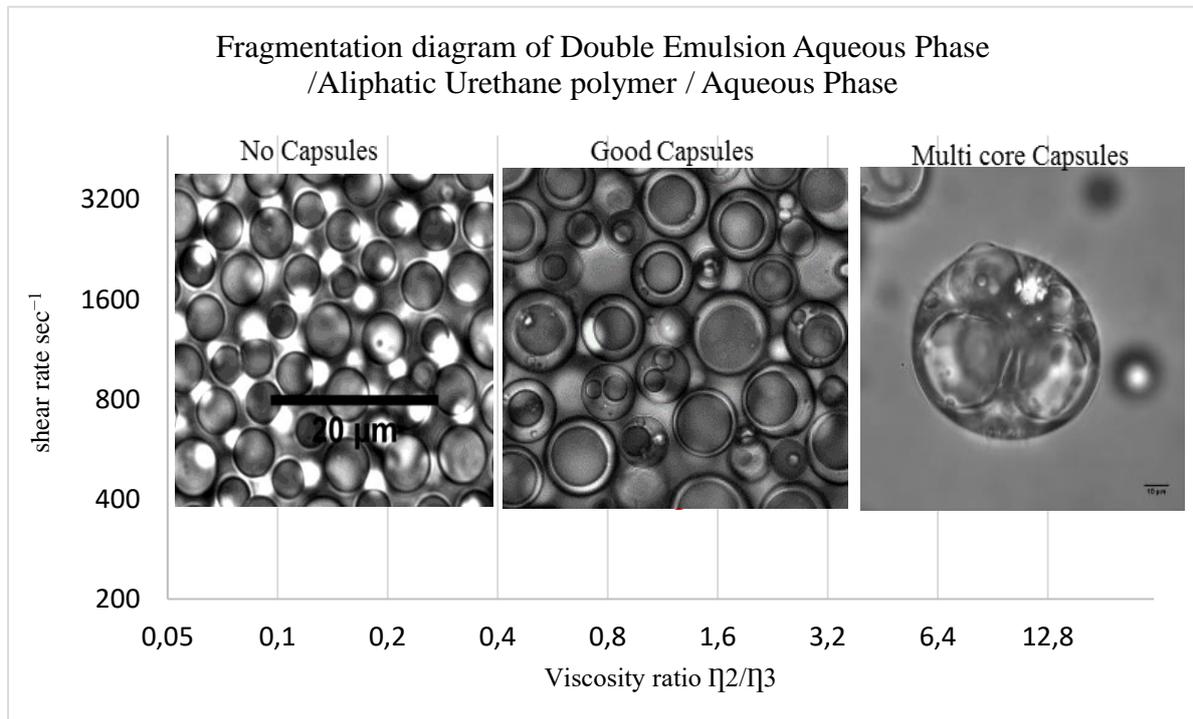


Figure 3-2-D. 25
Fragmentation diagram for double emulsion depending on the viscosity ratio between phase 2 and 3

Conclusion:

We can observe from the diagram that there are three different zones:

1- High viscosity between $\eta_2/\eta_3 = 18.3$

We observed poor fragmentation, leading to poly disperse capsules with multi core.

2- Optimum viscosity ratio $\eta_2/\eta_3 = 1.89$ to 1.24

We observed good fragmentation with nearly monodisperse capsules with single homogeneous core-shell structure.

3- Low viscosity ratio $\eta_2/\eta_3 = 0.18$

We observed very strong fragmentation which destroy the double emulsion and produce small droplets of aliphatic urethane acrylate polymer with size of $5\mu\text{m}$.

Effect viscosity ratio on the stability of double emulsion aqueous phase / acrylate shell / aqueous phase

No:	Description	Phase 2 viscosity pa.s at 10 sec ⁻¹	Phase 3 viscosity pa.s at 10 sec ⁻¹	Viscosity ratio phase2 / phase 3	Evaluation the emulsification
1	CN991 in Water	10.058	0.0017	5916.470	Very bad
2	CN991 in 3 % Alginate	10.058	0.122579	82.0532	Very bad
3	CN991 in 5% alginate	10.058	0.549588	18.3009	Very bad
4	CN991 in 7 % Alginate	10.058	2.11424	4.75726	Bad
5	CN991 in 8 % Alginate	10.058	3.223	3.12	Good
6	CN991 in 9 % Alginate	10.058	5.3216	1.89	Very good
7	CN991 in 10 % Alginate	10.058	8.28345	1.24	Very good
8	CN991 In 15 % Alginate	10.058	55.0585	0.18267	Very bad

Table 3-2-D. 1

Effect of the viscosity ratio on the stability for the second emulsion of aqueous phase / acrylate shell / aqueous phase

To confirm the best region of the optimum emulsification of the double emulsions when we used viscosity ratio close to 1

We made different trial of double emulsion emulsification of sodium alginate solution as a core, aliphatic urethane acrylate liquid polymer as a shell and sodium alginate solution as an external phase under different shear rate with using different viscosity value from low viscosity to high viscosity but with keeping always the viscosity ratio between the fluids η_1/η_2 and η_2/η_3 close to 1

The results that we got I plotted it in one graph as it shown:

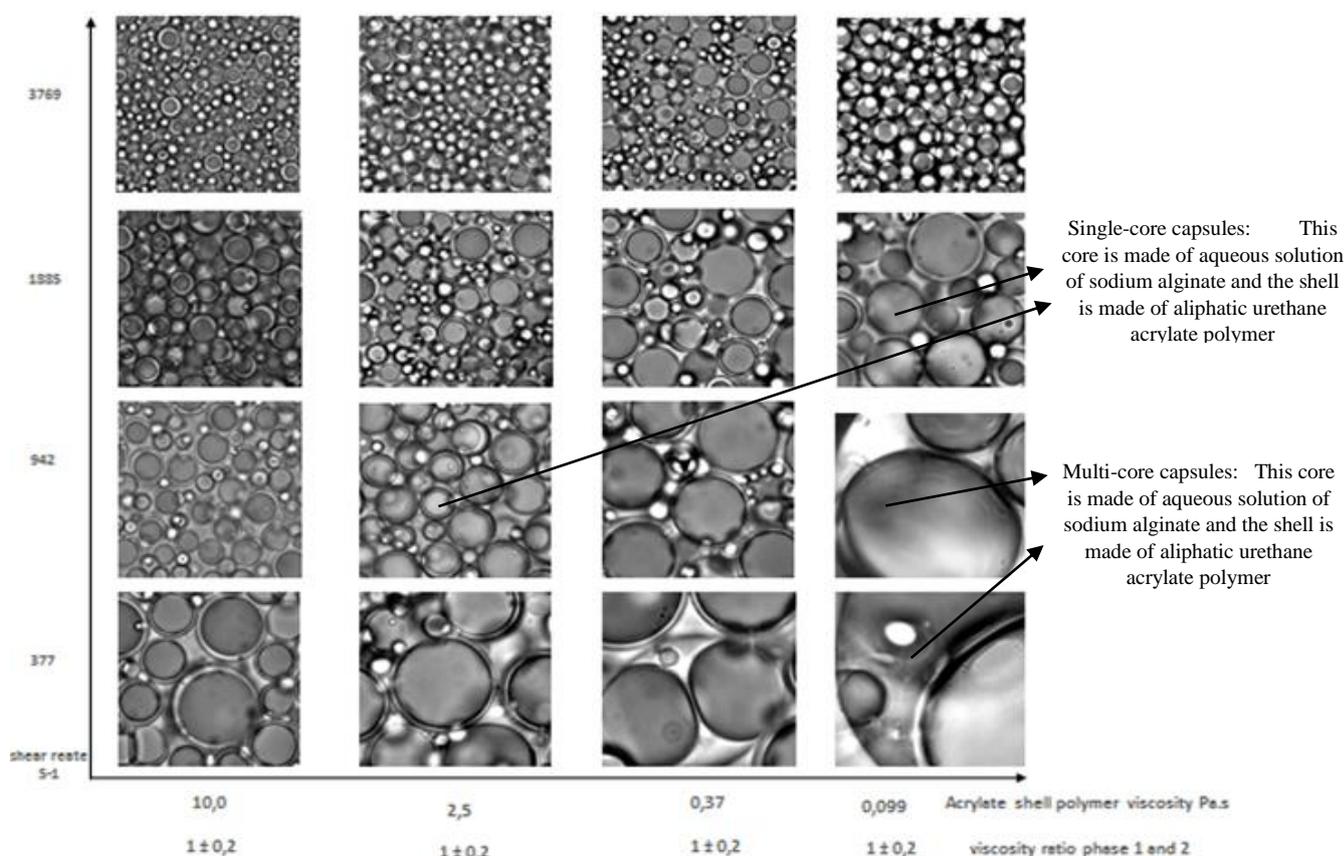


Figure 3-2-D. 26
Double emulsion fragmentation with using viscosity ratio close to 1 at different shear rate

From the results which presented as images were taken by using optical microscopy for the results of the emulsification of double emulsion at using optimum viscosity ratio η_2/η_3 close to 1

We observed good fragmentation of the capsules that made of single homogeneous core-shell structure depending on the shear that we applied so, if we used low viscosity values at low shear rate the fragmentation was not good because it can't fragment the double emulsion and it formed capsules with multi core of alginate solution.

So, we need to used high shear rate it help to fragment the double emulsions and it formed capsules with single core of alginate solution with shell of aliphatic urethane acrylate liquid polymer dispersed in alginate solution has the same viscosity value of the core.

Conclusion:

From the previous results we can conclude that:

- 1- If the viscosity ratio η_2/η_3 is too high = 18.3, the layer of aliphatic urethane acrylate liquid polymer has a higher viscosity value than the external phase of 5% of sodium alginate solution. This causes very poor fragmentation and it leads to poly disperse capsules with heterogeneous multi-cores.
- 2- If the viscosity ratio η_2/η_3 is 1.24 or 1.89, the layer of the aliphatic urethane acrylate liquid polymer has almost the same viscosity value as the external phase of 10% of sodium alginate solution, this causes good fragmentation and it leads to nearly mono disperse capsules with homogeneous single-cores.
- 3- If the viscosity ratio η_2/η_3 is too low = 0.18, the layer of the aliphatic urethane acrylate liquid polymer has lower viscosity value of the external phase of 15% of sodium alginate solution. At low shear rate the first emulsion was not dispersed in the very viscous external phase and it became a solid block cellular material made of droplets of alginate solution in aliphatic urethane polymer. At high shear rate for durations more than 2 minutes almost all the double emulsion capsules were ruptured, they lost their cores, and they became small droplets of aliphatic urethane acrylate polymer without cores.

3-2-D.2 Oil / polymer / Aqueous Phase Double Emulsion System

All the formulations of the double emulsion were made at the optimum viscosity ratio $\eta_1/\eta_2 = 1.08$ which is close to 1. The core of the capsules was made of (Oil PAO40) and the shell was a liquid polymer of epoxy urethane acrylate CN109.

Also, the viscosity ratio η_2/η_3 was constant at the optimum value = 0.93 which is close to 1 and the external phase in this case was aqueous phase of Glycerol.

- Materials and the Equipment:

Poly alpha olefin oil (PAO40), Epoxy urethane acrylate liquid polymer CN109, 1.6 Hexanediol diacrylate

Glycerol, Initiator for UV polymerization (2-hydroxy 2-methylpropiophenone)

Balance, Plastic beaker of 50 ml, 150 ml Glass beaker, Overhead mixer, UV oven, Glass slides and covers slip, Small plastic pipette

Double emulsion preparation

- 1- After the evaluation of the fragmentation of the first emulsion we conclude that the ideal viscosity ratio was= 1.08 which is close to = 1. The core of the capsules was made of (Oil PAO40) and the shell was a liquid polymer of epoxy urethane acrylate CN109.
- 2- In the plastic beaker of 50 ml place 14.5 g of epoxy urethane acrylate liquid polymer with 5.0 g of 1.6 Hexanediol diacrylate and 0.5 g of UV initiator 2-hydroxy 2-methylpropiophenone, mix them well with the overhead mixer at rotational speed 1000 rpm for a duration of 2 minutes.
- 3- Place 4 g of the precedent mixture and added to it 4g of the oil PAO40.
- 4- Mix them at a rotational speed 2000 rpm, for a duration of 2 minutes, using the overhead mixer with 4 blades propeller stirrer. This leads to the first emulsion.
- 5- For the second emulsification, we used the optimum viscosity ratio $\eta_2/\eta_3 = 0.93$.
- 6- Place 20 g of Glycerol in glass beaker of 150 ml and attach it under the overhead mixer. Stir it with the Anchor stirrer at a rotational speed of 200 rpm.
- 7- During the stirring of the first emulsion take 3.0 ml in a syringe and drop it in the Glycerol beaker. Stir at 2000 rpm for 1 minute.
- 8- Pour the emulsion in the Couette cylinder with gap 100 μm , injection speed 3, and control the rotation speed at 100 rpm.
- 9- Pour out the emulsion in a Petri dish to ensure homogeneous polymerisation and place it in the UV oven for 5.0 minutes.
- 10- Take a small droplet from the double emulsion after the polymerization in the small plastic pipette and place it on the glass slide under the cover slip and then observe it on the optical microscope using the objective lens 100X, in order to have images that show the structure of this emulsion.
- 11- Repeat the same experiment at increasing rotational speeds in the Couette instrument to 300 and 600 rpm.

The structures of these formulations observed with the optical microscope using bright field images are showing below:

This double emulsion was prepared with the Couette instrument at a rotational speed 100 rpm

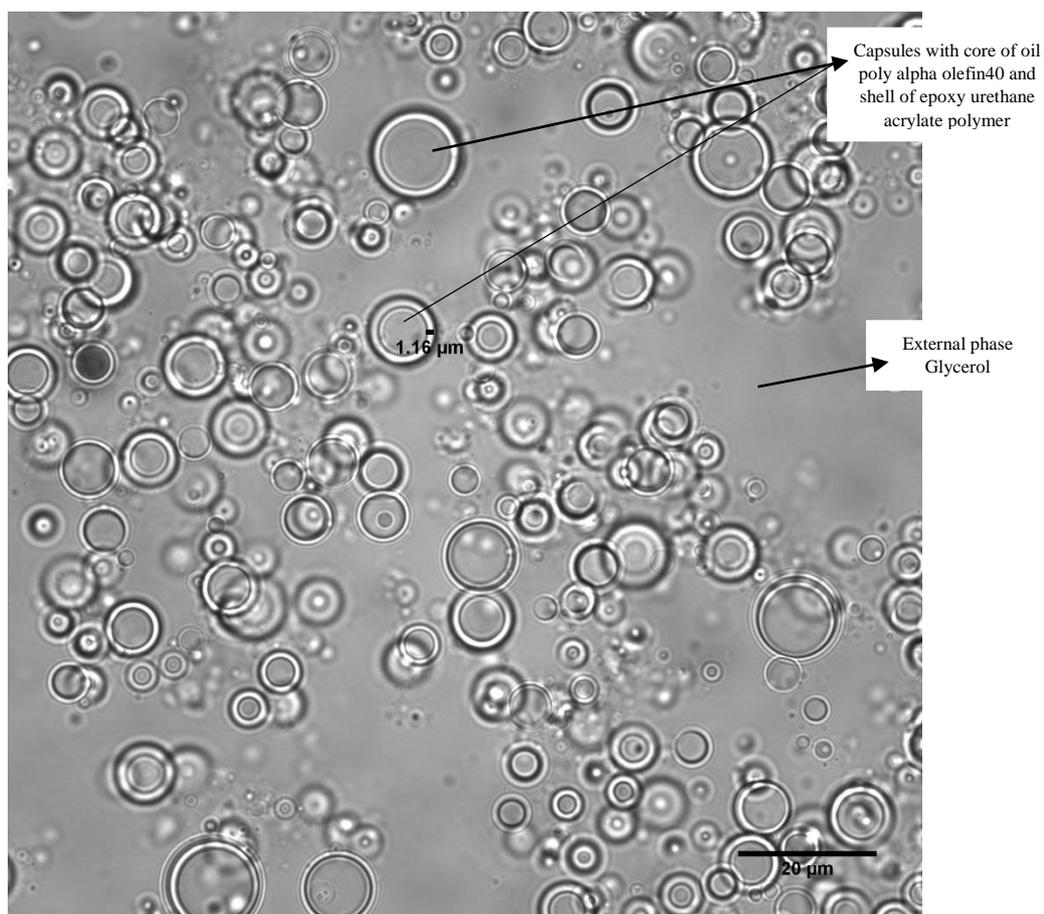


Figure 3-2-D. 27

The double emulsion had polydisperse capsules with cores of poly alpha olefin 40 and shells made of epoxy urethane acrylate polymer. Some of these capsules had sizes larger than 15μm.

The next double emulsion was prepared with the Couette instrument at a rotational speed 300 rpm

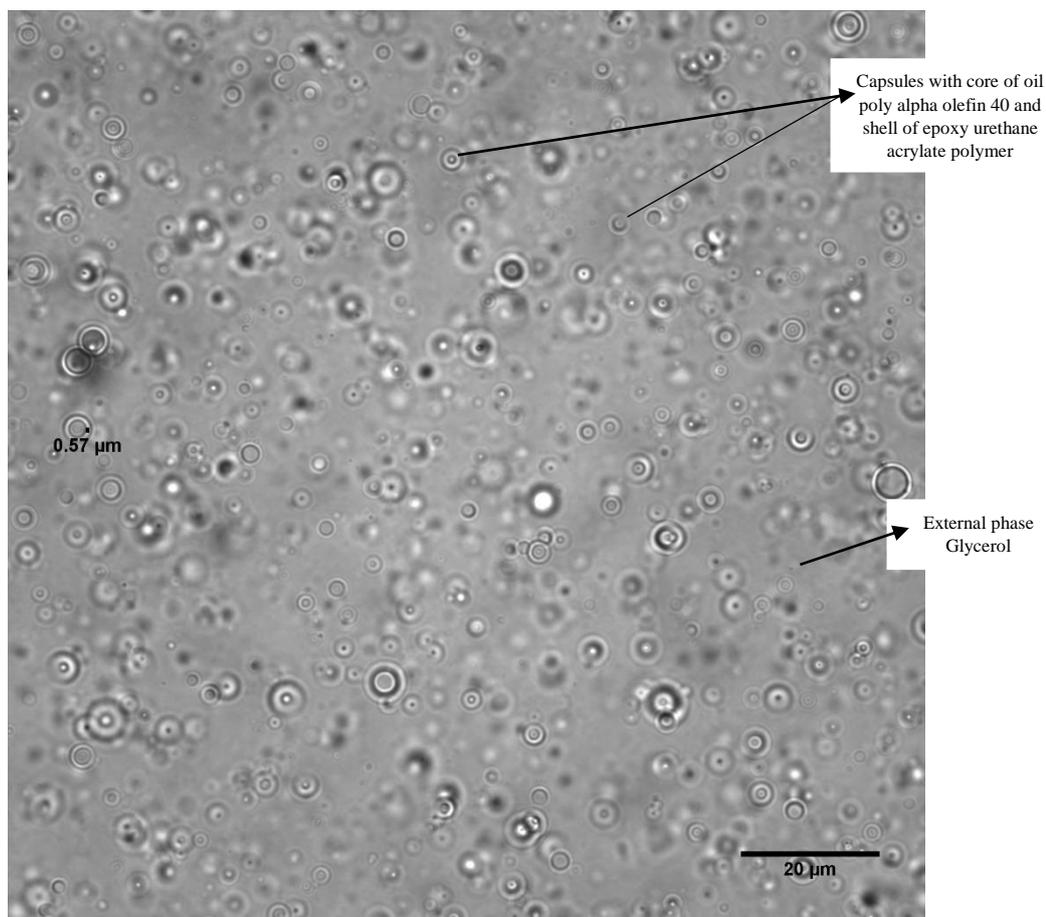


Figure 3-2-D. 28

The double emulsion had monodispersed capsules with cores of poly alpha olefin 40 and shells made of epoxy urethane acrylate polymer. These capsules had sizes of 5μm.

The next double emulsion was prepared with the Couette instrument at a rotational speed 600 rpm

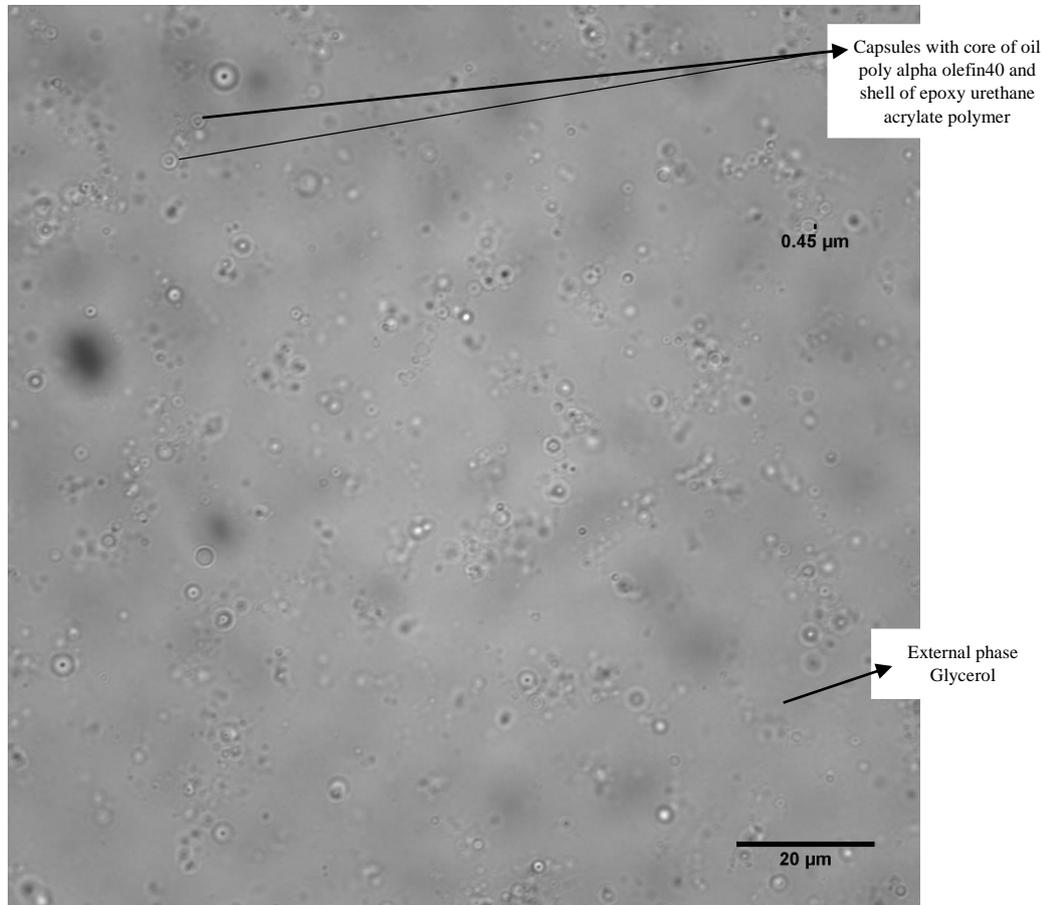


Figure 3-2-D. 29

The next double emulsion had monodispersed capsules with cores of poly alpha olefin 40 and shells made of epoxy urethane acrylate polymer. These capsules had sizes less than 5μm.

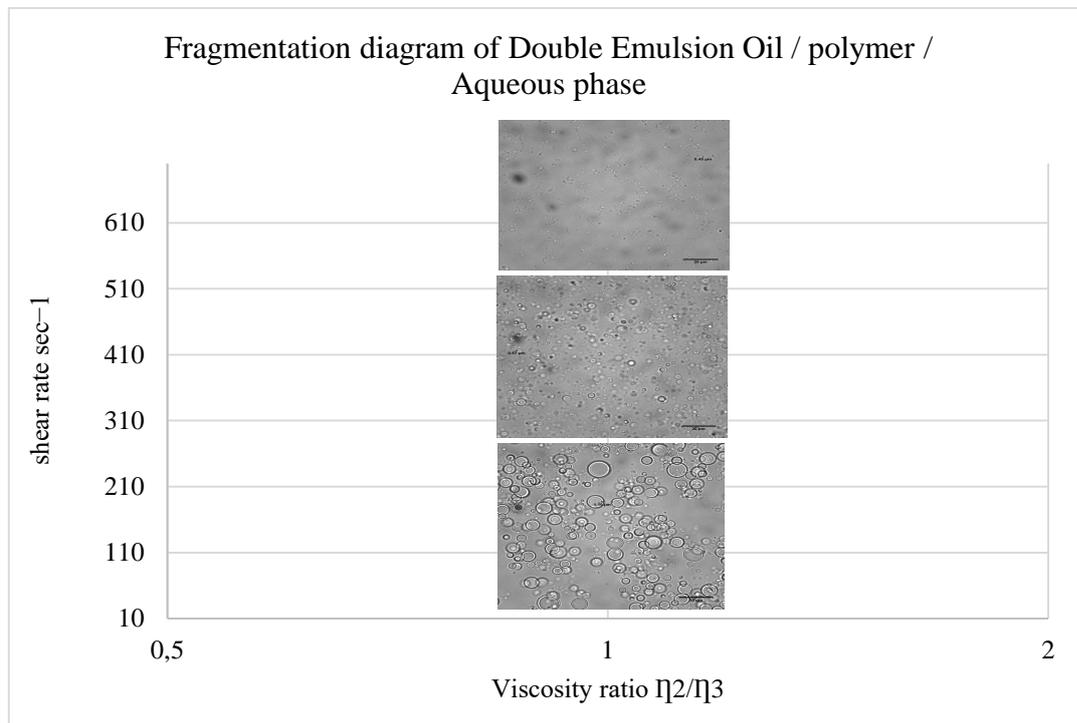


Figure 3-2-D. 30

Fragmentation diagram for double emulsion oil / acrylate shell / aqueous phase

Conclusion:

According to the diagram determined using the optimum viscosity ration $\eta_1/\eta_2 = 1.08$ which is close to 1 and the optimum viscosity $\eta_2/\eta_3 = 0.93$ which is close to 1, there are three different regions at different rotational speeds:

1- Rotational speed 100 rpm

We observed poor fragmentation which yields polydisperse double emulsions with sizes about 15 μm .

2- Rotational speed 300 rpm

We observed very good fragmentation which yields fairly monodisperse double emulsion with sizes about 5 μm .

3- Rotational speed 600 rpm

We observed high fragmentation which yields fairly monodisperse double emulsion with about 3 μm .

Viscosity ratio effect on the stability for the second emulsion oil / acrylate shell / aqueous phase

No:	Description	Phase 2 viscosity pa.s at 10 sec ⁻¹	Phase 3 viscosity pa.s at 10 sec ⁻¹	Viscosity ratio	Evaluation the emulsification
1	CN109 in Glycerol	0.85602	0.918148	0.9357	Very good

Table 3-2-D. 2

Effect of the viscosity ratio on the stability for the second emulsion oil / acrylate shell / aqueous phase

Conclusion:

From the previous results of double emulsion fragmentation, we can conclude that:

If we use the optimum viscosity ratios $\eta_1/\eta_2 = 1.08$ and $\eta_2/\eta_3 = 0.94$, we obtain double emulsions capsules with oil cores and shells made of epoxy urethane acrylate polymer, which are further fragmented homogeneously by the Couette instrument to even smaller capsules. The sizes depend on the rotational speed of the Couette instrument. We are able to obtain microcapsules with sizes below than 3 μ m.

Résumé du troisième chapitre

A- Conclusion de la fragmentation de la première émulsion

A-1- Les résultats de la phase aqueuse émulsifiante de solution aqueuse d'alginate de sodium dans un polymère liquide de l'uréthane acrylate aliphatique dépendent du rapport de viscosité entre les deux phases, comme suit :

1- Faible viscosité entre $\eta_1 / \eta_2 = 0,001$

Nous avons observé une fragmentation médiocre avec un taux de coalescence élevé et une séparation de phase presque complète.

2- Rapport de viscosité optimal $\eta_1 / \eta_2 = 0,8$. Ce qui est proche de 1

Nous avons observé une bonne fragmentation avec des gouttelettes presque monodispersées de solution aqueuse d'alginate de sodium dispersées dans de l'uréthane acrylate aliphatique en tant que phase externe.

3- Rapport de viscosité élevé $\eta_1 / \eta_2 = 5,5$

Nous avons observé une faible fragmentation avec des gouttelettes polydispersées et non sphériques de solution aqueuse d'alginate de sodium dispersées dans un polymère liquide d'uréthane acrylate aliphatique en tant que phase externe.

A-2- Les résultats de la phase huile émulsifiante de silicium dans un polymère liquide époxyuréthane acrylate dépendent du rapport de viscosité entre les deux phases, comme suit :

1- Rapport de faible viscosité $\eta_1 / \eta_2 = 0,02$

La phase interne (huile de silicone 10mpa.s) a une viscosité bien inférieure à celle de la phase polymère liquide époxy acrylate (47mpa.s)

Les résultats ont été médiocres en termes de fragmentation en raison de deux phénomènes : l'écoulement de la pointe qui produit de nombreuses petites gouttelettes et la coalescence des grosses gouttes d'huile. Au cours de l'émulsification, ces phénomènes conduisent à une séparation de phase, même à fort taux de cisaillement. Lorsque nous arrêtons le cisaillement, toutes les grosses gouttelettes d'huile se mélangent et flottent au sommet de la phase polymère liquide époxy acrylate. Les très petites gouttelettes d'huile restent stables pendant une demi-heure, mais finissent par se confondre avec les autres gouttelettes, remontent au sommet sous l'effet de leur densité et enfin, au bout d'un jour, elles forment deux phases.

2- Rapport de viscosité optimal $\eta_1 / \eta_2 = 1$

Nous avons une bonne fragmentation et un bon temps de stabilité pour la première émulsion utilisant une phase d'huile de silicone qui a presque la même viscosité que le polymère liquide époxyuréthane acrylate, de sorte que le rapport de viscosité $\eta_1 / \eta_2 = 1,08$. Nous nous disputons :

1- La stabilité de l'émulsion ne découle pas des valeurs de masse volumique, car l'huile de silicium (10 MPa.s) a une masse volumique = 0,93 g / cm³ et l'huile de silicium haute viscosité (PDMS) a presque la même densité = 0,97 g / cm³. Pourtant, ils se comportent très différemment.

2- La stabilité de l'émulsion ne résulte pas des tensions interfaciales car l'huile de silicium (10mpa.s) a une tension d'interface = 4,13 mN / m avec un polymère liquide époxy-uréthane, et l'huile de silicium à haute viscosité (PDMS) a presque même tension interfaciale avec un polymère liquide époxy-uréthane = 3,83 mN / m, et pourtant leur comportement est très différent.

Dans le cas d'un rapport de viscosité optimal, les gouttelettes d'huile de silicium de viscosité moyenne restent stables jusqu'à deux semaines sans séparation de phase.

3- Rapport de viscosité élevé $\eta_1 / \eta_2 = 8,6$

Le résultat d'une huile dispersante ayant une valeur de viscosité supérieure à celle du polymère liquide epoxy-uréthane acrylate est également une bonne émulsification, même si le rapport de viscosité est élevé. Ce comportement est totalement différent de celui observé par Grace, qui présentait un échec de l'émulsification à des valeurs élevées du rapport de viscosité. La bonne fragmentation peut être due aux caractéristiques suivantes (pas exclusivement) :

Les deux fluides sont newtoniens et ils ont une faible tension interfaciale, ce qui facilite la production de petites gouttelettes qui restent stables même après deux mois sans séparation de phase.

B- Conclusion de la fraction de masse maximale pour la première émulsion

B-1- Fraction massique maximale pour la première émulsion de phase aqueuse dans un polymère liquide d'acrylate d'uréthane aliphatique

La fraction massique maximale que nous pouvons utiliser pour préparer la première émulsion de solution aqueuse à 10% d'alginate de sodium, telle que la phase interne, ne dépasse pas 70% dans le polymère liquide uréthane acrylate aliphatique. Avec un rapport de phase interne plus élevé, on obtient une émulsion inverse qui a la solution aqueuse d'alginate de sodium comme phase externe et le polymère liquide uréthane acrylate aliphatique comme phase interne, avec un certain nombre de capsules co-existantes.

Afin de rester du côté sûr pour préparer la double émulsion, nous préférons commencer par une première émulsion contenant 50% de la solution aqueuse d'alginate de sodium à 10% dans un polymère liquide d'uréthane acrylate aliphatique.

Nous remarquons également que l'inversion de l'émulsion a lieu à une fraction massique de la phase interne nettement supérieure à 50% : 50%, alors que le rapport de viscosité est proche de 1.

B-2- Fraction massique maximale pour la première émulsion de phase huile / polymère époxy acrylique polymère.

En pratique, nous concluons que la fraction massique maximale que nous pouvons utiliser dans la première émulsion d'huile de polyalphaoléfine 40 dans un polymère liquide époxyuréthane acrylate ne représente pas plus de 50% de l'émulsion totale.

Il est tout à fait remarquable qu'avec une fraction massique de phase interne égale à 50%, on obtienne une émulsion composée exclusivement de gouttelettes d'huile de polyalphaoléfine 40 dans le polymère liquide époxyuréthane acrylate.

On n'observe cette belle asymétrie qu'avec 50% d'huile dans un polymère époxyuréthane acrylate

Si nous augmentons la fraction massique de la phase interne à 60%, nous obtenons une émulsion inversée de gouttelettes de polymère liquide d'époxy uréthane acrylate dans l'huile de polyalphaoléfine 40.

C- Schéma de fragmentation en double émulsion

C-1- Diagramme de fragmentation de l'émulsion double : Phase aqueuse / polymère acrylate d'uréthane aliphatique / phase aqueuse

Tout en maintenant le rapport de viscosité $\eta_1 / \eta_2 = 0,8$ et nous avons changé le rapport de viscosité entre les phases η_2 / η_3 en modifiant chaque fois la viscosité de la phase 3 de la phase externe.

D'après les résultats précédents, nous pouvons conclure que :

1- Si le rapport de viscosité η_2 / η_3 est trop élevé = 18,3, la couche de polymère liquide uréthane acrylate aliphatique a une valeur de viscosité supérieure à celle de la phase externe de 5% de solution d'alginate de sodium. Cela provoque une très faible fragmentation et conduit à des capsules poly dispersées à cœurs multiples hétérogènes.

2- Si le rapport de viscosité η_2 / η_3 est de 1,24 ou 1,89, la couche du polymère liquide uréthane acrylate aliphatique a presque la même valeur de viscosité que la phase externe de 10% de solution d'alginate de sodium, ceci entraîne une bonne fragmentation et conduit à capsules mono-dispersées à cœur unique homogène.

3- Si le rapport de viscosité η_2 / η_3 est trop bas = 0,18, la couche de polymère liquide uréthane acrylate aliphatique a une valeur de viscosité inférieure de la phase externe de 15% de solution d'alginate de sodium. À faible vitesse de cisaillement, la première émulsion n'était pas dispersée dans la phase externe très visqueuse et devenait un matériau cellulaire solide à blocs constitué de gouttelettes de solution d'alginate dans un polymère d'uréthane aliphatique. À fort taux de cisaillement pendant plus de 2 minutes, presque toutes les capsules à émulsion double ont été enlevées, elles ont perdu leur cœur et sont devenues de petites gouttelettes de polymère uréthane acrylate aliphatique sans cœur.

C-2- Diagramme de fragmentation de l'émulsion double : huile / polymère / phase aqueuse

Selon le diagramme déterminé en utilisant le rapport de viscosité optimal $\eta_1 / \eta_2 = 1,08$ qui est proche de 1 et la viscosité optimale $\eta_2 / \eta_3 = 0,93$ qui est proche de 1, il existe trois régions différentes à des taux de cisaillement différents avec l'instrument Couette à des différentes vitesses de rotation :

1- Vitesses de rotation 100 rpm

Nous avons observé une faible fragmentation qui donne des émulsions doubles polydisperses d'une taille d'environ 15 μm .

2- Vitesses de rotation 300 rpm

Nous avons observé une très bonne fragmentation qui donne une émulsion double relativement monodispersée avec des tailles d'environ 5 μm .

3- Vitesses de rotation 600 rpm

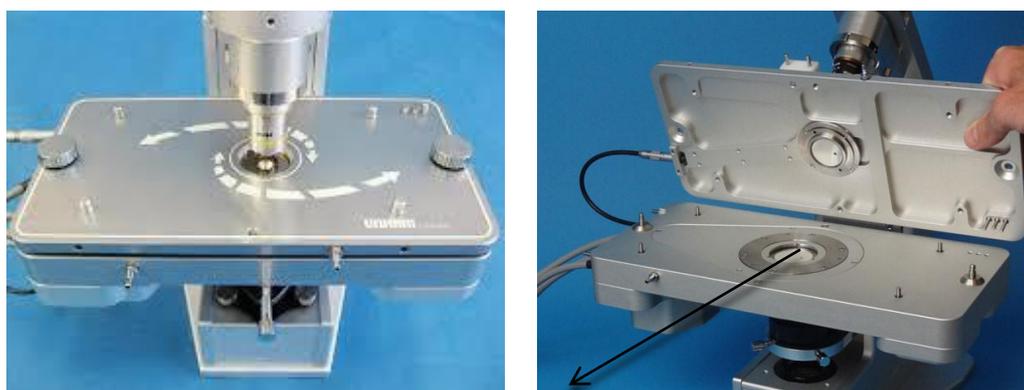
Nous avons observé une fragmentation élevée qui donne une émulsion double relativement monodispersée d'environ 3 μm .

Chapter 4

Visualization of Double Emulsion Fragmentation

4-1 Visualization of Double Emulsion Fragmentation

In this part we present four movies which show the mechanism of the fragmentation which produces double emulsions that have an aqueous core phase or oil core phase acrylate polymer dispersed in aqueous solution of sodium alginate or in Glycerol. We will show the effect of the viscosity ratio between phase1 and phase 2. For this visualisation we used a CSS450 Optical Rheology System.



Rotational shear chamber for emulsion fragmentations

Figure 4-1. 1

CSS450 Optical Rheology System

4-1- Aqueous Phase / Polymer Shell / Aqueous phase Capsules

In this section we present microscope images of double emulsions single capsules that are fragmented the shear

In order to improve the contrast of the capsules, we used Rhodamine 6 G to label the polymer shell of aliphatic urethane acrylate. Indeed, it has a much higher solubility in the aliphatic urethane acrylate than in the sodium alginate solution. In this way we display the localization of the acrylate polymer shell, while the aqueous phase containing alginate was almost non fluorescent.

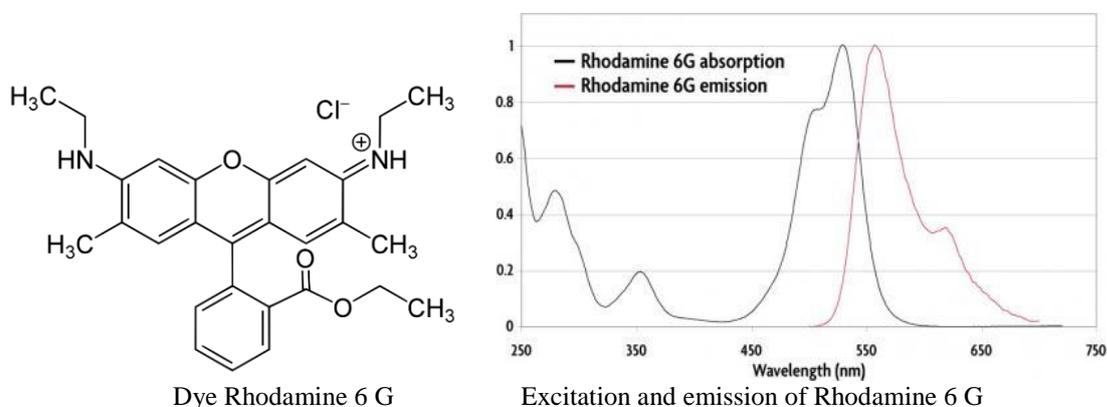


Figure 4-1. 2

Chemical structure of Rhodamine 6G and the excitation and emission spectra

Procedure:

Prepare the acrylate shell with the fluorescent dye

- Place 10g of aliphatic urethane acrylate polymer CN991 in a 50 ml beaker and add to it 0.001g of Rhodamine 6G. Mix them for 2 minutes at 2000 rpm with overhead mixer.
- Used the centrifuge at 6000 rpm to sediment the non-soluble Rhodamine 6G.
- Prepare the sodium alginate solutions:
- 7% of sodium alginate in water

Place 1.75 g of sodium alginate in a 50 ml plastic beaker and add to it 23.25 g of deionized water. Mix them with the overhead mixer for 5 minutes at 1000 rpm, transfer the resulting solution to a small bottle and let it rest for one day.

- 10% of sodium alginate in water

Place 2.5 g of sodium alginate in a 50 ml plastic beaker and add to it 22.5 g of deionized water. Mix them with the overhead mixer for 5 minutes at 1000 rpm, transfer the resulting solution to a small bottle and let it rest for one day.

- 15% of sodium alginate in water

Place 3.75 g of sodium alginate in a 50 ml plastic beaker and add to it 21.25 g of deionized water. Mix them with the overhead mixer for 5 minutes at 1000 rpm, transfer the resulting solution to a small bottle and let it rest for one day.

Preparing the setup

- Place 2 ml of 10% sodium alginate solution (external phase) in the glass rotation chamber of the CSS450 Optical Rheology System. Also spread a small layer of 10% sodium alginate solution on the cover to prevent the acrylate polymer from sticking to the glass surface.
- Place 2g of liquid acrylate polymer which was labeled with Rhodamine 6G in a small beaker of volume 10 ml, add to it 2g of aqueous solution of sodium alginate 7% and mix them gently with a small metallic spatula. This produces the first emulsion.
- Use a plastic cone (Clip Tip of micropipette) to take a small droplet of this first emulsion, place it on the aqueous phase which is in the glass rotation chamber and try to disperse the droplets gently with the Clip Tip. This produces the double emulsion.
- Put the cover back in place.
- Try to bring one droplet of double emulsion in the observation area by making manual rotations at low shear rate (vel 0.1 rad/s) in the Rotary mode.

Set up the instrument for controlled displacements (step shear).

For the shear experiment we used the following parameters as a Shear motor profile

Row	Mode	Gap	strain	Rate	Frequency	Dim	Time
1	step	200	3000.0	500.0	n/a	CW	n/a

Table 4-1. 1

- Switch on the fluorescence light and enter the parameters of the camera as follows:
Hc Image Live – profile/ Image Display

Histogram	Gain	Exposure time	Present size	Frame count	Best time
10 Bists	255	35.0 ms	1344×256	100	3.5057 sec

Table 4-1. 2

- Click the button stop live, click it once again to start recording, and at the same time click on the shear step button.
- Used ImageJ to create movies from the stored images.

4-1-A Low viscosity ratio between phase 1 and phase 2

In this experiment the values of the viscosity ratio are:

Viscosity ratio between phase 1 and 2 = $\eta_1/\eta_2 = 0.28$

Viscosity ratio between phase 2 and 3 = $\eta_2/\eta_3 = 1.25$



Figure 4-1-A 1
Fragmentation of double emulsion with low viscosity ratio $\eta_1/\eta_2 = 0.28$

What we learn from this experiment with low viscosity ratio $\eta_1/\eta_2 = 0.28$: A double emulsion droplet (capsule) with multi-cores was broken by the shear to small beads of aliphatic urethane acrylate polymer with multi-cores of 7% sodium alginate solution.

4-1-A.2 Optimum viscosity ratio between phase 1 and phase 2

In this experiment the values of the viscosity ratio are:

Viscosity ratio between phase 1 and 2 = $\eta_1/\eta_2 = 0.8$

Viscosity ratio between phase 2 and 3 = $\eta_2/\eta_3 = 1.25$

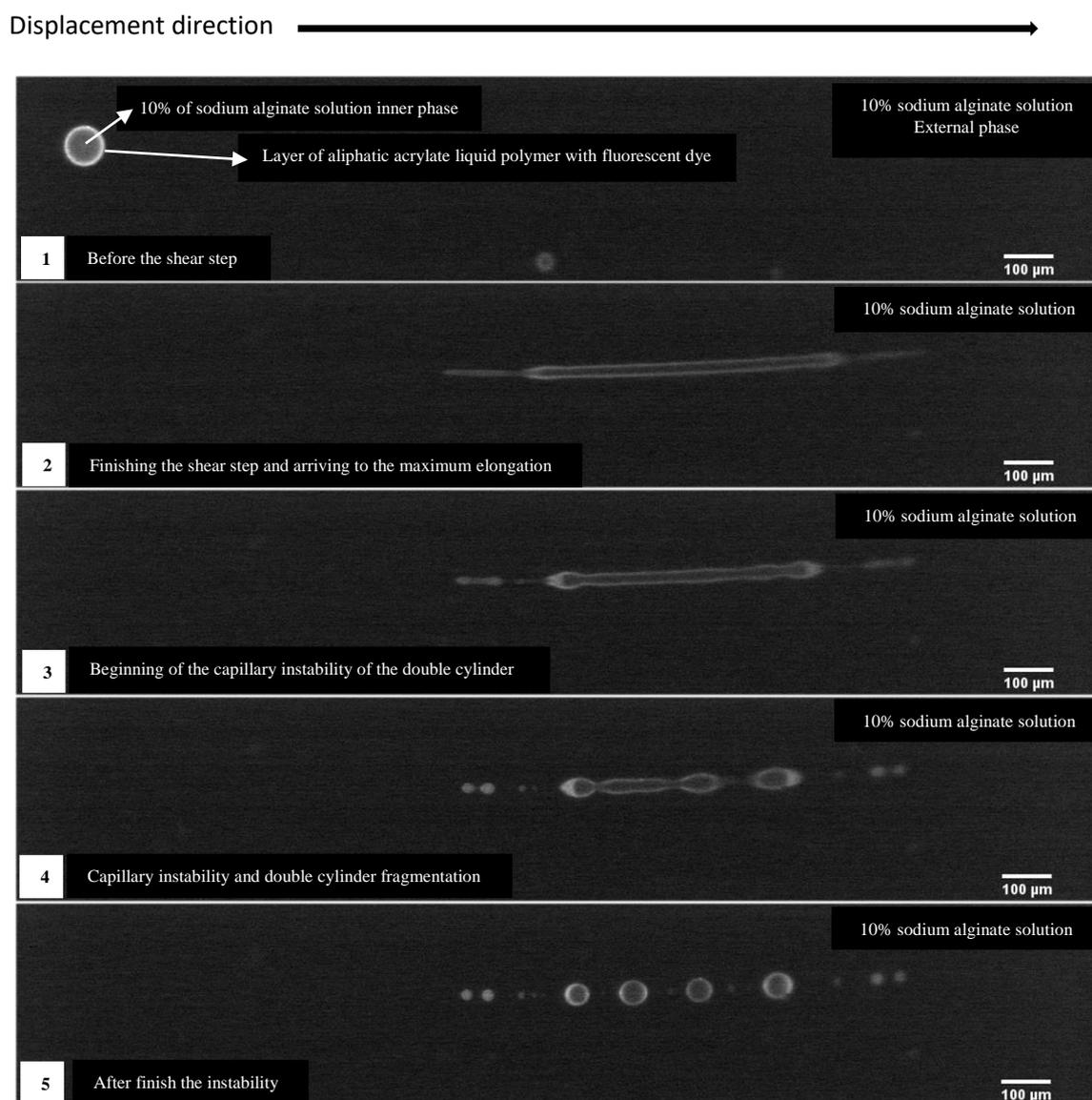


Figure 4-1-A 2
Fragmentation of double emulsion with viscosity ratio $\eta_1/\eta_2 = 0.80$

What we learn from this experiment with optimum viscosity ratio $\eta_1/\eta_2 = 0.8$ close to 1: A double emulsion droplet (capsule) with single-core was stretched by the shear and the capillary instability broke it into small capsules. We can see both the core and the shell being fragmented together. In addition, there are a few beads of aliphatic urethane acrylate polymer without core that originate from accumulation of shell polymer at both ends of the stretched capsule.

4-1-A.3 High Viscosity Ratio between Phase 1 and Phase 2

In this experiment the value of the viscosity ratio between the fluids are:

Viscosity ratio between phase 1 and 2 = $\eta_1/\eta_2 = 8.07$

Viscosity ratio between phase 2 and 3 = $\eta_2/\eta_3 = 1.25$

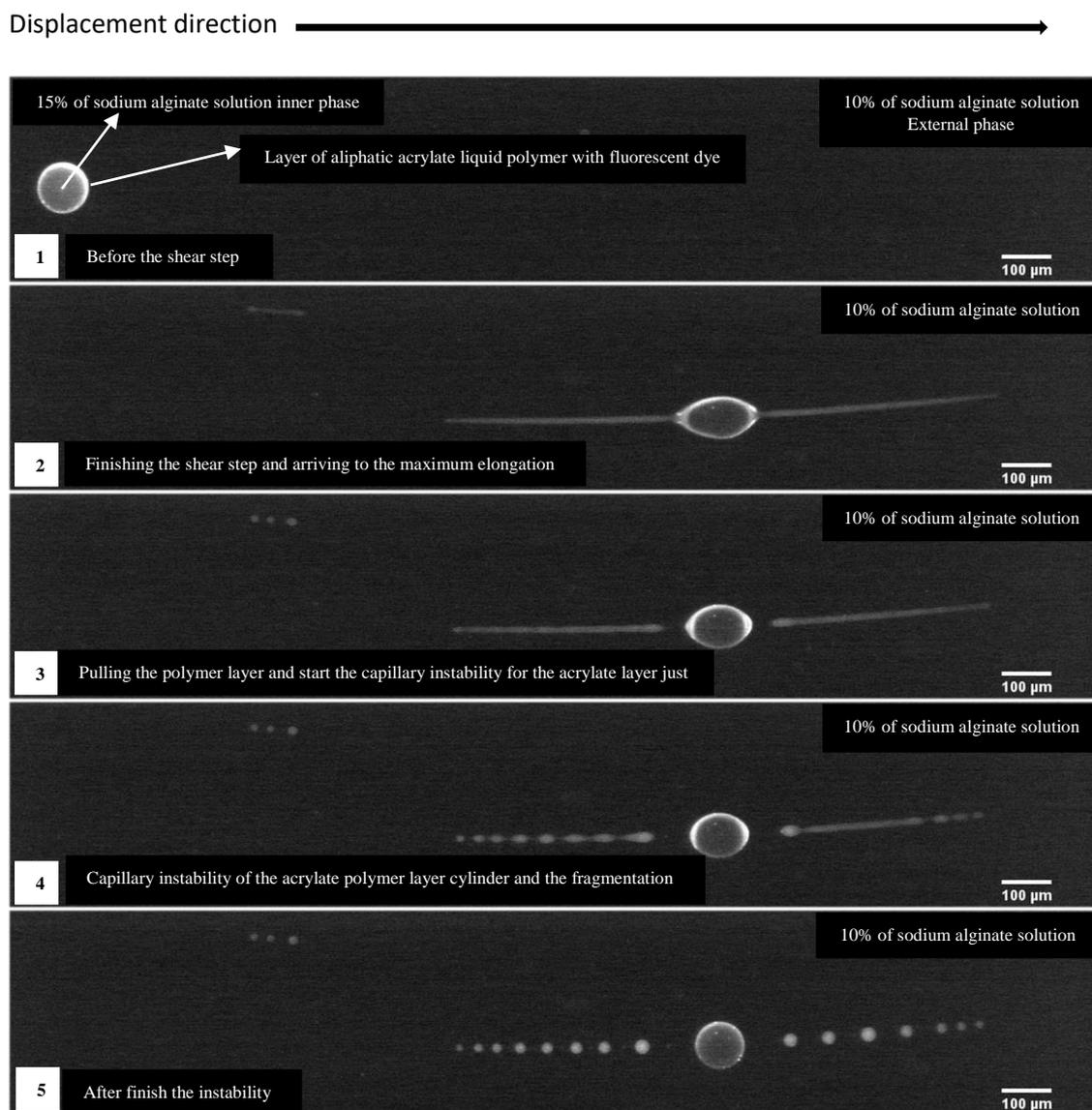


Figure 4-1-A 3
Fragmentation of double emulsion with viscosity ratio $\eta_1/\eta_2 = 8.07$

What we learn from this experiment with optimum viscosity ratio $\eta_1/\eta_2 = 8.07$, which is too high: A double emulsion droplet (capsule) with single-core was not fragmented because the core was too viscous. The shell was pulled to both ends of the capsule where it accumulated in the shape of two very thin cylinders. These cylinders subsequently detached from the capsule and fragmented. In the end it gives a few beads of aliphatic urethane acrylate polymer without core that originate from accumulation of shell polymer at both ends of the stretched capsule.

Conclusion:

From these movies of double emulsion fragmentations, we conclude:

- 1- Starting with first emulsion has low viscosity ratio $\eta_1/\eta_2 = 0.28$
We obtain double emulsions containing multi-cores capsules. This is not the single-core shell structure that we are trying to produce.
- 2- Using the optimum viscosity ratio for the first emulsion $\eta_1/\eta_2 = 0.8$ which is close to 1, we have an ideal fragmentation of the core and shell together which makes it possible to produce double emulsion with a core-shell structure.
- 3- Using a too high viscosity ratio for the first emulsion $\eta_1/\eta_2 = 8$
The core has a much higher viscosity than the shell polymer. Consequently, the core withstands the shear, it is not fragmented. Some of the acrylate urethane polymer shell is pulled away from the capsule and fragmented.

4-1-B Oil / Epoxy Urethane Acrylate Polymer shell / Aqueous Phase Capsules

In this experiment, the value of the viscosity ratio η_1/η_2 and η_2/η_3 was chosen to be close to 1

4-1-B.1 Optimum viscosity ratio

In this experiment the value of the viscosity ratio between the fluids are:

Viscosity ratio between phase 1 and 2 = $\eta_1/\eta_2 = 1.08$

Viscosity ratio between phase 2 and 3 = $\eta_2/\eta_3 = 0.93$

Procedure:

Prepare the acrylate shell with the fluorescent dye

- Place 10g of Epoxy urethane acrylate liquid polymer CN109 in a 50 ml beaker, add to it 0.001g of Nile red and mix them with the overhead mixer for 2 minutes at 2000rpm.
- Used the centrifuge to sediment the non-soluble Nile Red

Preparing the setup

- Place 2 ml of Glycerol (external phase) in the glass rotation chamber of the CSS450 Optical Rheology System. Also spread a small layer of Glycerol on the cover to prevent the epoxy acrylate polymer from sticking to the glass surface.
- Place 2g of liquid epoxy urethane acrylate polymer which was labeled with Nile red in a small beaker of volume 10 ml, add to it 2g of poly alpha olefin (PAO40 oil) and mix them gently with a small metallic spatula. This produces the first emulsion.
- Use a plastic cone (Clip Tip of micropipette) to take a small droplet of this first emulsion, place it on the aqueous phase which is in the glass rotation chamber and try to disperse the droplets gently with the Clip Tip. This produces the double emulsion.
- Put the cover back in place.
- Try to bring one droplet of double emulsion in the observation area by making manual rotations at low shear rate (vel 0.1 rad/s) in the Rotary mode.

Set up the instrument for controlled displacements (step shear).

Shear motor profile

Row	Mode	Gap	strain	Rate	Frequency	Dim	Time
1	step	100	3500.0	500.0	n/a	CW	n/a

Table 4-1-B. 1

- Turn on the light of the fluorescence and put the parameter of the camera in this option as flowing:

Hc Image Live – profile/ Image Display

Histogram	Gain	Exposure time	Present size	Frame count	Best time
10 Bists	255	35.0 ms	1344×256	100	3.5057 sec

Table 4-1-B. 2

- Click the button stop live and click it once again to start recording and in the same time click on shear step button
- Used ImageJ to change the images to movies
- In this experiment the value of the viscosity ratio between the fluids are:
 - Viscosity ratio between phase 1 and 2 = $\eta_1/\eta_2 = 1.08$
 - Viscosity ratio between phase 2 and 3 = $\eta_2/\eta_3 = 0.93$

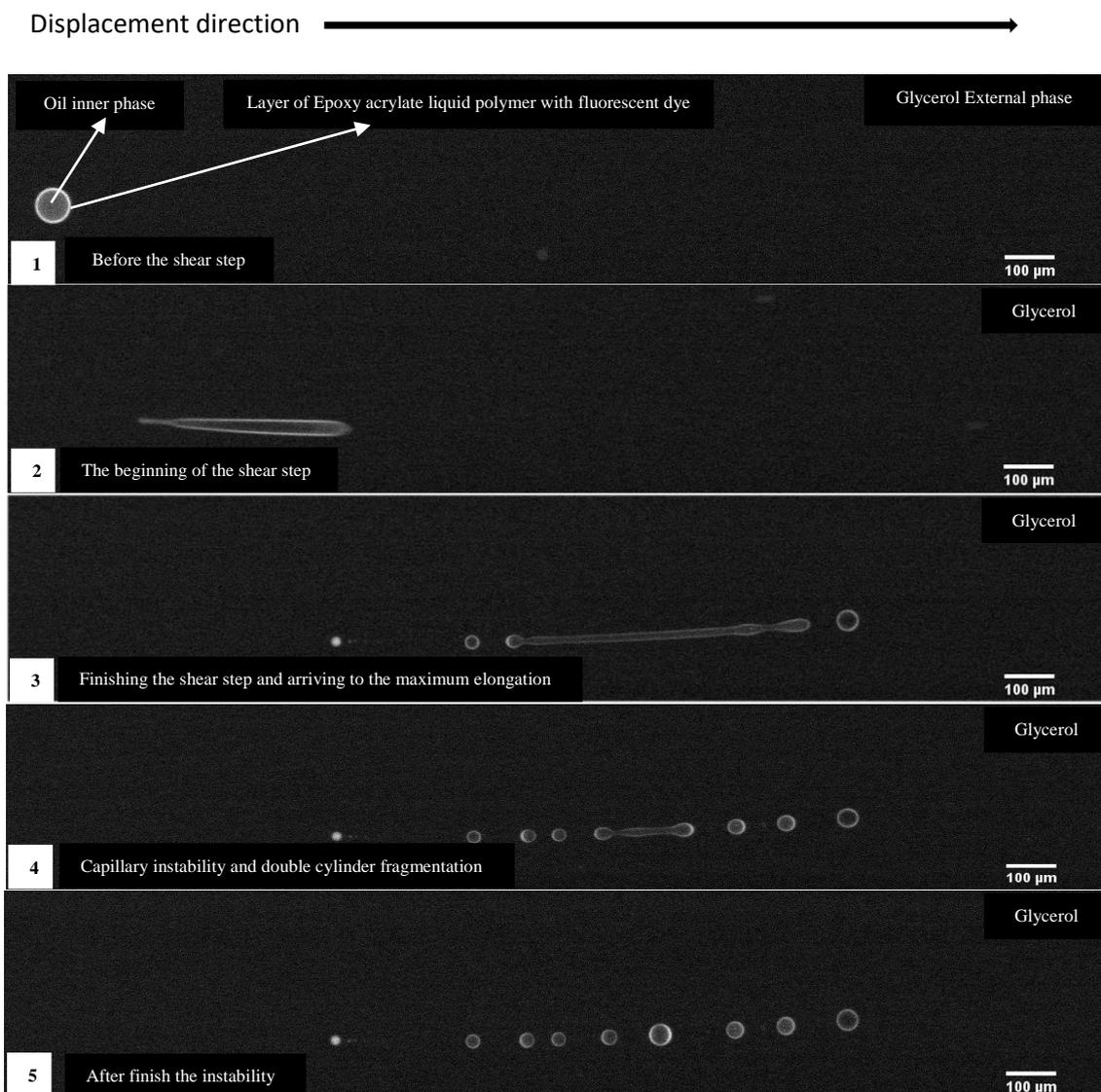


Figure 4-1-B. 1
Elongation fragmentation of double emulsion Oil acrylate membrane and Glycerol

What we learn from this experiment with optimum viscosity ratio $\eta_1/\eta_2 = 1.08$ and $\eta_2/\eta_3 = 0.93$ which is close to 1: A double emulsion droplet (capsule) with single-core was stretched by the shear and the capillary instability broke it into small capsules. We can see both the core and the shell being

fragmented together. In addition, there is one beads of epoxy urethane acrylate polymer without core that originated from accumulation of shell polymer at one end of the stretched capsule.

Conclusion:

From the movie of the fragmentation of double emulsions with oil cores, we conclude:

Using optimum viscosity ratio of first emulsion = 1.08, which is close to 1 we obtain ideal fragmentation of the oil core and shell together. It produces a double emulsion with smaller capsules that retain the core-shell structure.

Résumé du quatrième chapitre

Visualisation de la fragmentation en double émulsion

Pour cette visualisation, nous avons utilisé un système de rhéologie optique CSS450. Dans cette partie, nous présentons quatre films qui montrent le mécanisme de la fragmentation qui produit des émulsions doubles se compose d'un cœur aqueux ou huileux couvert par un polymère d'acrylate qui est dispersé dans une phase aqueuse laquelle solution aqueuse d'alginate de sodium ou dans du glycérol. Nous avons montré l'effet du rapport de viscosité entre phase1(cœur) et phase 2 (acrylate coque).

Conclusion de la fragmentation des émulsions doubles avec cœur aqueuse d'alginate de sodium :

De ces films de fragmentation des émulsions doubles avec des cœurs aqueux, nous concluons :

1- Le premier émulsion a un faible rapport de viscosité $\eta_1 / \eta_2 = 0,28$ et le rapport de viscosité $\eta_2 / \eta_3 = 1.25$ qui aussi proche de 1.

Nous obtenons des émulsions doubles contenant des capsules multi-cœurs. Ce n'est pas la structure de cœur -coquille unique que nous essayons de produire.

2- En utilisant le rapport de viscosité optimal pour la première émulsion $\eta_1 / \eta_2 = 0,8$ qui est proche de 1 et le rapport de viscosité $\eta_2 / \eta_3 = 1.25$ qui aussi proche de 1, nous avons une fragmentation idéale du cœur et de la coque qui permet de produire une émulsion double avec une structure cœur - coquille.

3- Utiliser un rapport de viscosité trop élevé pour la première émulsion $\eta_1 / \eta_2 = 8$ et le rapport de viscosité $\eta_2 / \eta_3 = 1.25$ qui proche de 1

Le cœur a une viscosité beaucoup plus élevée que le polymère coque. Par conséquent, le cœur résiste au cisaillement, il n'est pas fragmenté. Une partie de la coque en polymère acrylate-uréthane est retirée de la capsule et fragmentée.

Conclusion de la fragmentation des émulsions doubles avec cœur d'huile :

Du film de la fragmentation des émulsions doubles avec des cœur d'huile, nous concluons :

En utilisant le rapport de viscosité optimal de la première émulsion $\eta_1 / \eta_2 = 1,08$, ce qui est proche de 1 et le rapport de viscosité $\eta_2 / \eta_3 = 0,93$ qui aussi proche de 1, nous obtenons une fragmentation idéale du cœur d'huile et de la coque. Il produit une double émulsion avec des capsules plus petites qui conservent la structure cœur -coquille.

Chapter 5

Shell Polymerisation and Capsules Characterization

5-1 Polymerisation of Acrylate Shell

5-1-A Effects of Initiator Concentration and UV Exposure Duration

We observed the osmotic swelling of capsules filled with 10% NaCl and 10% of sodium alginate in pure water, and the rupture of the capsules at large swelling. From these observations we calculate the size and volume of the capsules and the initial osmotic pressure. We used these informations to study the acrylate shell polymerization and how it depended on the UV exposure time and on the initiator concentration.

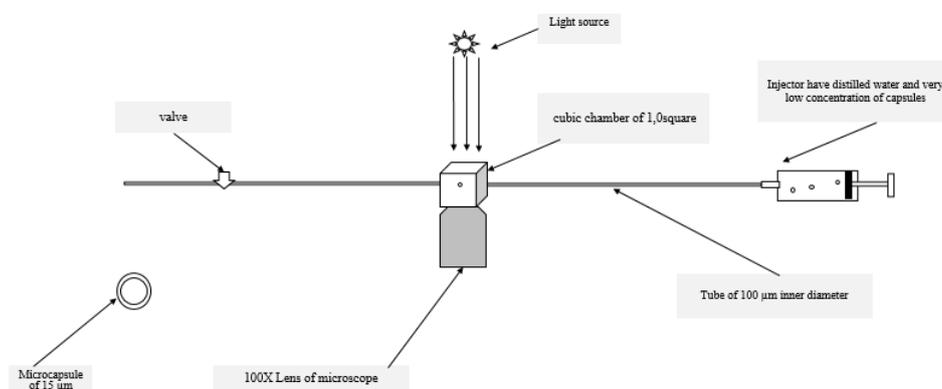


Figure 5-1. 1
Observation system that made by cubic chamber of 100 µm

Material and the Equipment

Sodium alginate, polymer aliphatic urethane acrylate CN991, Initiator 2 hydroxyl-2 methyl propiophenone, Sodium chloride, Plastic beaker 250 ml, Petri dish, Spatula, Beaker of 100 ml and 250 ml, UV oven, 2 over Head mixer, Balance with 0.001g accuracy, Microscopy with 100 x lines, Setup observation fixed on the microscope.

The procedure

Preparation of solutions

- 1- Prepare phase 2 (shell polymer). Place 10 g of polymer CN991 without Initiator in a plastic beaker of volume 100 ml.
- 2- Prepare phase 3 (external phase). Place 10g of Sodium Alginate with 90 g of deionized water in a plastic beaker of volume 250 ml and disperse it completely using the overhead mixer for 30 minutes at a rotational speed of 2000 rpm

- 3- Prepare phase 1 (Internal phase). Place 10 g of Sodium chloride with 83 g of deionized water in a plastic beaker of volume 250 ml, mix with the overhead mixer for 10 minutes, add 7 g of Sodium alginate and disperse it completely using the overhead mixer for 30 minutes at a rotational speed of 2000 rpm.

Emulsions preparation

First emulsion

- 1- Place 5g of polymer CN991 without initiator in a plastic beaker of volume 100 ml with 5g of sodium alginate solution 7%.
- 2- Mix them using overhead mixer with a rotational speed of 2000 rpm for 1 minute.

Double emulsion

- 1- Place 20 g of sodium alginate solution 10% in plastic beaker and attach it under the overhead mixer.
- 2- During the rotation of the first emulsion take 3.0 ml from it by using a syringe, drop it in the beaker of the alginate 10% and stir the mixture at a rotational speed of 500 rpm for 20 second.

Polymerisation step :

- 1- Drop a small quantity of the double emulsion into a Petri dish to make a small layer of double emulsion in order to have homogeneous polymerisation in the UV oven with different times of UV treatment 30 sec, 1.0 minutes, 3.0 minutes and 1.0 hour.

Washing and extraction of capsules

- 1- Place 2 g from the double emulsion in a Centrifuge tube and fill it with deionized water to 45g.
- 2- Shake it by hand for 20 second and then place it in the centrifuge with parameters: time 2 minutes, speed 2000 rpm and acceleration 2700 g.
- 3- Pour the solution in to the sink and fill the centrifuge tube with deionized water to 45g.
- 4- Redisperse the capsules into the water by shaking.

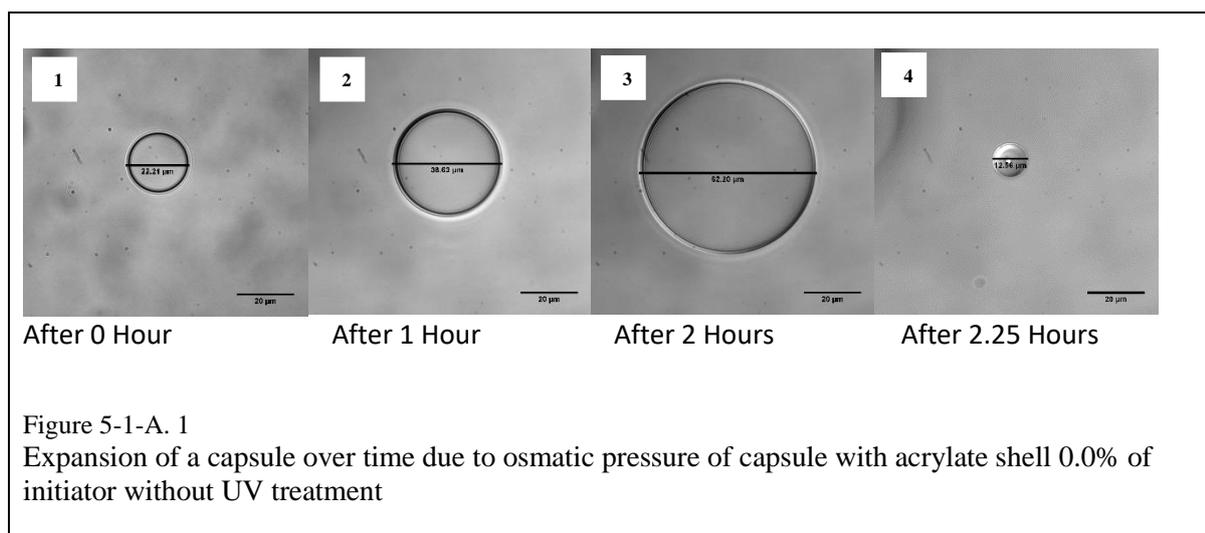
Capsules size observation

- 1- The observation setup is shown in Figure 5-1.1. It made of a cubic cell glued by UV glue to a glass slide. Two Teflon tube are connected to opposite sides of the cell, one of them is connected to a syringe and the other has a valve through which the assembly can be opened or closed.
- 2- The cell is placed on inverted microscope using the 100 x lens with index matching oil between the 100 x lens and cell.
- 3- Place the setup on the microscope using adhesive tape.

- 4- Place deionized water in the syringe, make sure that the valve is open, then fill the tubes and the cell with water to remove all air babbles.
- 5- Place one droplet of the redisperse capsules in the syringe to obtain a very diluted dispersion of capsules. Injection this dispersion through the syringe. The dilution must be such that there is only one capsule inside the cell.
- 6- Close the valve to maintain the capsule in the same position above the lens, and start the camera to acquire one image every 5 minutes.

Repeat this experiment with a fresh sample that has been prepared with a different set of polymerisation parameters for example keep a constant initiator concentration and change the UV exposure time to 30 sec, 3 minutes and 1 hour. Then increase the initiator concentration to 0.1%, 1% and 10% for each UV exposure time.

5-1-A.1 Initiator concentration 0.0%



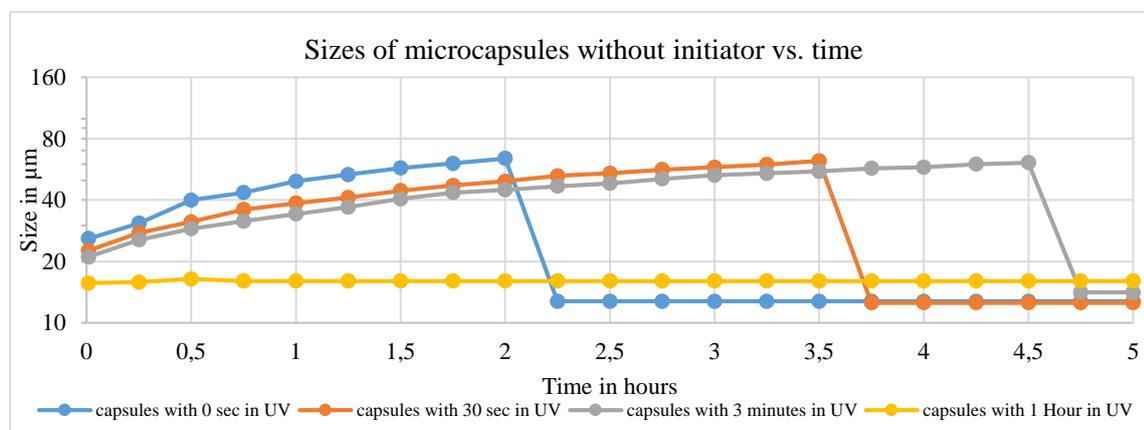


Figure 5-1-A. 2
Capsule size expansion over the course of time from the time of injection of the capsule in cell until rupture by osmotic pressure. Capsule: acrylate shell 0.0% of initiator with different exposure times of UV

We noted that when we used no initiator, the capsules have different behaviours depending on the UV exposure time:

Calculate the osmotic pressure of the capsules:

$$P = \frac{i n R T}{V}$$

P total = P sodium chloride + P sodium alginate

i= van't Hoff factor of the solution = for NaCl = 2 and for sodium alginate = 1

P = osmotic pressure

n= number of moles = mass / molecular mass = mol

R = gas constant = 0.08206 l atm K⁻¹ mol⁻¹

T = temperature in kelvin = 25 +273.15 = 298.15 K°

V = volume in litter = 0.1 l

Calculate the osmotic pressure for sodium chloride 10% in mass

$$\text{number of moles } n = \frac{10\text{g}}{58.44 \text{ g mol}} = 0.1711 \text{ mol}$$

$$\text{Concentration} = \frac{\text{number of moles}}{\text{volume in litter}} = \frac{0.1711 \text{ mol}}{0.1 \text{ litter}} = 1.711 \frac{\text{mol}}{\text{litter}}$$

Sodium chloride is a strong electrolyte solution



Each mole of NaCl produce two moles of particles So, $i = 2$

osmotic pressure for sodium chloride $P_{\text{NaCl}} = 2 * 1.711 \text{ mole litter}^{-1} * 0.08206 \text{ l atm K}^{-1} \text{ mol}^{-1}$

$$*298.15 \text{ K}^\circ = 83.728 \text{ atm}$$

Calculate the osmotic pressure for sodium alginate 10% in mass

Equation 22-16 in page 445. [24]

$$\Delta \pi = RT \left[\left(\frac{1}{2} - X \right) \frac{\phi^2}{v_s} + \left[(i \phi / v_s)^2 + 4 C_0^2 \right]^{1/2} - 2 C_0 \right]$$

Π = Pressure

$$R = 8.32 \text{ m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T = 25 + 273.15 = 298.15 \text{ K}^\circ$$

$$RT = 2,48\text{E}^{+03} \text{ m}^3 \text{ Pa mol}^{-1}$$

i is alginate polymer charge rate = 0,35

$X = 0$ the interactions, monomer-monomer and monomer-solvents are equivalent

$$C_0 \text{ Salt Concentration} = 1,71 \text{ moles L}^{-1} = 1,71\text{E}^{+03} \text{ mols m}^{-3}$$

$$v_s \text{ Water molecular volume} = 1,80\text{E}^{-05} \text{ m}^3 \text{ mole}^{-1}$$

$$\phi \text{ alginate polymer} = 0,1$$

$$i \phi / v_s = 0.35 * 0.1 / 0,000018 = 1,94\text{E}^{+03}$$

$$(i \phi / v_s)^2 = 3,78\text{E}^{+06}$$

$$(i \phi / v_s)^2 + 4 C_0^2 = 3,78\text{E}^{+06} + 4(1710)^2 = 3,78\text{E}^{+06} + 1,17\text{E}^{+07} = 1,55\text{E}^{+07}$$

$$\left[(i \phi / v_s)^2 + 4 C_0^2 \right]^{1/2} = 3,93\text{E}^{+03}$$

$$2 C_0 = 2 * 1710 = 3,42\text{E}^{+03}$$

$$\phi^2 / v_s = 0.1^2 / 1,80\text{E}^{-05} = 5,56\text{E}^{+02}$$

$$\left[(i \phi / v_s)^2 + 4 C_0^2 \right]^{1/2} - 2 C_0 = 3,93\text{E}^{+03} - 2 * 1,71\text{E}^{+03} = 5,14\text{E}^{+02}$$

$$\left(\frac{1}{2} - X \right) \frac{\phi^2}{v_s} = 2,78\text{E}^{+02}$$

$$\text{Pressure} = 1,96\text{E}^{+06} \text{ Pascal}$$

$$\text{Pressure} = 19,63 \text{ atm}$$

The osmotic pressure for sodium alginate solution $P_{\text{alginate}} = 19,63 \text{ atm}$

Total osmotic pressure

$$P_{\text{total}} = P_{\text{NaCl solution}} + P_{\text{alginate solution}}$$

$$= 83.728 \text{ atm} + 19.63 \text{ atm} = 103.358 \text{ atm}$$

- UV Exposure time 0 second

The capsule that had an initial size 22.21 μm increased in volume at an almost constant rate. The capsule started with a volume = 6.27 PL, the final volume before rupture was = 118.44 PL, so that the volume had increased by a factor of 18.88.

The mechanism of swelling was water diffusion through the aliphatic urethane acrylate shell under the effect of the difference of the osmotic pressure between the solution inside the capsule which had a calculated osmotic pressure = 83.789 atm and the external solution which had no osmotic pressure (distilled water).

The capsule ruptured after 2.25 hours and produced a small droplet of aliphatic urethane acrylate with size 13.56 μm

- UV Exposure time 30 second

The capsule that had an initial size 21.05 μm to final size 55.25 μm and increased in volume at an almost constant rate. The capsule started with a volume = 3.94 PL, the final volume before rupture was = 108.58 PL, so that the volume had increased by a factor of 27.55.

The mechanism of swelling was water diffusion through the aliphatic urethane acrylate shell under the effect of the difference of the osmotic pressure between the solution inside the capsule which had a calculated osmotic pressure = 83.789 atm and the external solution which had no osmotic pressure (distilled water).

The capsule ruptured after 3.5 hours and produced a small droplet of aliphatic urethane acrylate with size 13.56 μm .

- UV Exposure time 3 minutes

The capsule that had an initial size 21.05 μm to final size 61.04 μm and increased in volume at an almost constant rate. The capsule started with a volume = 3.08 PL, the final volume before rupture was = 102.32 PL, so that the volume had increased by a factor of 33.22.

The mechanism of swelling was water diffusion through the aliphatic urethane acrylate shell under the effect of the difference of the osmotic pressure between the solution inside the capsule which had a calculated osmotic pressure = 83.789 atm and the external solution which had no osmotic pressure (distilled water).

The capsule ruptured after 4.5 hours and produced a small droplet of aliphatic urethane acrylate with size 13.56 μm .

- **UV Exposure time 60 minutes**

The capsule shows almost no increase in volume during 4 hours despite the osmotic pressure difference between the solution inside the capsule which had a calculated osmotic pressure = 83.789 atm and the external solution which had no osmotic pressure (distilled water).

In fact, this capsule remained stable without rupture even the day after. Therefore, the polymer shell inhibited the flow of water into the capsule, and therefore it had been cross linked by the UV exposure. This confirms our suspicion that the liquid polymer from the factory has a very low concentration of initiator. This is why it is recommended to use the polymer within 6 months after its production and to avoid exposure to light and oxygen.

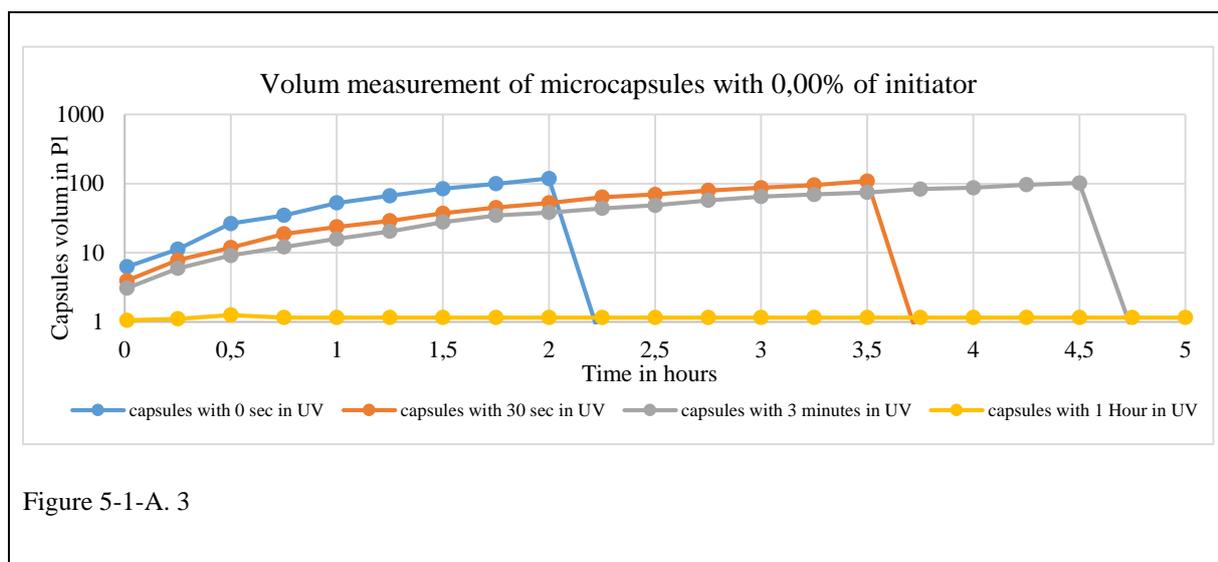


Figure 5-1-A. 3

5-1-A.2 Initiator concentration 0.01%

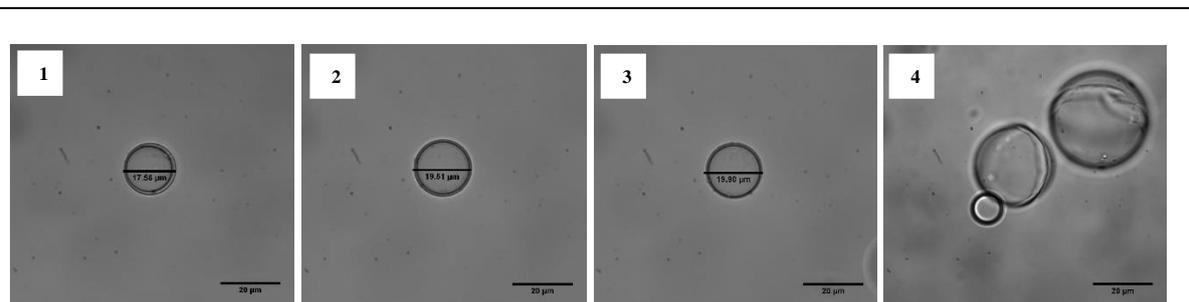


Figure 5-1-B. 1

After 0 Hour

After 1 Hour

After 2 Hours

After 12 Hours

Size expansion of aqueous capsules with polymer shell containing 0.01 % of initiator and exposure time of 3 minutes in UV oven.

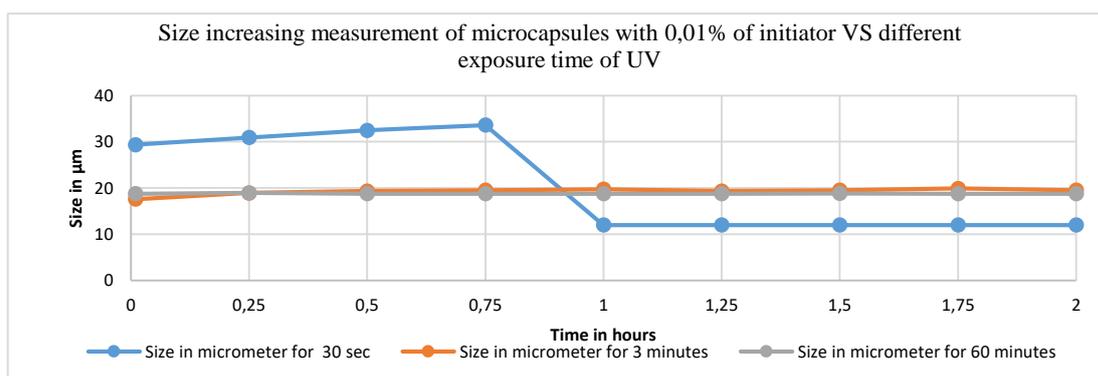


Figure 5-1-B. 2

Size expansion until crack over time by osmotic pressure of capsule with acrylate shell 0.01% of initiator with different exposure time in UV oven.

- UV Exposure time 30 second

With some initiator present in the polymer shell, the swelling of the capsule was much smaller. The capsule had an initial size = 29.36 µm and increased only to a final size = 33.61 µm. The capsule started with a volume = 9.59 PL, the final volume before rupture was = 15.01 PL, so that the volume had increased by a factor of 1.56.

The mechanism of swelling was water diffusion through the aliphatic urethane acrylate shell under the effect of the difference of the osmotic pressure between the solution inside the capsule which had a calculated osmotic pressure = 83.789 atm and the external solution which had no osmotic pressure (distilled water).

The capsule ruptured after a much shorter time = 0.75 hours and produced a small droplet of aliphatic urethane acrylate with size 11.98 μm .

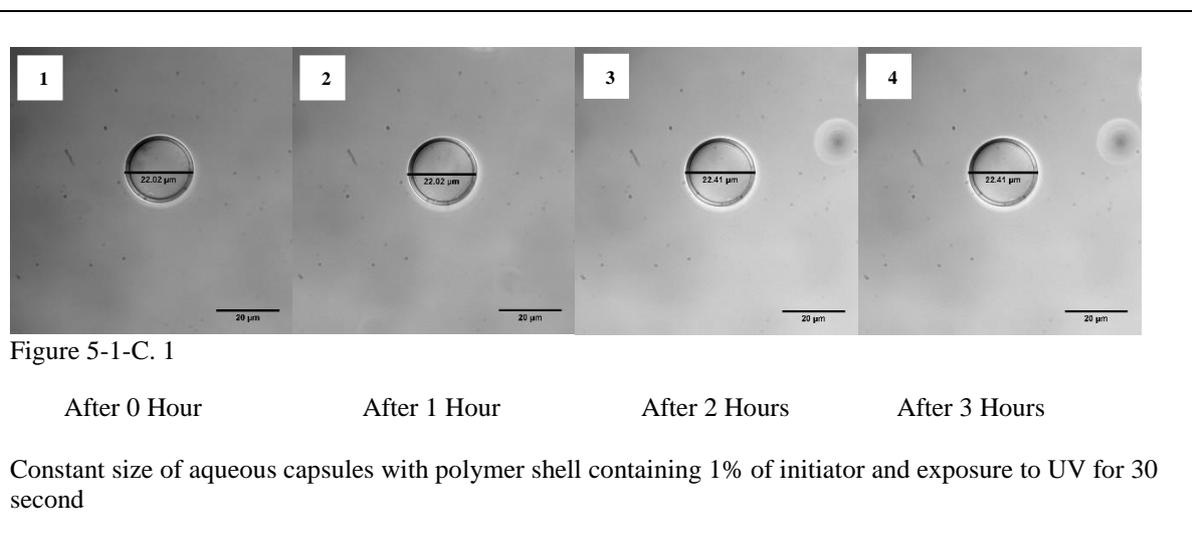
- **UV Exposure time 3 minutes**

This capsule remained stable with no increase in volume during 4 hours, but it ruptured the day after. In figure 5-1-B.1 we can see a fracture in the polymer shell. This is due to the difference in osmotic pressure between the solution inside the capsule which had a calculated osmotic pressure = 83.789 atm and the external solution which had no osmotic pressure (distilled water). It confirms that the polymer shell became stiff because of the number of cross links.

- **UV Exposure time 60 minutes**

The capsule shows almost no increase in volume during 4 hours despite the osmotic pressure difference between the solution inside the capsule which had a calculated osmotic pressure = 83.789 atm and the external solution which had no osmotic pressure (distilled water). In fact, this capsule remained stable without rupture even the day after. Therefore, the polymer shell inhibited the flow of water into the capsule, and therefore it had been cross linked by the UV exposure.

5-1-A.3 Initiator concentration 1 %



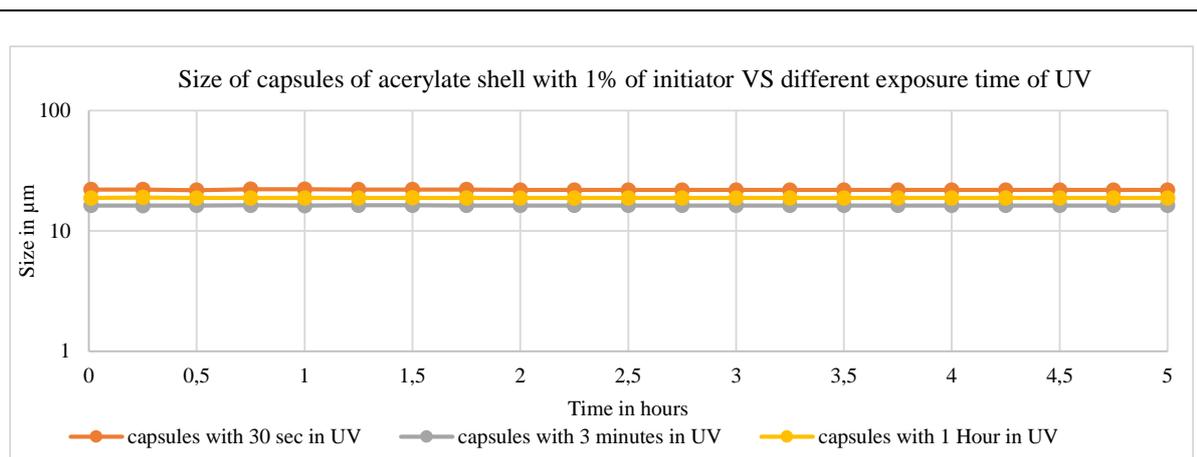


Figure 5-1-C. 2

Constant size of water capsules with polymer shell contains 1% of Initiator with different espouser time in UV oven

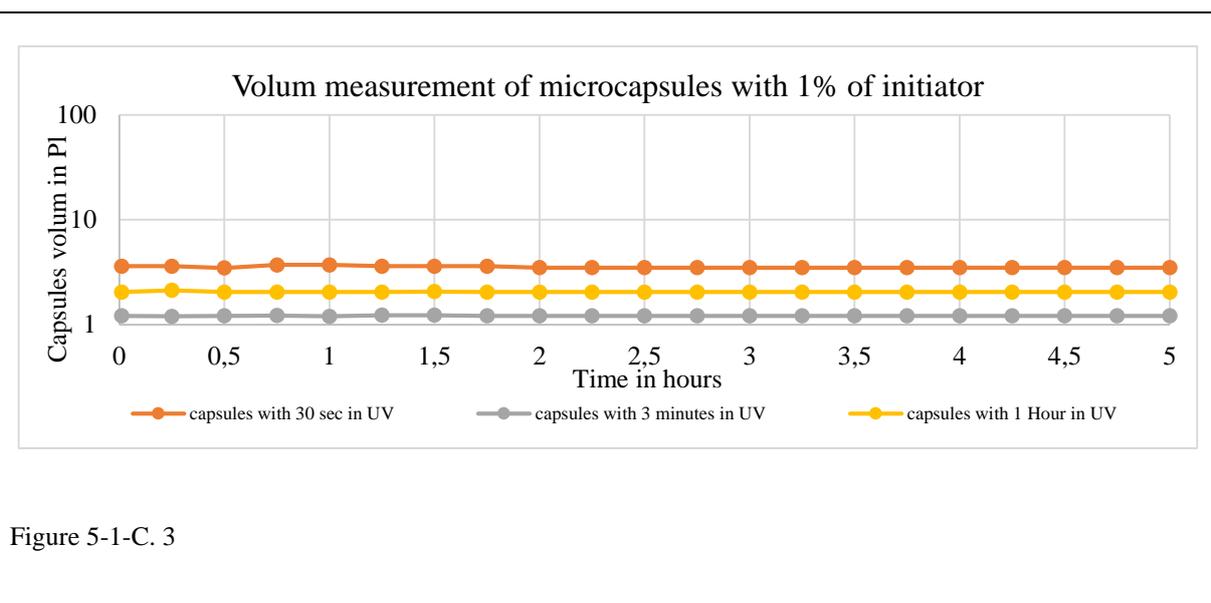


Figure 5-1-C. 3

All these capsules remained stable with no increasing in volume in duration of 4 hours without rupture even in the day after. Therefore, the polymer shell had been cross linked. We confirm that polymer shell with 1% of initiator exposed to UV for exposure times 30 second or 3 minutes or 60 minutes are fully cross linked and inhibit the flow of water into the capsules.

5-1-A.4 Initiator concentration 10.0%

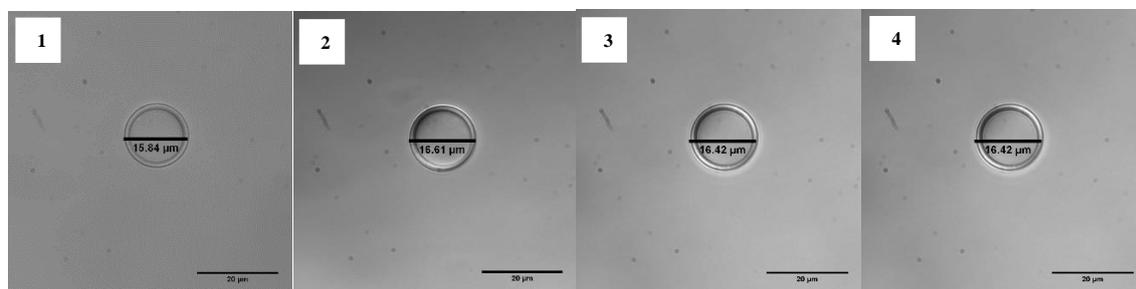


Figure 5-1-D. 1

After 0 Hour

After 1 Hour

After 2 Hours

After 3 Hours

No size expansion of osmatic pressure of capsule with acrylate shell 10 % of initiator with 30 second of espouser time in UV oven

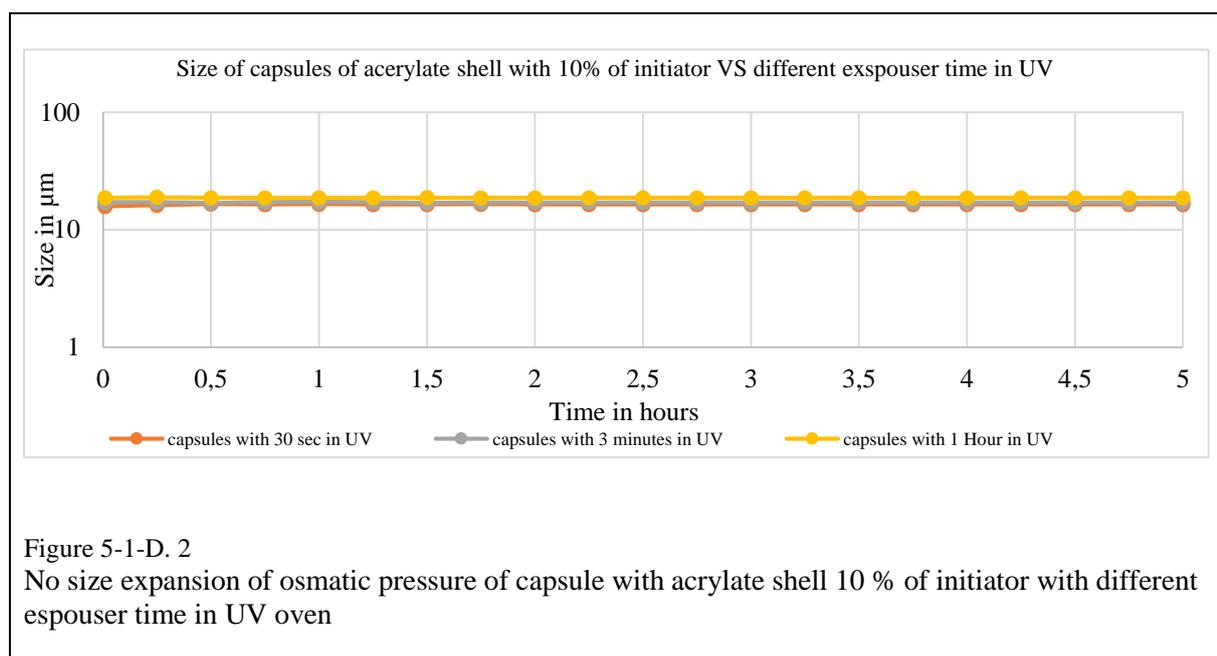
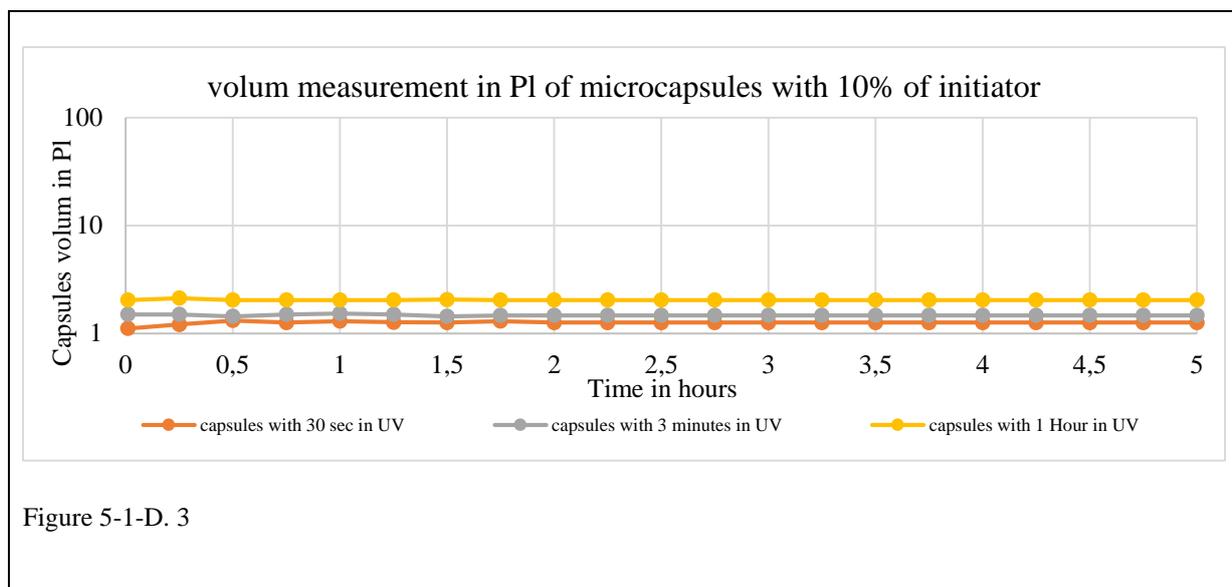


Figure 5-1-D. 2

No size expansion of osmatic pressure of capsule with acrylate shell 10 % of initiator with different espouser time in UV oven



All these capsules remained stable with no increasing in volume in duration of 4 hours without rupture even in the day after. Therefore, the polymer shell had been cross linked. We confirm that polymer shell with 10% of initiator exposed to UV for exposure times 30 second or 3 minutes or 60 minutes are fully cross linked and inhibit the flow of water into the capsules.

Conclusion

With these observations, we show that we can adjust the extent of cross linking of the shell polymer, so that its behaviour is either elasto-plastic or stiff depending on the initiator concentration and on the dose of UV exposure. At low concentration of cross links the response of the shell to an osmotic pressure different is elasto-plastic and it ruptures after substantial stretching. At higher concentration of cross links, the mechanical response of the shell is stiff and it ruptures after a small expansion. At very high concentration of cross links the shell does not rupture any longer.

5-2 Size distribution of Capsules

5-2-A Bright Field Images by Optical Microscopy

5-2-A.1 Aqueous Phase / Aliphatic Urethane acrylate shell / Aqueous Phase

We have used ImageJ, a software which make it possible to measure distances on the images provided by the optical microscope, in order to determine the diameter of the capsules and their shell thickness.

The images were taken using an optical microscope with objective lens 100X
The lens calibration was determined by following relation:

$$2019\text{Pix} = 130\ \mu\text{m}$$

In order to improve the quality of the contrast of the images we have washed the external phase which was solution of sodium alginate 10% with pure water.

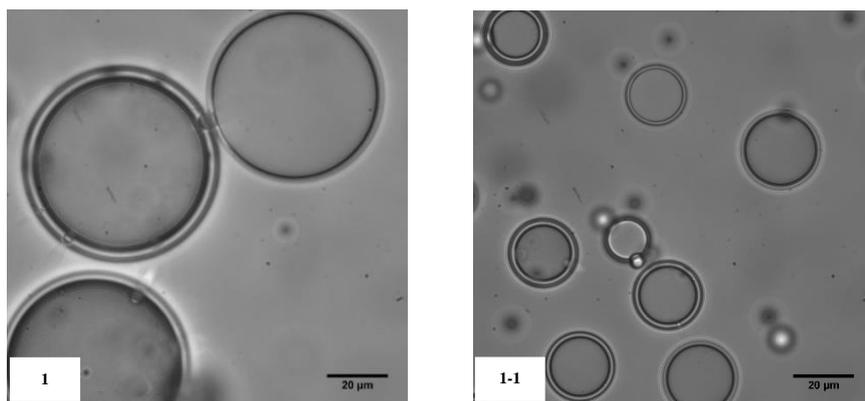


Figure 5-2-A. 1

Sample - 1 Capsules of aqueous of 10% sodium alginate / CN991 aliphatic urethane acrylate shell / water microcapsules prepared at a rotational speed 200 rpm. Average diameter = 65 μm , average shell thickness = 4 μm

Sample – 1-1 Capsules of aqueous of 10% sodium alginate / CN991 aliphatic urethane acrylate shell / water microcapsules prepared at a rotational speed 400 rpm. Average size = 25 μm , average shell thickness = 2 μm .

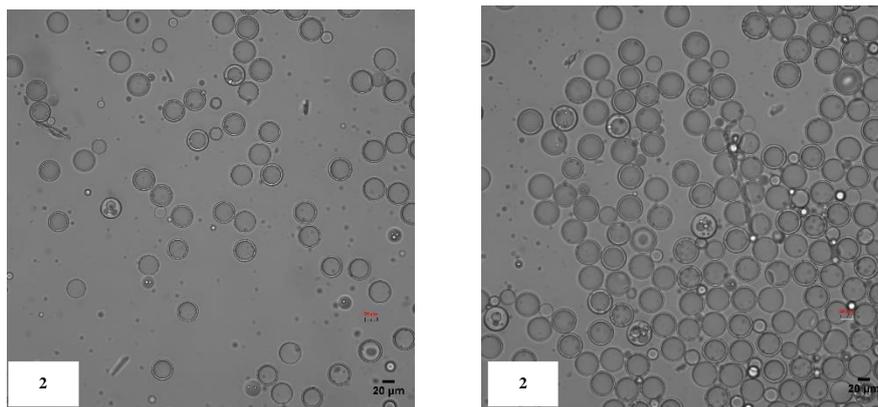


Figure 5-2-A. 2

Sample - 2 Capsules of aqueous solution of 10% sodium alginate / CN2035 poly ester urethane acrylate shell / water microcapsules prepared at a rotational speed 200 rpm. Average size = 42.08 μm , average shell thickness = 3.57 μm .

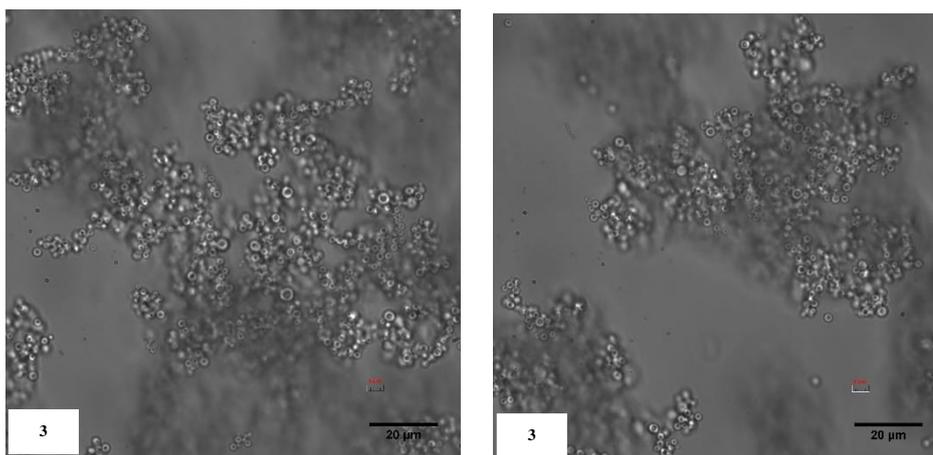


Figure 5-2-A. 3

Sample - 3 Capsules of aqueous solution of 10% sodium alginate // CN2555 poly ester urethane acrylate shell / water microcapsules prepared at a rotational speed 200 rpm. Average size = 2.13 μm , average shell thickness = 450nm.

When we use a di-functional polymer such as CN991 and CN2035 to make the shells, we obtain capsule diameters about 40 μm . However, when we use a tetra-functional polymer like CN2555 the size of the capsule decreases to 3 μm . Since the emulsification was performed in the same conditions, this reduction must result from lower interfacial tensions.

5-2-A.2 Oil / Epoxy Urethane acrylate shell / Aqueous Phase

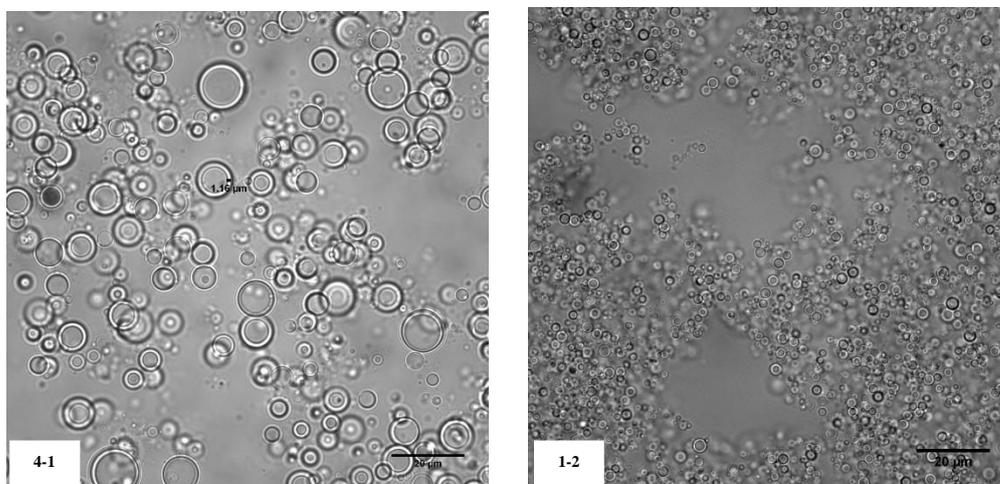


Figure 5-2-A. 4

Oil / Epoxy Urethane acrylate shell / Aqueous Phase

These microcapsules have been prepared with epoxy acrylate polymer, using the Couette with a gap of 100 μm with a rotational speed of 100 and 600 rpm

Capsules of poly alpha olefin 40 // CN109 epoxy urethane acrylate shell / glycerol microcapsules prepared at a rotational speed 100 rpm. Average size = 13.82 μm, average shell thickness = 1.17 μm.

Capsules of poly alpha olefin 40 / CN109 epoxy urethane acrylate shell / glycerol microcapsules prepared at a rotational speed 600 rpm. Average size = 2.41 μm, average shell thickness = 200 nm.

5-2-B Fluorescence Images Using Dissolved Dyes

5-2-B.1 Aqueous Phase / Aliphatic Urethane Acrylate Shell / Aqueous Phase System

In order to visualize the shells of the capsules we dissolved dyes in the urethane acrylate shell polymer. The dye concentration was quite low =0.001% in mass.

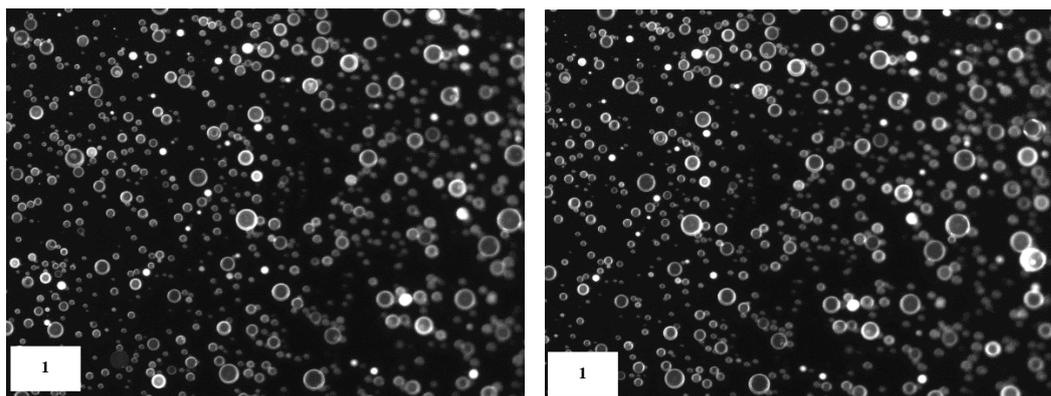


Figure 5-2-B. 1

Fluorescence images obtained by adding Rhodamine 6 G dissolved in the polymer shells (excitation 553 nm and emission 627 nm)

Sample – 1 Capsules of aqueous of 10% sodium alginate / CN991 aliphatic urethane acrylate shell with Rhodamine 6 G / water microcapsules prepared at a rotational speed 400 rpm. Average size = 25 μm , average shell thickness = 2 μm .

5-2-B.2 Oil / Epoxy Urethane Acrylate Polymer shell / Aqueous Phase

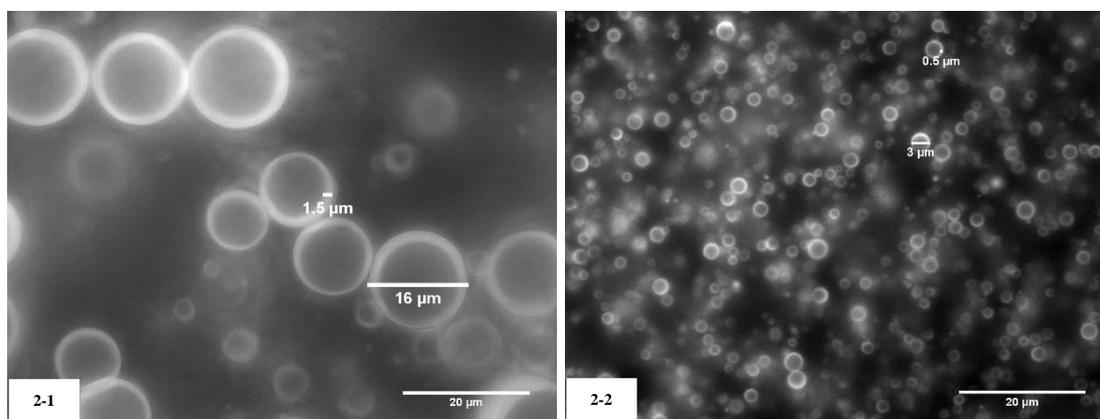


Figure 5-2-B. 2

Fluorescence image by adding Nile Red excitation 450 nm and emission 550 nm in the acrylate

shell for oil / Epoxy urethane acrylate shell / water system under shear rate 100 rpm and 600 rpm

Sample – 2-1 Capsules of Oil PAO 40 / CN109 Epoxy urethane acrylate shell / Aqueous phase microcapsules

The average of size discription = 16 μm

And the average of the shell thickness = 1.5 μm

Sample – 2-2 Capsules of Oil PAO 40 / CN109 Epoxy urethane acrylate polymer shell / water microcapsules

The average of size discription = 2.5 μm

And the average of the shell thickness = 300 nm

5-2-C Sizes Distribution of capsules through Laser Light Scattering

We used light scattering in the Mie regime to determine the complete size distribution of the capsules dispersed in aqueous phase.

The instrument was a Malvern (Master Sizer). This instrument makes measurement on diluted dispersions of capsules under slow stirring to avoid the sedimentation of the capsules.

5-2-C.1 Aqueous Phase / Aliphatic Urethane acrylate shell / Aqueous Phase

In this experiment we measured the complete size distribution of capsules made at the same shear rate for different duration of stirring.

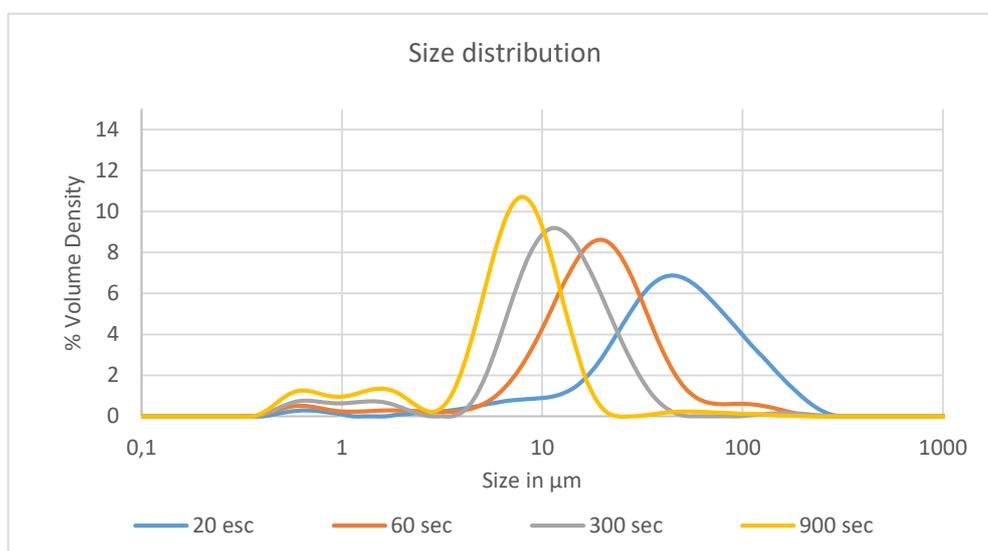


Figure 5-2-C. 1

Effect of the duration of the second emulsification. Sample: aqueous phase / aliphatic urethane acrylate shell / aqueous phase). Horizontal axis: diameters of the capsules in μm . Vertical axis: volume density of capsule populations.

We observe that the sizes of all objects in the dispersion are reduced when the duration of the shear is increased, most of these objects are presumably capsules, but there may be droplets of aliphatic urethane acrylate as well.

5-2-C.2 Oil / Epoxy Urethane Acrylate polymer Shell / Aqueous Phase

In this experiment we measured the complete size distribution of capsules of poly alpha olefin oil 40 made at different shear rates but for the same duration of stirring.

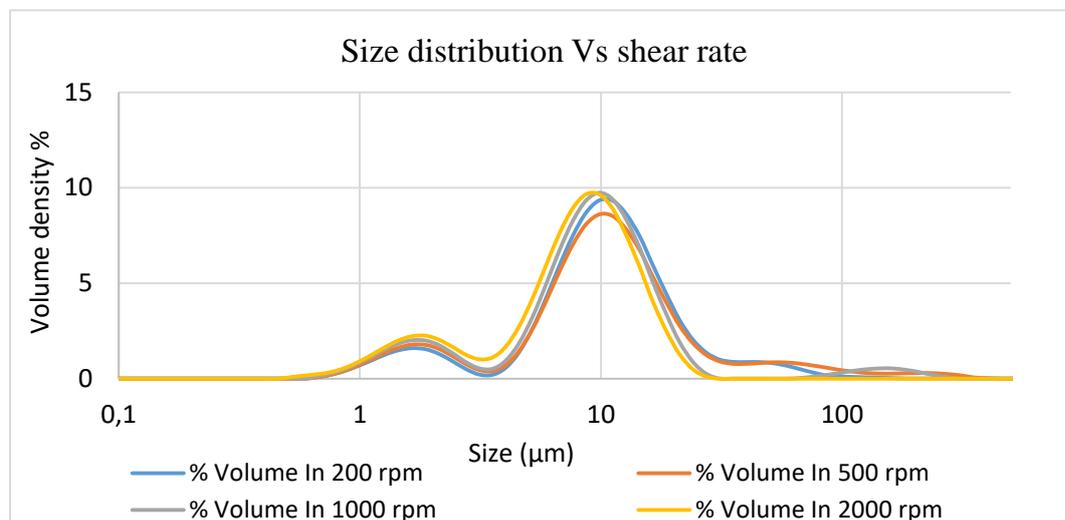


Figure 5-2-C. 2

Effect of the shear rate during the second emulsification. Sample: oil phase / epoxy urethane acrylate shell / aqueous phase). Horizontal axis: diameters of the capsules in μm . Vertical axis: volume density of capsule populations.

We observe that the sizes of the capsules remain the same at all shear rates when using the overhead mixer. The mechanism of the second emulsification is inefficient in this case, presumably because the viscosity of the external phase was too low and the gap between the blades and the beaker was too large (2500 micrometre). This effect was corrected when the dispersion was sheared in the Couette instrument that has a smaller gap (100 micrometre) as shown in the Figure 5-2-B.2.

5-2-D Transmission electron microscopy

In a few cases we produced capsules that were smaller than 5 μm . In order to resolve their structures, we had to use electron microscopy. But electrons don't do well in liquid water; therefore, we have to dry the capsules. In order to avoid aggregation of the capsules during drying we had dilute them with large volume of water.

5-2-D.1 Aqueous Phase / Aliphatic Urethane acrylate shell / Aqueous Phase

These capsules were synthesised with tetra functional poly ester urethane acrylate shell polymer, and they were found to be quite small with size less than 5 μm (see Figure 5-2-A.3). In order to resolve their structures, we had to use electron microscopy.

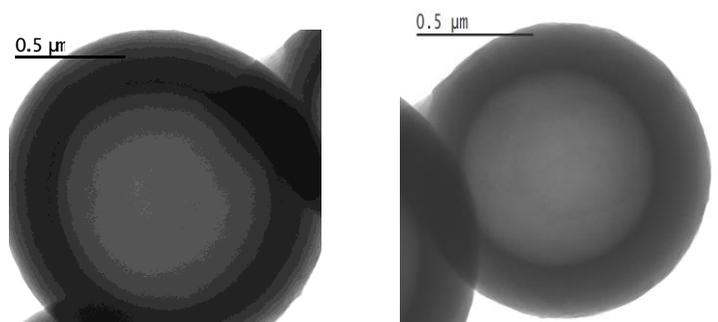


Figure 5-2-D. 1

Transmission Electron Microscope images of two capsules made with aqueous phase / CN2555 acrylate shell / water. The darker regions are the shells made of the tetra functional polyester CN2555.

We imaged a large number of capsules with TEM. The average sizes found for the tetra functional polymer capsules was 1.24 μm and their average shell thickness was 261nm.

5-2-D.2 Oil / Epoxy Urethane acrylate shell / Aqueous Phase

These capsules were synthesised with a core of silicone oil covered by a wax layer inside a shell of di functional epoxy urethane acrylate polymer. The capsules were found to be quite small. In order to resolve their structures, we had to use electron microscopy.

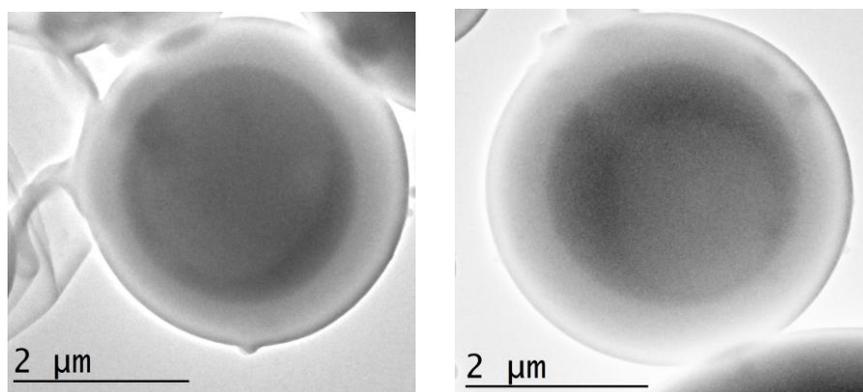


Figure 5-2-D. 2

Transmission Electron Microscope images of two capsules made with silicon oil core and layer of wax inside shell of CN109 epoxy urethane acrylate shell / water. The lighter regions are the shells made of the di functional epoxy urethane acrylate polymer CN109.

We imaged a large number of capsules with TEM. The average sizes found for the di functional polymer capsules were 4 µm and their average shell thickness was 500 nm

5-2-D.3 Aqueous Phase / Epoxy Urethane Acrylate Shell / Oil Phase

These capsules were synthesised with a core of 10% sodium alginate solution inside a shell of di functional epoxy urethane acrylate polymer dispersed in external phase Castor oil. The capsules were found to be quite small. In order to resolve their structures, we had to use electron microscopy.

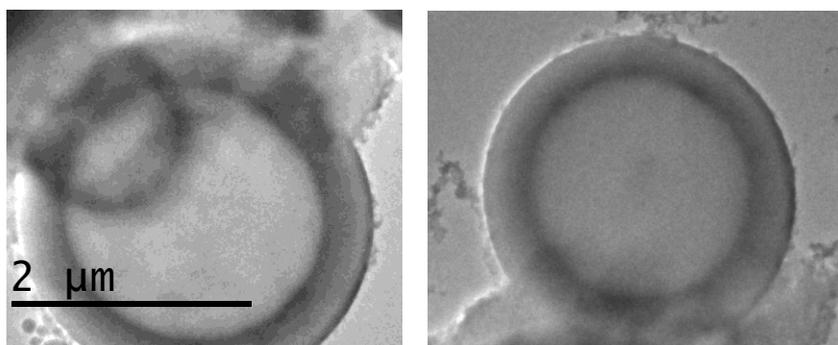


Figure 5-2-D. 3

Transmission Electron Microscope images of two capsules made with 10% aqueous solution of sodium alginate as a core inside shell of CN109 epoxy urethane acrylate shell / water. The lighter regions are the shells made of the di functional epoxy urethane acrylate polymer CN109.

We imaged a large number of capsules with TEM. The average sizes found for the di functional polymer capsules were 3 μm and their average shell thickness was 300 nm

5-3 Encapsulation efficiency

The aim of this experiment is to evaluate the encapsulation efficiency which is defined as (encapsulated material/ (encapsulated + lost in the external phase)).

For this purpose, we dissolved a fluorescent dye in the internal phase that was used to make the capsules, and we measured the quantity of dye that was lost in the external phase.

5-3-A Aqueous Phase / Aliphatic Urethane Acrylate polymer shell / Aqueous Phase

In this case the dye dissolved in the internal phase was Sulforhodamine 101, and its encapsulation efficiency was measured with a Tecan plate reader.

We found that the encapsulation efficiency was 70 % if we sheared the emulsion for 20 second and 30% if we sheared it for 15 minutes. According in the movie that presented in Figure 4-1-A.2, the loss of dye molecules to the external phase was caused by erosion of the capsules in the shear flow, followed by rupture of some capsules. This instability was due to the fact that phase 1 and phase 3 had no interfacial tension since they were chemically identical and soluble.

5-3-B Oil phase / Epoxy Urethane acrylate polymer shell / Aqueous phase

In this case the dye dissolved in the internal phase was Nile Red, and its encapsulation efficiency was measured with a Tecan plate reader.

The encapsulation efficiency was 100 % even if we sheared the emulsion for 15 minutes

This stability of the double emulsion originated from the high interfacial tension between the oil core phase 1 and the external phase (glycerol, phase 3) which was 22.41 mN/m.

5-4 Methods for triggering the rupture of capsules

In this section we present four methods that cause the release of encapsulated material. These methods use different chemical or physical properties of the encapsulated material and of the polymer shell.

5-4-1 Rupture by osmotic stress

In this case the capsules contained as a core an aqueous solution of sodium alginate (10%) and NaCl (10%). The shell polymer was aliphatic urethane acrylate with 0.01% of initiator cured for 3 minutes in the UV oven. The external phase was deionized water. The osmotic pressure between phase 1 and phase 3 was calculated to be = 83.728 atm.

Images of this phenomenon have been presented in the Figure 5-1- B.1

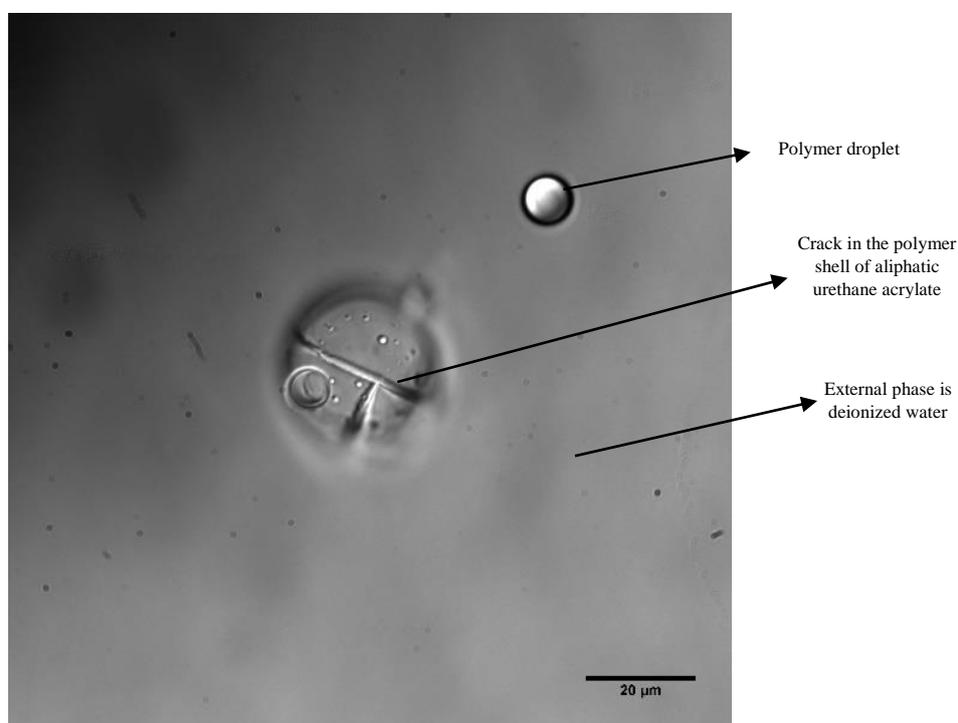


Figure 5-4- 1

Capsule ruptured after 12 hours. We can see that the polymer shell has cracked and ruptured under the effect of the osmotic pressure difference.

5-4-2 Rupture by mechanical pressure

In this method we placed the capsule in the gap between the two glass slides of the CSS450 Optical Rheology System. Then we reduced progressively the gap value from 60 to 0 micrometers which applied a mechanical pressure to the capsule.

We prepared two types of capsules with polymer shell of different rigidity (rubbery and glassy). These capsules behaved differently under mechanical pressure.

5-4-2. A Capsules contain aqueous core phase, Rubbery polymer shell CN991 aliphatic urethane di acrylate and external phase of water between two glass slides

The rupture is due to applying pressure and reducing the gap between the two glass slides of the CSS450 Optical Rheology System.

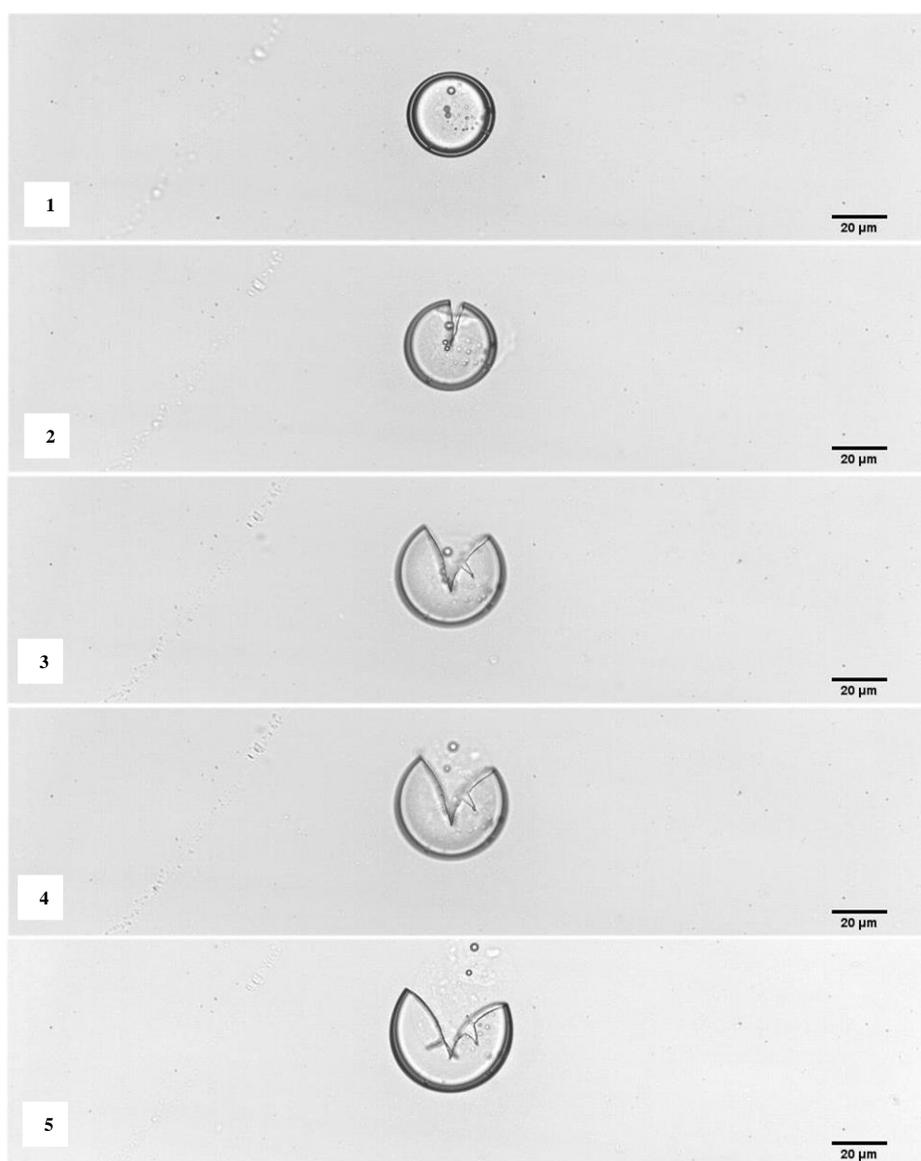


Figure 5-4-2-A 1

According to these images the capsule was cracked and its content was totally released but the polymer shell remained in one piece.

5-4-2. B Capsules contain aqueous core phase, Glassy polymer shell CN2035 aliphatic urethane di acrylate and external phase of water between two glass slides

The rupture is due to applying pressure and reducing the gap between the two glass slides of the CSS450 Optical Rheology System.

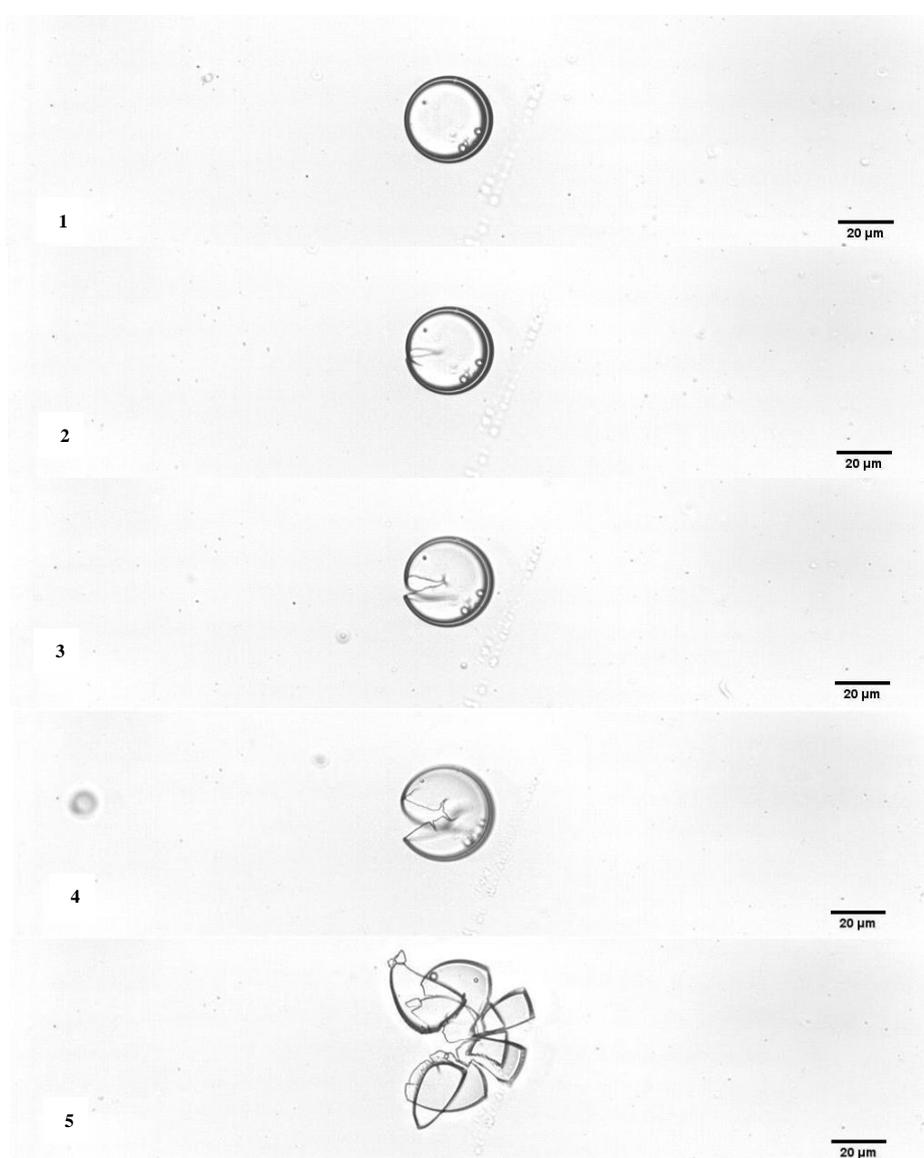


Figure 5-4-2-A 2

According to these images the capsule was cracked and its content was totally released, but in this case the glassy polymer shell was fragmented in to many small parts.

5-4-3 Rupture by ultrasound

In this case the capsules contained an aqueous core of sodium alginate 10%, a glassy polymer shell made of CN2035 aliphatic urethane di acrylate and an external phase of water.

This image was taken after applying ultrasonic for 15 minutes



Figure 5-4-3. 1

We can see that the ultrasound broke all the capsules and that the polymer shells were fragmented to many small pieces. The release was total.

5-4-4 Rupture by thermal expansion of the core

In this case the capsules contained a wax as a core, a polymer shell of CN109 epoxy urethane diacrylate and an external phase of water.

This capsule was heated up to 75 °C by using a heater plate with digital temperature control

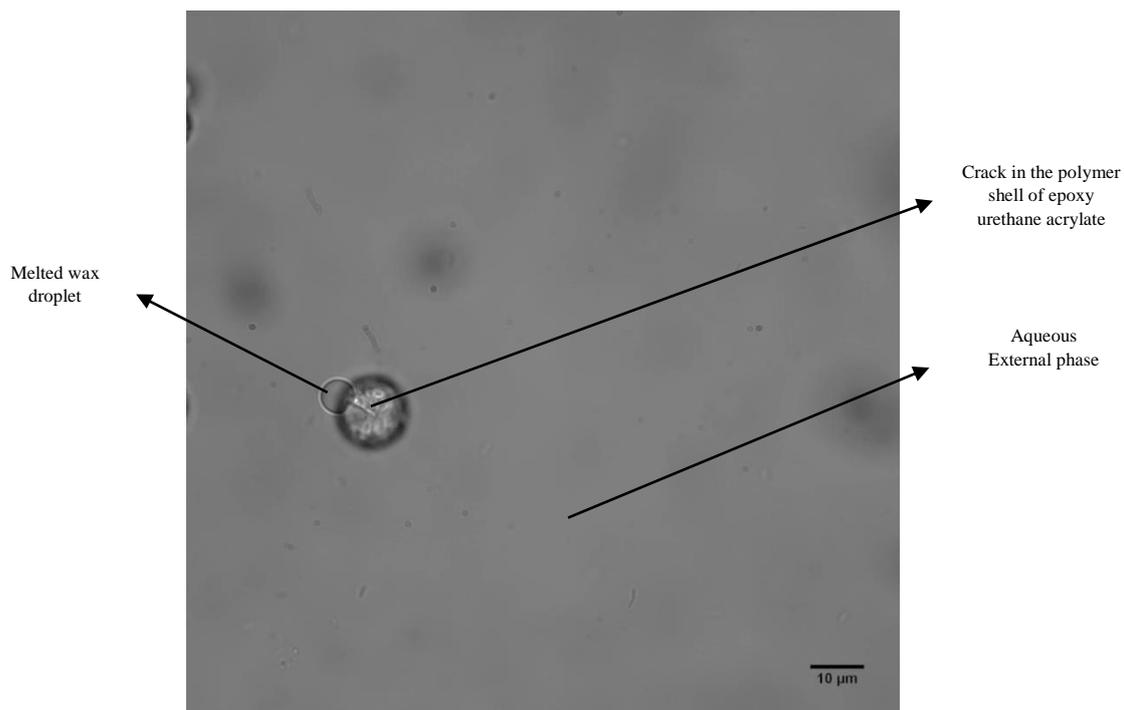


Figure 5-4-4. 1

From the image we can see that the capsule was cracked and that a droplet of melted wax leaked out through the crack. This crack was caused by the expansion (about 10%) of the wax when it melted. This result confirms the feasibility of thermal expansion release capsules.

Summary for the fifth chapter in french language

Résumé du cinquième chapitre

A- Polymérisation de coquille en polymère d'acrylate

Effets de la concentration en initiateur et de la durée d'exposition aux UV

Nous avons observé le gonflement osmotique de gélules remplies de 10% de NaCl et de 10% d'alginate de sodium dans de l'eau pure et la rupture des gélules à fort gonflement. À partir de ces observations, nous calculons la taille et le volume des capsules et la pression osmotique initiale. Nous avons utilisé ces informations pour étudier la polymérisation de la coque d'acrylate et son évolution en fonction du temps d'exposition aux UV et de la concentration en initiateur.

Avec ces observations, nous montrons que nous pouvons ajuster l'ampleur de la réticulation du polymère en coque, de sorte que son comportement soit élasto-plastique ou rigide, en fonction de la concentration en initiateur et de la dose d'exposition aux UV. A faible concentration de croix, la réponse de la coque à une pression osmotique différente est élasto-plastique et se rompt après un étirement important. À une concentration plus élevée de liaisons transversales, la réponse mécanique de la coque est raide et elle se rompt après une petite expansion. Lorsque la concentration des liaisons croisées est très élevée, la coque ne se rompt plus.

B- Distribution de taille des capsules

Images en champ clair par microscopie optique

Phase aqueuse / Coque en acrylate d'uréthane aliphatique / Phase aqueuse

Lorsque nous utilisons un polymère di-fonctionnel tel que CN991 et CN2035 pour fabriquer les coques, nous obtenons des diamètres de capsule d'environ 40 μm . Toutefois, lorsque nous utilisons un polymère tétra-fonctionnel tel que CN2555, la taille de la capsule diminue à 3 μm . L'émulsification étant réalisée dans les mêmes conditions, cette réduction doit résulter de tensions interfaciales plus faibles.

Phase d'huile / Coque acrylate d'uréthane époxy / Phase aqueuse

Ces microcapsules ont été préparées avec un polymère époxy acrylate, en utilisant la Couette avec un intervalle de 100 μm avec une vitesse de rotation de 100 et 600 tr / min.

Capsules de microcapsules de coque / glycérol de coque poly (alpha-oléfine 40 / CN109) époxy-uréthane préparées à une vitesse de rotation de 100 tours / minute. Taille moyenne = 13,82 μm , épaisseur moyenne de la coque = 1,17 μm .

Capsules de microcapsules de coque / glycérol de poly-alpha-oléfine 40 / CN109 époxy-uréthane préparées à une vitesse de rotation de 600 tr / min. Taille moyenne = 2,41 μm , épaisseur moyenne de la coque = 200 nm.

Images de fluorescence utilisant des colorants dissous

Afin de visualiser les enveloppes des capsules, nous avons dissous les colorants dans le polymère d'enveloppe d'acrylate d'uréthane. La concentration de colorant était assez faible = 0,001% en masse.

Tailles distribution des capsules par diffusion de la lumière laser

Nous avons utilisé la diffusion de la lumière dans le régime de Mie pour déterminer la distribution de taille complète des capsules dispersées en phase aqueuse.

L'instrument était un Malvern (Master Sizer). Cet instrument mesure les dispersions diluées de capsules sous agitation lente afin d'éviter la sédimentation des capsules.

La microscopie électronique à transmission

Dans quelques cas, nous avons produit des gélules inférieures à 5 μm . Afin de résoudre leurs structures, nous avons dû utiliser la microscopie électronique. Mais les électrons ne fonctionnent pas bien dans l'eau liquide ; par conséquent, nous devons sécher les capsules. Afin d'éviter l'agrégation des gélules lors du séchage, nous les avons diluées avec un grand volume d'eau.

Phase aqueuse / Coque en acrylate d'uréthane aliphatique / Phase aqueuse

Nous avons imagé un grand nombre de capsules avec TEM. Les tailles moyennes trouvées pour les capsules de polymère tétra-fonctionnel étaient de 1,24 μm et leur épaisseur de coque moyenne était de 261 nm.

Phase d'huile / Coque acrylate d'uréthane époxy / Phase aqueuse

Images au microscope électronique à transmission de deux capsules constituées d'un noyau d'huile de silicium et d'une couche de cire à l'intérieur de l'enveloppe en coquille CN109 époxy uréthane acrylate / eau. Les régions les plus claires sont les coques constituées du polymère CN109 époxyuréthane acrylate di-fonctionnel.

Nous avons imagé un grand nombre de capsules avec TEM. Les tailles moyennes trouvées pour les capsules de polymère di fonctionnelles étaient de 4 μm et l'épaisseur moyenne de leur coquille était de 500 nm.

Efficacité d'encapsulation

Le but de cette expérience est d'évaluer l'efficacité d'encapsulation qui est définie comme (matériau encapsulé / (encapsulé + perdu dans la phase externe)).

À cette fin, nous avons dissous un colorant fluorescent dans la phase interne utilisée pour fabriquer les capsules et nous avons mesuré la quantité de colorant perdue dans la phase externe.

Phase aqueuse / Coque en acrylate d'uréthane aliphatique / Phase aqueuse

Dans ce cas, le colorant dissous dans la phase interne était la sulforhodamine 101 et son efficacité d'encapsulation a été mesurée avec un lecteur de plaques Tecan.

Nous avons trouvé que l'efficacité d'encapsulation était de 70% si nous cisailions l'émulsion pendant 20 secondes et de 30% si nous les cisailions pendant 15 minutes. Selon le film présenté à la figure 4-1-A.2, la perte de molécules de colorant dans la phase externe était due à l'érosion des capsules dans le flux de cisaillement, suivie de la rupture de certaines capsules. Cette instabilité était due au fait que les phases 1 et 3 n'avaient pas de tension interfaciale puisqu'elles étaient chimiquement identiques et solubles.

Phase d'huile / Coque acrylate d'uréthane époxy / Phase aqueuse

Dans ce cas, le colorant dissous dans la phase interne était le rouge de Nil et son efficacité d'encapsulation a été mesurée avec un lecteur de plaques Tecan.

L'efficacité d'encapsulation était de 100% même si nous avons cisailé l'émulsion pendant 15 minutes. Cette stabilité de la double émulsion provient de la tension interfaciale élevée entre la phase 1 du noyau de l'huile et la phase externe (glycérol, phase 3) qui était de 22,41 mN / m.

Méthodes pour déclencher la rupture de capsules

Dans cette section, nous présentons quatre méthodes qui entraînent la libération de matériau encapsulé. Ces méthodes utilisent différentes propriétés chimiques ou physiques du matériau encapsulé et de l'enveloppe polymère.

- 1- Rupture par stress osmotique
- 2- Rupture par pression mécanique
- 3- Rupture par ultrasons
- 4- Rupture par expansion thermique du cœur

Final conclusion

From this work we show:

- 1- In this thesis we showed the possibility to make encapsulation surfactant-free by using viscos material with viscosity ratio close to 1 even without applying the wetting law.

we show that we are able to make double emulsion without using any surfactant to make microcapsules by controlling the viscosity ratio between the fluids also with applying the right shear rate, we show the effect of the viscosity ratio on the fragmentation of the double by four movies which show the fragmentations of the double emulsion, from these movies we concluded that we have optimum symmetric fragmentation between the core and the liquid polymer shell if we used viscosity ratio close to 1 between the fluids.

- 2- We showed the high stability and containment of the encapsulated materials inside the microcapsules
- 3- We showed different possibility to control the release depending on the nature of the material

Also we present four methods that cause the release of encapsulated material. These methods use different chemical or physical properties of the encapsulated material and of the polymer shell.

Methods for triggering the rupture of capsules: rupture by osmotic stress, rupture by mechanical pressure, rupture by ultrasound and rupture by thermal expansion of the core.

- 4- There are many wide range of application from cosmetic ingredient, home care product, petroleum additive

Conclusion finale

Nous montrons à partir de ce travail :

- 1- Possibilité de rendre le surfactant sans encapsulation en utilisant un matériau visqueux avec un rapport de viscosité proche de 1 même sans appliquer la loi de mouillage.

Donc nous sommes capables de produire une émulsion double sans utiliser des tensioactifs pour fabriquer des microcapsules en contrôlant le rapport de viscosité entre les fluides, même en appliquant le taux de cisaillement correct. Nous montrons ensuite l'effet du rapport de viscosité sur la fragmentation du double par quatre films montrant la fragmentation de la double émulsion, nous avons conclu que nous avons une fragmentation symétrique optimale entre le cœur et la coque en polymère liquide si nous utilisons un rapport de viscosité proche de 1 entre les fluides.

- 2- Haute stabilité et confinement des matériaux encapsulés à l'intérieur des microcapsules.
- 3- Possibilité différente de contrôler le rejet en fonction de la nature du matériau

Nous présentons également quatre méthodes qui entraînent la libération de matériau encapsulé. Ces méthodes utilisent différentes propriétés chimiques ou physiques du matériau encapsulé et de l'enveloppe polymère.

Méthodes de déclenchement de la rupture des capsules : rupture par contrainte osmotique, rupture par pression mécanique, rupture par ultrasons et rupture par dilatation thermique du cœur.

- 4- Large domaine d'application des ingrédients cosmétiques, produits de soins à domicile, additifs de pétrole

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Data sheet of the material that were used

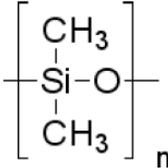
1- Silicone oil


sigma-aldrich.com

3050 Spruce Street, Saint Louis, MO 63103, USA
 Website: www.sigmaaldrich.com
 Email USA: techserv@sial.com
 Outside USA: eurtechserv@sial.com

Product Specification

Product Name:
Silicone oil - viscosity 10 cSt (25 °C)

Product Number:	378321	
CAS Number:	63148-62-9	
MDL:	MFCD00132673	
Formula:	(-Si(CH ₃) ₂ O-)n	

2- Sodium chloride

Product Specification

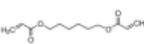
Product Name:
Sodium chloride - BioXtra, ≥99.5% (AT)

Product Number:	S7653	NaCl
CAS Number:	7647-14-5	
MDL:	MFCD00003477	
Formula:	ClNa	
Formula Weight:	58.44 g/mol	

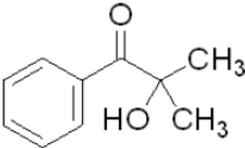
3- 1,6-Hexanediol diacrylate

Product Specification

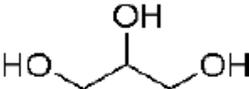
Product Name:
1,6-Hexanediol diacrylate - technical grade, 80%

Product Number:	246816	
CAS Number:	13048-33-4	
MDL:	MFCD00008631	
Formula:	C ₁₂ H ₁₈ O ₄	
Formula Weight:	226.27 g/mol	

4- 2 hydroxy 2 methylpropiophenone

Product Specification	
Product Name: 2-Hydroxy-2-methylpropiophenone - 97%	
Product Number:	405655
CAS Number:	7473-98-5
MDL:	MFCD00040710
Formula:	C ₁₀ H ₁₂ O ₂
Formula Weight:	164.20 g/mol
	

5- Glycerol

Product Specification	
Product Name: Glycerol - BioXtra, ≥99% (GC)	
Product Number:	G6279
CAS Number:	56-81-5
MDL:	MFCD00004722
Formula:	C ₃ H ₈ O ₃
Formula Weight:	92.09 g/mol
	

6- Rhodamine 6G

SECTION 1: Identification of the substance/mixture and of the company/undertaking	
1.1 Product identifiers	
Product name	: Rhodamine 6G
Product Number	: 56226
Brand	: Sigma-Aldrich
REACH No.	: A registration number is not available for this substance as the substance or its uses are exempted from registration, the annual tonnage does not require a registration or the registration is envisaged for a later registration deadline.
CAS-No.	: 989-38-8
1.2 Relevant identified uses of the substance or mixture and uses advised against	
Identified uses	: Laboratory chemicals, Manufacture of substances
1.3 Details of the supplier of the safety data sheet	
Company	: Sigma-Aldrich Chimie Sarl L'Isle D'Abeau Chesnes F-38297 ST. QUENTIN FALLAVIER
Telephone	: 0800 211408
Fax	: 0800 031052
1.4 Emergency telephone number	
Emergency Phone #	: +33 (0)9 75 18 14 07 (CHEMTREC) +33 (0)1 45 42 59 59 (I.N.R.S.)

7- Nile red

SECTION 1: Identification of the substance/mixture and of the company/undertaking	
1.1 Product identifiers	
Product name	: Nile Red
Product Number	: 72485
Brand	: Sigma
REACH No.	: A registration number is not available for this substance as the substance or its uses are exempted from registration, the annual tonnage does not require a registration or the registration is envisaged for a later registration deadline.
CAS-No.	: 7385-67-3
1.2 Relevant identified uses of the substance or mixture and uses advised against	
Identified uses	: Laboratory chemicals, Manufacture of substances
1.3 Details of the supplier of the safety data sheet	
Company	: Sigma-Aldrich Chimie Sarl L'Isle D'Abeau Chesnes F-38297 ST. QUENTIN FALLAVIER
Telephone	: 0800 211408
Fax	: 0800 031052
1.4 Emergency telephone number	
Emergency Phone #	: +33 (0)9 75 18 14 07 (CHEMTREC) +33 (0)1 45 42 59 59 (I.N.R.S.)

8- Sodium alginate

Product Specification	
Product Name:	Sodium alginate
Product Number:	W201502
CAS Number:	9005-38-3
MDL:	MFCD00081310

9- Polyalphaolefin 40

Product Datasheet



SpectraSyn™ 40

Polyalphaolefin (PAO) Fluid

Product Description

SpectraSyn™ High Viscosity Polyalphaolefin (PAO) basestocks feature low temperature properties (pour point and viscosity), low volatility, and improved thermal stability. SpectraSyn™ High Viscosity PAO products high viscosity indicas translate into improved flow at low temperatures and increased film thickness at high temperatures. SpectraSyn™ High Viscosity PAO basestocks are particularly suited for industrial oils requiring high stability under extreme operating conditions. SpectraSyn™ High Viscosity PAO products are frequently used in conjunction with lower viscosity fluids (PAO, mineral oils) as a viscosity booster to achieve a wide range of ISO VG industrial and automotive gear oils.

General

Availability ¹	<ul style="list-style-type: none"> • Africa & Middle East • Asia Pacific 	<ul style="list-style-type: none"> • Europe • Latin America 	<ul style="list-style-type: none"> • North America
Revision Date	• 08/10/2009		

Basics	Typical Value (English)	Typical Value (SI)	Test Based On
Specific Gravity (60.1°F (15.6°C))	0.850	0.850	ASTM D4052
Appearance (0°F (-18°C))	Bright & Clear	Bright & Clear	Visual
Color	< 0.5	< 0.5	ASTM D1500
Kinematic Viscosity			ASTM D445
212°F (100°C)	39.0 cSt	39.0 mm ² /s	
104°F (40°C)	396 cSt	396 mm ² /s	
32°F (0°C) ²	4840 cSt	4840 mm ² /s	
-4°F (-20°C) ²	40500 cSt	40500 mm ² /s	
Viscosity Index	147	147	ASTM D2270
Pour Point	-33 °F	-36 °C	ASTM D5950/D97
Flesh Point, COC	538 °F	281 °C	ASTM D92
Water	< 50 ppm	< 50 ppm	ASTM D6304
Refractive Index ² (77°F (25°C))	1.4680	1.4680	ASTM D1218
Total Acid Number	< 0.10 mg KOH/g	< 0.10 mg KOH/g	ASTM D974 (mod)

Flow	Typical Value (English)	Typical Value (SI)	Test Based On
Brookfield Viscosity ² (-15°F (-26°C))	102000 cP	102000 cP	ASTM D2983
Surface Tension ² (75°F (24°C))	31.5 dyne/cm	31.5 dyne/cm	ASTM D1331A

Thermal	Typical Value (English)	Typical Value (SI)	Test Based On
Density Correction Factor ²	6.05E-4 (g/cm ³)/°C	6.05E-4 (g/cm ³)/°C	ASTM D1250
Fire Point, COC ²	604 °F	318 °C	ASTM D92
Evaporation Loss ² (302°F (150°C), 22.0 hr)	0.4 wt%	0.4 wt%	ASTM D972
Evaporation Loss ² (401°F (205°C), 6.5 hr)	2.5 wt%	2.5 wt%	ASTM D972 (mod)
Vapor Pressure ² (392°F (200°C))	0.9 mm Hg	0.9 mm Hg	ASTM D2879

Performance	Typical Value (English)	Typical Value (SI)	Test Based On
Dielectric Constant ² (77°F (25°C))	2.15	2.15	ASTM D924
Dielectric Strength ²	38.9 kV	38.9 kV	ASTM D877

Solubility	Typical Value (English)	Typical Value (SI)	Test Based On
Aniline Point ²	319.3 °F	159.6 °C	ASTM D611

Additional Information

Technical White Mineral Oil, 21 CFR 178.3620(b)
National Sanitation Foundation (NSF) White book, category code H1, Lubricants with incidental food contact

Legal Statement

For detailed Product Stewardship information, please contact Customer Service.

10- Silicone oil RTV 615



GE Silicones

RTV615

RTV615 High Strength Transparent Silicone Rubber Compound

Product Description

RTV615 silicone rubber compound is clear liquid which cure at room temperature to high strength silicone rubber with the addition of curing agents. This two-component product is supplied with curing agent in matched kits which are designed for use at a convenient 10:1 ratio by weight.

The compound is clear and colourless. It is a low viscosity, easily pourable liquid with nominal viscosity ranging between 3000 and 7000 cps.

RTV615 silicone rubber compound has been used for protection of electronic components and assemblies against shock, vibration, moisture, ozone, dust, chemicals, and other environmental hazards by potting or encapsulation of the components and assemblies.

The optical clarity of this silicone rubber compounds suggests evaluation for applications such as potting solar cells for maximum light transmission and electronic assemblies where component identification is necessary or desirable.

Key Performance Properties

- Convenient 10:1 mixing ratio for use in automatic dispensing or hand operations
- Low viscosity allows easy flow in and around complex parts, providing excellent electrical insulation and shock resistance
- Cure rate can be accelerated by heat
- Will cure in deep sections or enclosed assemblies without exotherm and with low shrinkage
- Chemical composition contains no solvents for ease of use on production lines
- Reversion resistance and hydrolytic stability permit use in high humidity environments at elevated temperatures
- Clarity permits visual inspection for easy identification and repair of encapsulated parts
- Retention of elastomeric properties at temperatures up to 204 °C

11- Aliphatic urethane diacrylate CN991



Technical data sheet

CN991

October 2008

DESCRIPTION

CN991 is an *aliphatic urethane diacrylate* for use in ultra violet and electron beam curing compositions. This product offers the following key properties to your formulations :

- excellent weatherability
- good abrasion resistance
- good chemical resistance

CN991 is particularly suitable for the following applications :

- outdoor applications
- screen inks
- plastic coatings
- metal coatings

SALES SPECIFICATIONS

Viscosity (mPa.s at 25°C)	6 000 – 12 000
Maximum colour (Pt/Co)	100

TYPICAL PROPERTIES

Appearance	Clear liquid
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RECOMMENDATION FOR USE

To achieve application viscosity and to influence film properties, it is suggested that CN991 is modified with an appropriate blend of monomers and/or oligomers. In formulations for UV curing applications, a suitable photoinitiator system must be incorporated.

Further information and technical advice on formulating UV and EB coatings can be obtained by contacting us.

SHELF LIFE STABILITY

These products should be used within 6 months of receipt for optimum product results. Inhibitors, such as MEHQ, have been added to enhance shelf life stability in the presence of air.

STORAGE

These materials can polymerize under improper storage conditions. To avoid polymerization and to standardize the properties of the products, the following precautions are necessary :

- store materials away from direct sunlight and the presence of oxidizing agents and free radicals : use baked phenolic lined carbon steel drums or opaque, dark coloured polyethylene lined drums. Caution : head space should be present in storage containers to support the oxygen requirements of the inhibitor,
- store drums at temperatures above 10°C and below 35°C. Recommended bulk storage temperatures should remain within the 15-27°C range.

HEALTH AND SAFETY

Particular care should be taken to prevent contact of CN991 with the skin or eyes. If CN991 does contact the skin or clothing, remove contaminated clothing and wash affected area thoroughly with soap and water for at least 15 minutes. Seek medical attention.

Full health and safety data sheets in accordance with EEC regulations are available on our web site www.sartomereurope.com

12- Epoxy urethane diacrylate CN109

	<h2>Technical data sheet</h2>						
<h3>CN109</h3>							
<p>December 2003</p>							
<h4>INTRODUCTION</h4>	<h4>SHELF LIFE STABILITY</h4>						
<p>CN109 is a thixotropic modified epoxy acrylate oligomer for use in UV and EB curing compositions. High reactivity, chemical resistance and film hardness make it a useful component in varnish formulations for wood coatings.</p>	<p>These products should be used within 6 months of receipt for optimum product results. Inhibitors, such as MEHQ, have been added to enhance shelf life stability in the presence of air.</p>						
<h4>SALES SPECIFICATION</h4>	<h4>CONDITIONS OF STORAGE</h4>						
<table border="0"> <tr> <td>Viscosity (Pa.s 25°C)</td> <td style="text-align: right;">23 - 26</td> </tr> <tr> <td>Maximum acid value (mg KOH/g)</td> <td style="text-align: right;">2</td> </tr> <tr> <td>Maximum colour (Gardner)</td> <td style="text-align: right;">2</td> </tr> </table>	Viscosity (Pa.s 25°C)	23 - 26	Maximum acid value (mg KOH/g)	2	Maximum colour (Gardner)	2	<p>Store in baked phenolic lined carbon steel drums, opaque or dark coloured polyethylene lined drums. Caution : Head space should be present in storage containers to support the oxygen requirements of the inhibitor.</p>
Viscosity (Pa.s 25°C)	23 - 26						
Maximum acid value (mg KOH/g)	2						
Maximum colour (Gardner)	2						
<h4>TYPICAL PROPERTIES</h4>	<h4>STORAGE HAZARDS & SAFETY PRECAUTIONS</h4>						
<table border="0"> <tr> <td>Appearance</td> <td style="text-align: right;">Clear, viscous liquid</td> </tr> <tr> <td>Flash point (closed cup °C)</td> <td style="text-align: right;">> 100</td> </tr> </table>	Appearance	Clear, viscous liquid	Flash point (closed cup °C)	> 100	<p>These materials can polymerise under improper storage conditions. Store material away from direct sunlight and the presence of oxidizing agents and free radicals. Storage temperatures should not exceed 35°C.</p>		
Appearance	Clear, viscous liquid						
Flash point (closed cup °C)	> 100						
<h4>RECOMMENDATION FOR USE</h4>	<h4>STORAGE TEMPERATURE</h4>						
<p>To achieve application viscosity and to influence film properties such as hardness, it is suggested that CN109 is modified with suitable monomers, oligo(ether) acrylates and blends thereof. In formulations for UV curing applications, a suitable photoinitiator system must be incorporated.</p>	<p>Store drums at temperatures above 10°C and below 35°C. Recommended bulk storage temperatures should remain within the 15-27°C range. These precautions are necessary to standardise the properties of the product and to avoid premature polymerisation.</p>						
<p>Further information and technical advice on formulating ultra violet and electron beam coatings can be obtained by contacting us.</p>	<h4>HEALTH AND SAFETY</h4>						
	<p>Particular care should be taken to prevent contact of CN109 with the skin or eyes. If CN109 does contact the skin or clothing, remove contaminated clothing and wash affected area thoroughly with soap and water for at least 15 minutes. Seek medical attention.</p>						
	<p>Full health and safety data sheets in accordance with EEC regulations are available on our web site www.sartomereurope.com</p>						

13- Collected informations of polymers CN991, CN109 and CN2035 polyester acrylate

Specialty Oligomers SARTOMER

CN991
Aliphatic Urethane Diacrylate

Aliphatic Urethane Acrylates

Suggested Applications
Outdoor applications
Industrial coatings
Inks

Features
Excellent weatherability
Low viscosity
Good flexibility

Typical Properties

Functionality	2
Viscosity @ 25°C	9 Pa.s
Colour	100 Pt/Co max
Molecular weight	1500 g/mol

Film Properties

Young modulus	13 MPa
Elongation at break	15%
Tensile strength	1.5 MPa
Tg	15°C

Specialty Oligomers SARTOMER

CN109
Epoxy Acrylate

Epoxy Acrylates

Suggested Applications
Wood coatings

Features
Recommended to help controlling rheology of coatings

Typical Properties

Functionality	2
Viscosity @ 25°C	25 Pa.s
Colour	2 Gardner max
Acid value	2 mg KOH/g max
Molecular weight	900 g/mol

Film Properties

Young modulus	1700 MPa
Elongation at break	7%
Tensile strength	46 MPa

Specialty Oligomers SARTOMER

CN2035
Polyester Acrylate

Polyester Acrylates

Suggested Applications
Offset inks
Coatings

Features
Adhesion to plastics
Good pigment wetting
PETIA free

Typical Properties

Functionality	2
Viscosity @ 25°C	95 Pa.s
Colour	2 Gardner max

Film Properties

Young modulus	600 MPa
Elongation at break	10%
Tensile strength	14 MPa
Tg	30°C

RÉSUMÉ

Fabrication de microcapsules par émulsification sans tensioactif

Cette thèse présente un nouveau procédé de fabrication de microcapsules basé sur l'émulsification de fluides non miscibles, sans utilisation de tensioactif. Les seules conditions sont des énergies interfaciales favorables, un rapport de viscosité proche de 1 entre la phase interne (phase 1) et le fluide qui sert à faire la coque (phase 2), et un rapport de viscosité entre ce fluide (phase 2) et la phase externe (phase 3) qui est également proche de 1.

Dans ce travail, nous avons fabriqué des capsules avec un cœur qui est une solution aqueuse d'alginate de sodium ou qui est une huile polyalphaoléfine 40. La coque est fabriquée à partir d'un polymère aliphatique ou époxyuréthane acrylate liquide qui est ensuite réticulé par irradiation au rayon UV. Ces capsules sont dispersées dans une solution aqueuse. Nous nous concentrons sur la synthèse de ces microcapsules.

Dans un premier temps, nous caractérisons les propriétés physiques des fluides qui sont utilisés pour faire les émulsions : densité, tension interfaciale, viscosité en fonction de la vitesse de cisaillement. Ensuite, nous déterminons expérimentalement le diagramme de fragmentation des émulsions simples et doubles en faisant varier les rapports de viscosité et les vitesses de cisaillement. Nous trouvons qu'il existe un rapport de viscosité optimal η_1 / η_2 entre les phases 1 et 2 : ce rapport vaut 0,8, proche de 1. Nous constatons également que pour la double émulsion le rapport de viscosité optimal η_2 / η_3 entre les phases 2 et 3 vaut 1.24, également proche de 1. Nous présentons des images de microscopie et des vidéos de la fragmentation des gouttelettes d'émulsion double pour les deux types de capsules.

Nous avons utilisé le gonflement osmotique des capsules pour étudier la polymérisation de la coque d'acrylate et nous montrons comment ce gonflement dépend du temps d'exposition aux UV et de la concentration en initiateur. Nous caractérisons les microcapsules en mesurant leur distribution de tailles. Nous déterminons l'efficacité de l'encapsulation pour les deux types de capsules. Dans le cas des capsules à cœur aqueux, l'efficacité de l'encapsulation est de 70%. Cette perte d'efficacité est due au fait que la tension interfaciale entre les phases 1 et 3 est nulle. Dans le cas des capsules à cœur huileux, ce taux est de 100%. Cette stabilité de la double émulsion était due à la tension interfaciale élevée entre le cœur huileux (phase 1) et le glycérol (phase 3). Enfin, nous présentons quatre méthodes qui permettent de déclencher la rupture des capsules et la libération du matériau encapsulé. Ces méthodes utilisent différentes propriétés chimiques ou physiques du matériau encapsulé et de la coque.

MOTS CLÉS

Émulsion, énergie interfaciale, viscosité, sans tensioactif, agitateur suspendu, polymère polymérisable aux UV, microcapsules, système de rhéologie optique, pression osmotique, efficacité, encapsulation.

ABSTRACT

Fabrication of Microcapsules through Surfactant-Free Emulsification

This thesis presents a new process for the fabrication of microcapsules which is based on emulsification of non-miscible fluids, without using any surfactant. The only requirements are favorable interfacial energies, a viscosity ratio close to 1 between the inner phase (phase 1) and the liquid polymer that is used to make the shell (phase 2), and a viscosity ratio close to 1 between this liquid polymer (shell, phase 2) and the outer phase (phase 3).

In this work, we designed capsules with a core made either of an aqueous solution of sodium alginate or of poly alpha olefin 40 oil. The shell is made of a free radical cross linkable aliphatic or epoxy urethane acrylate liquid polymer. These capsules are dispersed in an aqueous solution. We focus on their synthesis.

In a first step, we characterize the physical properties of the fluids that are used to make the emulsions: density, interfacial tension and viscosity vs shear rate. Next, we determine experimentally the fragmentation diagram for single and the double emulsions by varying the viscosity ratios and the shear rates. We find that there is an optimum viscosity ratio η_1/η_2 between phase 1 and 2: this ratio= 0.8, which is close to 1. We also find that for the double emulsion the optimum viscosity ratio η_2/η_3 between phase 2 and 3 = 1.24, which is close to 1. We present microscope images and movies of the fragmentation of double emulsion droplets for both types of capsules.

We used osmotic swelling to study the polymerization of the acrylate shell and we show how it depends on UV exposure time and initiator concentration. We characterize the microcapsules by measuring their size distribution. We determine the encapsulation efficiency for both types of capsules. In the case of capsules with an aqueous core it is 70%. This loss of efficiency is due to the fact that phase 1 and phase 3 have no interfacial tension since they are chemically identical. In the case of capsules with an oil core, it is 100%. This stability of the double emulsion originates from the high interfacial tension between the oil core (phase 1) and the glycerol (phase 3). Finally, we present four methods that make it possible to trigger the rupture of the capsules and the release of encapsulated material. These methods use different chemical or physical properties of the encapsulated material and of the polymer shell.

KEYWORDS

Emulsion, Interfacial Energy, Viscosity, Surfactant- Free, Overhead stirrer, UV curable polymer, Microcapsules, Optical rheology system, Osmotic pressure, Efficiency, Encapsulation