Stellingen

1. De conclusies die Poncelet trekt uit de berekeningen gedaan aan de hand van zijn model van wandgroei bij microcapsules, zijn, bij gebrek aan goede waarden voor de parameters, in tegenspraak met de conclusies die volgen uit experimenten. 
dit proefschrift

2. De membraandikte is proportioneel aan de hoeveelheid monomeer dat beschikbaar is en niet evenredig met de wortel van de amine concentratie.
dit proefschrift

3. Het verdient aan beveling de doorlaatbaarheid van membranen, toegepast als wand van microcapsules, en de invloed van procescondities te meten aan vlakke membranen in plaats aan microcapsules.
dit proefschrift

4. Mathiowitz concludeert dat de doorlaatbaarheid van membranen met cross-links lager is dan voor membranen zonder cross-links. Dit is niet het geval.
dit proefschrift

5. Niet de reactiesnelheid maar het massatransport is de limiterende factor bij de vorming van polymeer membranen door grensvlak polycondensatie.
dit proefschrift

6. Het gebruik van ionwisselende membranen in electrolyse cellen moet indien mogelijk voorkomen worden.

8. Het wetsartikel over het zelfstandig uitvoeren van een promotieonderzoek moet zodanig uitgebreid worden met de bepaling dat de aanstelling van een assistent-in-opleiding geschiedt bij een vakgroep die gespecialiseerd is op het onderzoeksonderwerp.

9. In de huidige samenleving is een rechtsbijstandverzekering onontbeerlijk bij het verkrijgen van een rechtsmatige afhandeling in geval de tegenpartij een financieel draagkrachtige organisatie vertegenwoordigt. Dit getuigt niet van gelijkberechtiging.

10. De aantrekkingskracht van een sport is niet afhankelijk van de mate van activiteit op het speelveld maar van de spanning die deze activiteit met zich meebrengt.

11. Het gebruiken van citaten als stelling bij een proefschrift is niet verantwoord.

12. Het bezitten en gebruiken van klassieke automobielen moet gesubsidieerd worden.
Encapsulation and membrane formation by interfacial polycondensation - Léon Janssen

559089

TR diss 2124
ENCAPSULATION AND MEMBRANE FORMATION
BY INTERFACIAL POLYCONDENSATION

Proefschrift

Ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van de Rector Magnificus, prof. drs. P.A. Schenck, in het openbaar te verdedigen ten overstaan van een commisie, aangewezen door het College van Dekanen, op 30 oktober, 1992 te 19.00 uur

door
Leonard Johannes Joseph Maria Janssen
geboren te Geldrop

Scheikundig Ingenieur
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Rerum cognoscere causas

4.1. Introduction

4.2. Experiments

4.2.1. Analysis

4.2.2. Wall thickness

4.2.3. Hydrolysis experiments

4.3. Results

4.3.1. GC analysis

4.3.2. Wall thickness as a function of time

4.3.3. Influence of the process conditions on the wall properties

4.3.4. Hydrolysis of TDC

4.4. Discussion

4.4.1. Wall formation

4.4.2. Wall thickness during encapsulation

4.4.3. The effect of $C_{a,tdc}/C_{a,dena}$ on the polymer properties

4.4.4. Hydrolysis of encapsulated TDC

4.5. Conclusions

4.6. References

5. MICRO ENCAPSULATION: THE INFLUENCE OF THE PROCESS CONDITIONS ON THE WALL PERMEABILITY

5.1. Introduction

5.2. Theory

5.2.1. Models to describe the capsule wall formation

5.2.1.1. Model 1: diffusion with a constant flux of water

5.2.1.2. Model 2: diffusion with a flux of water depending on the amine flux

5.2.2. Addition of diamine to the aqueous phase

5.2.3. Effect of crystallinity

5.2.4. Effect of cross-linking

5.3. Experimental

5.3.1. Production of uniform droplets

5.3.2. Production of micro capsules

5.3.3. Process conditions
5.3.4. Permeability measurements
5.4. Results & discussion
5.4.1. Concentration measurements
5.4.1.1. The influence of the organic phase
5.4.1.2. Influence of addition of diamine to the aqueous phase
5.4.2. Thickness measurements
5.4.2.1. The influence of the organic phase
5.4.2.2. The influence of addition of EDA to the aqueous phase
5.4.3. Assessment of both models
5.4.4. Permeability measurements
5.4.5. Comparison of diffusion coefficient calculated from concentration, thickness and permeability measurements
5.5. Conclusions
5.6. References

6. MEMBRANE PERMEABILITY AND GROWTH
6.1. Introduction
6.2. Permeability measurements
6.2.1. Experimental
6.2.1.1. Production of polyterephthalamide membranes
6.2.1.2. Diffusion measurements
6.2.1.3. Thickness measurements
6.2.1.4. Characterisation of membranes by DSC, FTIR, WAXS
6.2.2. Results & discussion
6.2.2.1. Influence of $C_{tdc}/C_{deta}$
6.2.2.2. Addition of diamines
6.2.2.3. Characterisation
6.2.2.4. NaCl release from micro capsules
6.2.3. Conclusions
6.3. Growth measurements by light microscopy
6.3.1. Experimental
6.3.1.1. Growth measurements
6.3.1.2. Process conditions
6.3.2. Results & discussion
6.3.2.1. Model for wall growth
6.3.2.2. Growth versus time
6.3.2.3. Influence of $C_{tdc}/C_{deta}$
6.3.2.4. Addition of diamines 71
6.3.2.5. Influence of the organic phase 71
6.3.3. Conclusions 72
6.4. The early stage of wall growth by light transmission microscopy 72
6.4.1. Experimental 73
6.4.1.1. Experimental setup 73
6.4.1.2. Absorbance measurements 73
6.4.2. Results & discussion 74
6.4.2.1. Growth of the membrane, absorbance versus time 74
6.4.2.2. Influence of $C_{tdc}/C_{deta}$ 76
6.4.2.3. Addition of diamine 76
6.4.2. Effect of diamine 76
6.4.3. Conclusions 78
6.5. Discussion membranes & micro capsules 78
6.6. References 79

7. MICROENCAPSULATION OF A WATER-IN-OIL EMULSION 80
7.1. Introduction 80
7.2. Theory for the growth of the capsule wall 80
7.2.1. The growth of the capsule wall for TDC/DETA micro capsules 81
7.2.1.1. Model 1: the constant flux of water 81
7.2.1.2. Model 2: the flux of water proportional to the flux of amine 83
7.2.3. The growth of the capsule wall for TDC/DETA/EDA microcapsules 84
7.2.3.1. Model with a constant flux of water; EDA/DETA 84
7.2.3.2. A model for a flux of water proportional to the flux of amine; EDA/DETA 86
7.3. Experimental 87
7.3.1. Introduction 87
7.3.2. Production of micro capsules 87
7.3.3. Process conditions 88
7.3.4. Thickness measurements 88
7.4. Results and discussion 88
7.4.1. Concentration calculations 88
7.4.2. Influence of addition of diamines to the aqueous phase 91
7.4.3. Influence of the diamine/trichloride ratio 94
7.4.4. Assessment of both models 95
7.5. Comparison with o/w capsules 96
7.6. Conclusions 97
7.7. References 97

8. GENERAL CONCLUSIONS 98

Summary 101

Samenvatting 104

Symbols 107

Curriculum Vitae 110

Dankwoord 111
CHAPTER 1

INTRODUCTION

1.1. OBJECTIVES

Micro encapsulation is the envelopment of small particles, liquid droplets or gas bubbles with a coating and a size between 1 and 1000 µm. Micro capsules can be used as one of several polymeric controlled release systems [1]. Within the core of the micro capsule a component is present which can be released at a certain moment (e.g. carbon black in copying paper) (release control) or with a certain release rate (e.g. pesticides, medicines) (transfer control).

The coating is made of e.g. polysaccharide, protein, cellulose ether, (cross-linked) polymers, glycerides. The processes of encapsulation are e.g. spray drying, polymer–polymer phase separation, in-situ polymerisation, interfacial polymerisation [2]. The encapsulation of a liquid phase by interfacial polycondensation is an easy to manage production process. An emulsion of e.g. an organic phase in an aqueous phase produces a coating of polymer by polycondensation which occurs at and near the interface [3].

In case of transfer control the coating of the micro capsules acts like a membrane. This enables the micro capsules to control the release rate of an encapsulated compound. The release rate is determined by the structure [4,5] and composition [6] of the membrane.

The diffusion of a compound through a polymer membrane depends on the structure of the membrane and the compound to membrane interactions. The various types of diffusion can be ascertained by comparing the rate of diffusion to the rate of rearrangement of polymer molecules. This can be done by the diffusion Deborah number [7]. The diffusion Deborah number is defined by the ratio of the characteristic time of the fluid (\(\lambda_m\)) and the characteristic time of the diffusion process (\(\phi_0\)). For large values of the diffusion Deborah number, there is no variation of the polymeric structure during the diffusion process. The diffusing solvent molecule moves in a material which appears to have properties of an elastic solid. For small values of the diffusion Deborah number, the molecular relaxation process is fast compared to the diffusive transport. The polymer and solvent behave like viscous fluids [7]. The fraction of crystalline phase [8] and the cross-link density [9,10,11] affect the diffusion of solvent through a polymer.
The process of interfacial polycondensation in relation to micro encapsulation and to membrane formation is studied. This thesis is focused at the mechanism and kinetics of the formation of the membrane (wall) and the influence of the process conditions on the permeability of the capsule wall and the membranes. The kinetics of the formation of the membrane wall is described by a model, which relates the decrease of the core monomer (diacid chloride (o-i-w emulsion) or an amine (w-i-o emulsion)) and the increase of the wall thickness with time to the diffusion of one monomer (amine) through the growing membrane. The model is evaluated by concentration and thickness measurements. The membrane structure, studied with SEM, shows the existence of macro voids for which the model is extended to describe the formation of pores within the capsule walls.

1.2. SCOPE OF THIS THESIS

The interfacial polycondensation of an acid chloride, dissolved in a phthalate ester, and an amine, dissolved in water, is applied to three systems: 1) encapsulation of an oil-in-water emulsion, 2) production of a flat membrane and 3) encapsulation of a water-in-oil emulsion.

In chapter 2 the process conditions and the process of interfacial polycondensation is discussed. The mechanism of the interfacial polycondensation, the polycondensation reaction, the kinetics of the reaction and side reactions are discussed. The effect of process conditions on the formation of capsules and the geometry independence of the process of membrane formation are shown. The quantities which determine the diffusion process and the rate of diffusion in relation have been reviewed and related to the process conditions during the polycondensation. In addition, a model which describes the process of polycondensation during micro encapsulation and membrane production is reviewed.

Chapters 3 and 4 deal with the model for encapsulation in case of the production of macro capsules (diameter of 1 to 5 mm), the influence of hydrolysis during encapsulation, the analysis of the core and wall thickness. It is also shown how the process conditions can influence the permeability of the membrane of macro capsules.

In case of micro encapsulation (diameter 1 to 1000 µm), as shown in chapter 5, the model is extended to describe the formation of macro voids within the membrane by two means: 1) the macro voids are produced as a result of a constant flux of water which is incorporated within the membrane, 2) the macro voids are the result
of hydrational water which is transported with amine. The production of uniform sized droplets and the consecutive formation of micro capsules is discussed. The influence of the organic phase and the addition of diamines to the solution of triamine on the permeability of the membrane is shown.

Chapter 6 deals with the permeability of flat membranes to NaCl in relation to the process conditions. Methods to characterize the cross-link density and the fraction of crystallites of the membranes are discussed. The growth of the flat membranes is studied by microscopy and the early stage of membrane formation measured with light transmission is presented.

Chapter 7 discusses the influence of the inversion of the phases on the model for micro encapsulation and the influence of the process conditions on the permeability of the micro capsule membranes in case of the reverse encapsulation system: water-in-oil emulsion.

1.3. REFERENCES

CHAPTER 2

MEMBRANE FORMATION BY INTERFACIAL POLYCONDENSATION

2.1. INTRODUCTION

According to Arshady [1], interfacial polycondensation involves the condensation polymerization of two monomers (e.g., acid chloride and amine) each soluble in one phase of a two-phase system. The polycondensation reaction begins at the interface, as each of the monomers is present in only one of both phases. The initial place of polymerization is at, or on one side of, the interface, which depends on the partition coefficients of both monomers in a two-phase system. Wittbecker and Morgan [2] and Morgan and Kwolek [3] were the first to describe the principles of interfacial polycondensation. The production of polyamide by interfacial polycondensation was described by Beaman et al. [4].

The formation of micro capsules by interfacial polycondensation was first described by Chang [5]. The process of interfacial polycondensation can be used to produce solid (monolithic) or hollow (reservoir) type microspheres. The latter is frequently used for the production of micro capsules containing proteins or pharmaceuticals [6].

2.2. SYSTEM & REACTANTS

The polycondensation starts and proceeds at and near the interface of two immiscible liquids: 1) an organic phase in which an acid chloride is dissolved, 2) an aqueous phase in which an amine is dissolved in combination with NaOH.

In the present study the organic phase is dimethyl-, diethyl- or dioctylphthalate (DMP, DBP and DOP) in which terephthaloyldichloride (TDC) is dissolved. The aqueous phase is a solution of NaOH and diethylenetriamine (DETA) in water, or a solution of NaOH and DETA and ethylenediamine (EDA) or hexamethylenediamine (HMDA). During the polycondensation HCl is produced which reacts with the -NH₂ group to form -NH₃⁺; since the mechanism of the reaction with TDC is S_N² (see reaction (a) in chapter 3 and Wittbecker and Morgan [2]) the reaction cannot proceed with all the amine groups protonated. To neutralize the HCl NaOH is added.

4
2.3. INTERFACIAL POLYCONDENSATION

2.3.1. Mechanism

The mechanism of polymer formation by interfacial polycondensation is described by Morgan and Kwolek [3]. When an organic solution of diacid chloride is brought into contact with an aqueous solution of diamine, polymer is produced by the reaction of diacid chloride with the diamine. The relatively higher tendency of diamines to transfer into the organic phase rather than diacid chlorides to transfer into the aqueous phase causes the polycondensation to take place in the organic phase near the interface.

As the polycondensation proceeds, the concentration of oligomers increases until the oligomers couple to produce polymer which precipitates. The period in which the polymer chains are not precipitated depends on the interaction of the polymer and the solvent.

After the formation of the first polymer film the rate of polycondensation is strongly reduced. There is a secondary growth of polymer of lower molecular weight at the organic side of the interface.

These three steps of membrane formation by interfacial polycondensation are described by Arshady [1] to be: 1) the initial period of polycondensation; polymer is produced but not yet precipitated, 2) the formation of a primary membrane; the polymer precipitates and 3) the subsequent growth of the membrane; polymer formation and precipitation by diffusion of amine through the primary membrane.

This reaction scheme is confirmed by work of Hodnett [7], MacRitchie [8], Enkelmann and Wegner [9-11], Nikonov and Savinov [12] and P.L. Madan [13].

2.3.2. Reaction

The reaction between a diacid chloride and a diamine is an example of a Schotten-Baumann reaction; the reaction takes place by an $S_n^2$ mechanism. At first a protonated amide is produced, which rapidly eliminates the proton to a proton acceptor (usually a base added to the aqueous phase). This process produces a polyamide and the salt of the base and HCl, which is produced during the polycondensation. Beaman et al. [4] give examples which show that the structure and properties of the reactants are not limiting the process of polycondensation. Both diamine and diacid chloride may be aliphatic, alicyclic or aromatic and have a long or short chain. Also the production of polyamides having functional groups is possible by interfacial polycondensation [14]. Morgan et al. [3] describe optimum conditions to produce high molecular weight polymer. The optimum concentration
ratio hexamethylenediamine/sebacoyl chloride is about 6.5 for \( \text{CCl}_4 \) as organic solvent. Solvents which decrease the partition coefficient of the diamine reduce the optimum concentration. Mathiowitz reports [31] in the production of micro capsules an amine/chloride ratio of 15 or 30 to obtain micro capsules which behave like free flowing powders. Furthermore, the polymer produced by Morgan was continuously drawn from the interface, whereas in producing micro capsules this is not the case. This strongly influences the concentration at the site of reaction.

2.3.3. **Kinetics of polycondensation**

The polycondensation reaction of diacid chloride and diamine is very fast. Bradbury et al. [15] studied the reaction between TDC and piperazine. Precipitation of polymer at the interface affects the rates of transport of reactants to the zone of reaction. This effect is minimized by using low concentration of both TDC and piperazine (\( 10^{-2} - 10^{-6} \) M), thus producing only small amounts of polymer. The rate of consumption of TDC by the polyamidation reaction is first order with respect to TDC.

2.3.4. **Side reactions**

Except for the Schotten-Baumann reaction between the diacid chloride and the diamine, other reactions are the hydrolysis of the diacid chloride [16-18] and the formation of diamine hydrochlorides [19]. It was shown that hydrolysis of the acid chloride groups is the basic chain termination reaction in interfacial polycondensation [16]. Crawford and Bradbury [17] describe the hydrolysis of TDC under conditions where little polymer is produced. It was shown that hydrolysis takes place in the aqueous phase. Sokolov and Nikonov [18] describe the effect of a hydrolyzing agent on the polymer composition and conclude that it depends on the relative intensity of the hydrolysis with respect to the reaction rate of diacid chloride and diamine. The formation of diamine hydrochlorides is neutralized by a strong HCl acceptor in the aqueous phase [18, 19].

2.3.5. **Capsule formation**

Micro capsules produced by interfacial polycondensation are usually made from an emulsion. An emulsion of the core material is made by stirring, which is followed by the addition of e.g. diamine to the continuous phase. The interfacial polycondensation starts and micro capsules are produced [1, 21-26, 30]. Kondo et al. [27-28] studied the effects of polycondensation conditions on the characteristics of micro capsules. The effect of the organic phase (the partition coefficient of
the diamine), the addition of Span 85 and the stirring speed on the micro capsule diameter and the micro capsule diameter distribution are studied. By an increase of the stirring speed or of the Span 85 concentration capsules are produced with a more narrow diameter distribution. An increase of the mean capsule diameter with stirring speed was also reported by Dietrich et al. [29].

2.4. MEMBRANE FORMATION

Enkelmann [10] used the interfacial polycondensation of hexamethylene diamine and sebacoyl chloride to produce membranes, which can be used in dialysis, osmosis and reverse osmosis processes. The mechanism of membrane formation was studied by measuring the membrane thickness as a function of time [9–11]. Cadotte et al. [20] used interfacial synthesis in preparing reverse osmosis membranes as desalination membranes. On a microporous polysulfone support a membrane of polyethylene imine or piperazine and isophthaloyl chloride is produced. The interfacial polycondensation process can be used to produce membranes at the interface of two immiscible liquids. This process is essentially equal for different geometries of the interface. The geometry of the interface determines whether membranes (flat interface) or micro capsules (spherical interface, oil-in-water or water-in-oil capsules) are produced.

2.5. DIFFUSION THROUGH MEMBRANES

The release of encapsulated compounds is controlled by the membrane properties of the capsule wall and the interactions of the polymer and the release compound. The role of the polymer permeability is reviewed by Richards [32]; it is characterized by the type of membrane, viz. 1) non-porous, 2) microporous or 3) hydrogel membranes.

In case of non-porous membranes Peppas et al. [33,34] describe that the diffusion coefficient of the solute depends on the swelling of the polymer, the cross-link density and the size of the solute. The diffusion takes place through the matrix of the polymer.

The diffusion in microporous membranes mainly takes place through the pores within the membranes. According to Siegel [35] the diffusion through the matrix of the polymer can be neglected with respect to the diffusion through the pores. The
effective diffusion coefficient ($D_{eff}$) can be described as:

$$D_{eff} = D_{lw} \left( \frac{\varepsilon K_p}{\tau} \right)$$  \hspace{1cm} (2.1)

where $D_{lw}$ is the diffusion coefficient of the solute in water, $\varepsilon$ is the porosity of the membrane, $\tau$ is the tortuosity of the pores and $K_p$ is the partition coefficient of the solute between the pores and the polymer matrix.

If the size of the solute ($r_s$) approaches the size of the pores ($r_p$) the effects of the pore wall become effective [35]. The Faxen theory is used to describe this process. Aruna and Sastri [37] corrected the Faxen equation into:

$$\frac{D_m}{D_{lw}} = \left( 1 - \lambda \right)^2 \frac{1 - 0.235 \lambda}{1 + 20.23 \lambda}$$  \hspace{1cm} (2.2)

with $D_m$ is the diffusion coefficient in the membrane and $\lambda$ is $r_s/r_p$.

Polyamide membranes are reported to be non-porous [31, 38] or microporous having pore diameters of 25 Å [37] or 18 Å [39].

2.6. CAPSULE MEMBRANE FORMATION MODEL

Poncelet describes a model for membrane formation for water-in-oil micro encapsulation [40]. This model takes into account protonation of neutral amine, which decreases 1) the concentration of amine available for the polycondensation and 2) the partition of neutral amine between the aqueous phase and the membrane, which both decrease the concentration gradient over the membrane. The flux of amine through the membrane is described by Ficks 1st law. Because of the complexity of the model no analytical solution was present. The membrane thickness as a function of time was calculated, which showed a decreased rate of membrane growth with time. The effect of the diamine diffusion coefficient, the solvent, the diamine concentration, the pH and temperature on the membrane formation was calculated according to the model assumptions.
2.7. REFERENCES


CHAPTER 3
MACRO ENCAPSULATION AND A MODEL FOR WALL GROWTH

3.1. INTRODUCTION

A characteristic property of micro capsules is their capability to control the release of an encapsulated compound (transfer control). The capsule wall acts as a membrane; its structure [1,2] and the material it consists of [3] influence the release characteristics of the encapsulated compound.

A model system is used to produce capsules by polycondensation of terephthaloyldichloride (TDC) and diethylenetriamine (DETA) at the interface of an oil-in-water emulsion [4] (Fig. 3.1 shows their chemical structures). The polymer envelopes the oil droplet (dibutylphthalate, DBP) and a capsule is formed. During the growth of the wall, the polymer layer acts like a membrane, which, as shown in Fig. 3.2 (photographs 1-3), consists of a dense top- and a porous sub layer. In the early stages of polymer production the dense top layer is formed, which is followed by the growth of a porous sub layer. The sub layer grows due to diffusion of amine molecules through the polymer wall into the oil phase, followed by reaction with TDC; this sub layer has an open cellular structure.

![Chemical structure of TDC and DETA](image)

Figure 3.1. The chemical structures of TDC (a) and DETA (b).

A model, which describes the relationship between the wall growth, the decrease of the TDC concentration inside the capsule and the diffusion of the amine through the wall, is presented. This chapter also describes the production device, the production of capsules, the wall structure and the analysis of the wall structure.
Figure 3.2. SEM photographs of cross sections of the capsule wall, which show the increase in pore size with maturation. Micrographs 1-3 are taken after 6, 25, and 60 min. of wall maturation respectively.

3.2. MODEL

3.2.1. Model for wall formation and wall growth in capsule production

The wall of the capsules consists of a polymer formed by a polycondensation reaction at the oil/water interface according to the reaction (a). At or close to
the organic side of the interface the reaction between TDC and DETA takes place and polymer precipitates at the interface [5]. Initially no polymer exists and the polycondensation, with a rate constant of \( k_r = 10^4 - 10^6 \text{ m}^3\text{skmol}^{-1} \), is limited by the transport rate of DETA molecules from the aqueous phase into the oil phase. This results in the production of a thin top layer of polymer. After the formation of this top layer in the oil phase, \( \text{H}_2\text{O} \) and NaOH diffuse into the polymer, so that the membrane swells with the aqueous phase. At the same time DETA diffuses through the polymer [5] into the oil phase; consequently DETA and TDC proceed reacting under the formation of the sub layer. HCl, which is formed in reaction (a), is neutralized by NaOH transported from the aqueous phase.

The formation of a capsule wall can be described by two stages: at first growth is limited by transfer of DETA molecules from the aqueous phase into the oil phase, whereas afterwards growth is limited by diffusion of DETA through the first layer of polymer. The diffusion of the smaller NaOH molecules through the polymer layer is faster than the diffusion of the larger DETA molecules, so the produced hydrochloric acid is neutralized immediately. The following model is proposed to describe the wall growth, after the formation of the top layer.

### 3.2.2. Model for polymer formation in capsules

A model for the capsule is drawn schematically in Fig. 3.3. The ratio of the wall thickness and the capsule diameter is only about \( 10^{-5}\text{m}/4\times10^{-3}\text{m} \approx 0.0025 \). This allows us to consider the capsule wall as a flat sheet. The final wall thickness is determined by the initial amount of TDC in the droplet as this determines the maximum amount of polymer which can be formed. The capsule diameter depends on process conditions.

By the following reaction polymer is produced inside the capsules:

\[
\text{TDC} + r_t \text{DETA} \rightarrow \text{polymer} + \text{HCl}
\]

(a)

In the case of \( r = 1 \) linear polymer will formed (then in the polymer the ratio of atoms \( C/N = 4 \)); in this case no cross-linking takes place. On the other hand, when \( r_t = 2/3 \), a network will be produced and \( C/N = 5.33 \) [6]; in that case also all secondary amine groups of the DETA molecules will react with the acid chloride groups of TDC. For all conditions \( (2/3 \leq r_t \leq 1) \) the reaction rate is determined by the diffusion rate of DETA through the produced polymer wall into the capsule. Ficks 1st law [7] is used to describe the mole transfer rate of DETA through the membrane wall (see Fig. 3.4). During encapsulation no hydrolysis of TDC by \( \text{H}_2\text{O} \)
Figure 3.3. The model of the capsule with enlarged the composition of the capsule wall (1 = top layer, 2 = sub layer) and the inner (3) and outer (0) phase.

Figure 3.4. Detail of the model of the capsule wall (top and sub layer) and the concentration gradients across the capsule wall.

takes place [8] and on the average $r_t$ molecules of DETA react with one molecule of TDC. The rate of decrease of the TDC concentration is proportional to the flux of DETA molecules into the capsule and to the area/volume ratio of the capsule (the capsule is assumed to be spherical). The mass balance of TDC over an oil drop, after the formation of a top layer with thickness $d_1$, yields the following relationship for the TDC concentration in a capsule as a function of time (with the
assumption that \( C_{01,\text{deta}} = C_{0,\text{deta}} \):

\[
- V_c \frac{\partial C_{3,\text{tdc}}(t)}{\partial t} = \frac{C_{0,\text{deta}} - C_{12,\text{deta}}(t)}{\rho_t d_1} D_{1,\text{deta}} A_c \tag{3.1}
\]

The left hand side of equation (3.1) is equal to the number of moles of TDC which react per unit of time, the right hand side indicates the product of the flux of DETA per unit of area into the capsule, the capsule surface area \( A_c \) and \( 1/\text{molar reaction ratio (1/}\rho_t) \).

With the assumption that no accumulation takes place between the top- and sublayer (the flux through the top layer is equal to the flux through the sub layer), and as \( C_{23,\text{deta}} = 0 \), we have:

\[
\frac{C_{0,\text{deta}} - C_{12,\text{deta}}(t)}{d_1} D_{1,\text{deta}} = \frac{C_{12,\text{deta}}(t)}{d_2(t)} D_{2,\text{deta}} \tag{3.2}
\]

Due to the transfer of DETA and the subsequent reaction with TDC the thickness of the sub layer \( d_2 \) will increase, thus decreasing the mass-transfer rate of DETA. The growth of \( d_2 \) is proportional to the molar flux of DETA and the molar volume \( V_{pol} = M_u/\rho_{pol} \) and inversely proportional to the reaction ratio \( (1/\rho_t) \) and volume fraction of polymer in the sub layer \( (\beta) \) of the polymer formed:

\[
\frac{\partial d_2}{\partial t} = \frac{C_{12,\text{deta}}(t)}{\rho_t d_2(t)} D_{2,\text{deta}} \frac{M_u}{\rho_{pol} \beta} \tag{3.3}
\]

\( \beta \) is the volume fraction of polymer in the porous sub layer, swollen with water, the top layer is considered to be homogeneous. From equation (3.2) \( C_{12,\text{deta}}(t) \) is obtained as a function of \( d_2(t) \), which can be substituted into equation (3.3). As \( r_t, D_{1,\text{deta}}, D_{2,\text{deta}}, M_u, \rho_{pol} \) and \( \beta \) are independent with \( t \), after integration with \( d_2 = 0 \) at \( t = t_1 \) we obtain:

\[
d_2(t) = - \frac{D_{2,\text{deta}}}{D_{1,\text{deta}}} + 2 \left( \frac{D_{2,\text{deta}}}{d_1 D_{1,\text{deta}}} \right)^2 + 2 \frac{d_{2,\text{deta}}}{D_{2,\text{deta}}} C_{0,\text{deta}} \frac{M_u}{\rho_t \rho_{pol} \beta} \left( t - t_1 \right) \tag{3.4}
\]

From equations (3.2) and (3.4) a relationship between \( C_{12,\text{deta}}(t) \) and time is obtained, which will be substituted into equation (3.1). Since \( C_{3,\text{tdc}}(t) = C_{3,\text{tdc}}(t_1) \) at \( t = t_1 \), integration yields:

15
\[ C_{3,tde}(t) = C_{3,tde}(t_1) - \frac{\varepsilon \rho_{pol} R}{d_e M_u} d_2(t) \] (3.5)

Equation (3.5) describes the change of the \( C_{3,tde}(t) \) inside the capsules as a function of the diffusion of DETA and of the increasing thickness of the sub layer of the wall. It has been found first that the change of the concentration of \( C_{3,tde}(t) \) is linear in \( \sqrt{t} \) for \( t \gg t_1 \) and secondly that \( t - t_1 \gg (D_{2,deta} d_1^2 r_t \rho_{pol} \beta)/(2 C_{0,deta} D_{1,deta} M_u) \).

3.3. EXPERIMENTAL

3.3.1. Materials

A solution of terephthaloyldichloride (TDC, Janssen Chimica) in dibutylphthalate (DBP, Merck) was prepared by stirring TDC and DBP at room temperature. A white precipitate (terephthalic acid, TDA) was removed over a glass filter (Pyrex P4, 10-16 \( \mu \)m). Diethylenetriamine (DETA, Janssen Chimica) and sodium hydroxide (NaOH, Merck) were dissolved in deionized water. All chemicals used were analytical grade.

3.3.2. Capsule production

Three solutions were used for the production of capsules:

- \( O_1 \): solution of TDC in DBP (0.1 - 1.0 kmol/m\(^3\))
- \( S_1 \): solution of DETA and NaOH in water (0.1 - 0.8 kmol/m\(^3\) DETA, 1.0 kmol/m\(^3\) NaOH)
- \( S_2 \): solution of NaCl in water (1.7 kmol/m\(^3\))

The diameter of the droplets produced at the needle tip was determined by the flow rate of \( O_1 \). The mean diameter varied between 3 and 5 mm depending on the flow rate.

3.3.3. Device

Micro capsules were prepared one at a time [9,10] in the apparatus shown in Fig. 3.5 [11]. A solution of NaOH and DETA in water (solution \( S_1 \)) was pumped through inlet \( W_1 \) into the reaction vessel with a tube pump (Masterflex). Simultaneously a solution of NaCl (solution \( S_2 \)) was pumped into the reaction vessel through inlet \( W_2 \) with the same volumetric flow rate as that of solution \( S_1 \) (5 \( \times \) 10\(^{-7} \) m\(^3\)/s). The oil solution was pumped through inlet \( O_1 \) passing a needle
(inside diameter = 0.25 mm) to form oil drops at the needle tip. The droplets rose due to the difference in the densities of the oil solution ($O_1$, the density of a 1.0 M solution is 1.09 g/ml) and the salt solution ($S_2$, the density is 1.13 g/ml) in the lower part of the reactor. In the top part of the reactor, above QQ, the oil droplets continued to rise because the mixture of solutions $S_1$ and $S_2$ had a higher density than the oil solution. In the top part of the reactor filled with the amine solution $S_1$ and the salt solution $S_2$ polycondensation of TDC and DETA at the interface started and proceeded to form capsules. The temperature of the aqueous solution in the top part varied between 20 and 22 °C.

![Diagram](image)

**Figure 3.5.** The device for the capsule production. The amine solution ($S_1$) enters through inlet $W_1$, the oil solution ($O_1$) through inlet $O_1$. Below QQ no amine is present in the inner tube and the wall production starts above QQ.

### 3.3.4. Analysis

At several time intervals samples (i.e. capsules) were taken to analyze the capsule contents (i.e. the TDC concentration) with a capillary gas chromatograph, the wall structure (with SEM) or the wall composition (with FTIR).
3.3.5. **Wall-structure**

By SEM photography (JEOL JSM-35) the structure and the thickness of the wall could be determined. For that purpose a capsule was frozen in liquid nitrogen and cut into two halves; then both halves were put into ethanol to remove the oil. To make SEM pictures of a cut cross section the capsule halves were frozen in water and with the aid of a microtome (Reichert-Jung, model 2700) thin slices were cut off at -20 °C. The result was a sharp cross-section at the remaining part by which it was possible to make SEM pictures of both the top and sub layer.

3.3.6 **Membrane sub layer porosity**

The volume of the capsule wall is the volume of the shell between the inner and outer boundary of the capsule wall. The factor $\beta$ is a correction factor for the presence of holes in the sub layer. The left hand side of Eq. (3.3) represents the thickness of the capsule wall whereas the right hand side is the product of the thickness of the polymer and the factor $\beta$. The fraction of polymer equals $\beta$ and the fraction of holes equals 1-$\beta$. The porosity of the capsule wall (= the fraction holes) was measured with an image analyzer. From pictures of a cut cross section of the capsule wall, the area of the holes within a frame was measured. The porosity is equal to the ratio of the holes area and the frame area.

3.3.7 **Light microscopy**

The growth of the membrane was studied with the aid of a light microscope. At one edge of a covering glass, which laid on top of an object glass, a drop of solution $O_1$ was put and at the opposite side a drop of solution $S_1$. As a consequence of the capillary forces both liquids flowed between the two glass plates and produced an interface, at which point a membrane was formed.

3.4 **RESULTS**

The capsules which were produced with the device shown in Fig. 3.5 varied in diameter due to a variation of the drop size. The drop size varied due to fluctuations in the oil flow. The cut cross area of a number of capsules was measured with an image analyzer, from which the capsule diameter was calculated. A characteristic distribution of the capsule diameter is shown in Fig. 3.6. This shows that capsules are formed with a mean diameter of 4.77 mm, a length/width ratio smaller than 1.05 and a standard deviation of $3.05 \times 10^{-2}$;
Figure 3.6. The characteristic distribution of capsule diameters of a batch of capsules. The deviation of the diameters is due to pump fluctuations.

90% of the capsule diameters are in a range of $4.52 \leq d \leq 5.04$ mm, so a narrow distribution has been obtained.

During maturation of the membrane capsule wall the pore size diameter increased. Photographs 1-3 in Fig. 3.2 show a cut cross section of the capsule membrane at increasing maturation times; from the top layer of the membrane into the capsule the pore sizes increase. This reveals that during the maturation the polycondensation takes place in the organic phase. Photo 1 was taken after 6 minutes of wall maturation, at which time the first pores were formed; the largest pore has a diameter of $5 \mu m$. Photo 2 shows the wall structure after 25 minutes of maturation; the maximum pore size is $20 \mu m$. After 60 minutes of maturation the maximum pore size increased to $27 \mu m$.

The experiments with a light transmission microscope showed that at the organic side of the membrane small drops appeared. The membrane, which is produced in the organic phase, will swell by the aqueous phase. When polymer is formed the volume of the oil phase decreases; as a consequence the capsules were filled with drops of the aqueous phase on the organic side of the wall. These drops tended to coalesce and to form larger drops; the coalescence stopped by precipitation of the polymer produced. As the membrane thickness increased, more drops coalesced and consequently larger drops were formed. Fig. 3.7 shows schematically the formation of the pores in the membrane sub layer. From the initial interface between the organic and aqueous phase in the organic phase larger drops were formed before the
polymer precipitated. It appears that the size of the drops determines the size of the holes in the membrane of photos 1-3 Fig. 3.2, since at longer maturation times larger holes were formed, as a consequence of the larger droplets formed.

Introduction of bifunctional amines (ethylenediamine EDA, hexamethylenediamine HEDA) in addition to or instead of DETA in the aqueous phase resulted in a different behaviour of the wall formation, because of the lower degree of cross-linking. Measurements with the light microscope did not show the formation of droplets.

\[
\begin{array}{c}
\text{toplayer} \\
(a)
\end{array} \quad \begin{array}{c}
\text{sublayer} \\
(d)
\end{array}
\]

\[
\begin{array}{c}
\text{sublayer} \\
(c)
\end{array} \quad \begin{array}{c}
\text{toplayer} \\
(b)
\end{array}
\]

**Figure 7. Schematic growth of the sub layer.**

a) **After the formation of the top layer small drops appear at the organic side of the membrane.**

b) **Due to polymer precipitation at the drop/oil interface small pores of the size of the droplets are formed.**

c) **As the membrane thickness increases, the rate of polymer formation decreases. Consequently larger drops are formed as a result of the longer coalescence time.**

d) **Polymer precipitation at the drop/oil interface of the larger drops causes larger holes to be formed.**

According to the model described, the concentration of TDC inside the capsule is given by:

\[
A(t) = a \left[ -b + \sqrt{b^2 + c(t - t_1)} \right]
\]  \hspace{1cm} (3.6)

where \( A(t) = C_{tdc}(t_1) - C_{tdc}(t) \)
\[ a = \frac{6 \rho_{\text{pol}} \beta}{d_\text{c} M_u} \]  
\[ b = \frac{d_\text{e}}{D_{1, \text{dela}}} \]  
\[ c = 2 r_t D_{2, \text{dela}} C_{0, \text{dela}} \frac{M_u}{\rho_{\text{pol}} \beta} \]

After \( t_1 \) seconds the top layer of the membrane (capsule wall) has been produced. For \( t < t_1 \) the transport of DETA from the aqueous phase into the oil phase is determined by the diffusion of DETA in the aqueous phase, through the interface and into the oil phase. For \( t > t_1 \) the transport of DETA into the capsule is limited by the diffusion of DETA through the polymer wall.

Assuming that the decrease of the TDC concentration due to the formation of the top layer, is small, then \( C_{3, \text{tde}}(t_1) \approx C_{3, \text{tde}}(0) \), so that:

\[ A'(t) = C_{3, \text{tde}}(0) - C_{3, \text{tde}}(t) \approx ab + \frac{a^2c}{2 \sqrt{(ab)^2 + a^2c (t - t_1)}} \]  

To analyze the dependence of the TDC concentration on time, equation (3.10) is differentiated with respect to \( t \):

\[ \frac{\partial}{\partial t} A'(t) = \frac{a^2c}{2 \sqrt{(ab)^2 + a^2c (t - t_1)}} \]  

Or:

\[ \left( \frac{\partial}{\partial t} A'(t) \right)^{-2} = \frac{4(ab)^2 + 4a^2c (t - t_1)}{\left( a^2c \right)^2} = \frac{\left( \frac{b}{ac} \right)^2 + \frac{4}{a^2c} \left( t - t_1 \right)}{\left( a^2c \right)^2} \]

From equation (3.12) it appears that the left hand side is proportional to time \( t \), with a slope equal to \( 4/(a^2c) \), provided \( r_t, D_{1, \text{dela}}, D_{2, \text{dela}}, M_u, \rho_{\text{pol}} \) and \( \beta \) are constant. Fig. 3.8 shows a characteristic plot of \((\partial A'(t)/\partial t)^{-2}\) versus \( t \); a linear relation exists, at least for the first 35 minutes. After this time \( C_{3, \text{tde}} \) becomes too low to obtain reliable results. Fig. 3.8 confirms the relation given in Eq. (3.12); hence, we may conclude that the model is consistent with Fig. 3.8.

Analysis of Fig. 3.8 shows that the intercept of the straight line with \((\partial t/\partial A'(t))^2\)-axis is very small and can be neglected for the time range measured.
Consequently equation (3.10) can be simplified into:

\[ A'(t) = \sqrt{a^2c} \cdot t \]  

(3.13)

This is shown in Fig. 3.9, \( A'(t) \) appears to be proportional to \( \sqrt{t} \). The slope of the line in Fig. 3.9 is equal to \( \sqrt{a^2c} \).

**Figure 3.8.** Evaluation of equation (3.12) showing the validity of the model.

\[ \text{Figure 3.9. The 'consumed' TDC concentration as a function of the reaction time.} \]
3.5. DISCUSSION

The polycondensation reaction between diethylenetriamine and terephthaloyl-dichloride takes place in the organic (dibutylphthalate) phase and close to the interface between the organic and aqueous solution. High molecular weight polymer is formed by coupling the increasing number of oligomers in the organic solution near the interface [5]. In order to react, DETA molecules have to diffuse from the aqueous phase into the organic phase and, when the first polymer has been precipitated at the interface, also through the polymer membrane. Because of the high reaction rate between DETA and TDC the consumption rate of TDC molecules inside a capsule is limited by the transfer rate of DETA from the aqueous phase into the organic phase.

The production of the asymmetric membranes consists of two stages: the first stage is the polycondensation reaction which forms the polymer, that, after precipitation, forms the top layer of the membrane. In the second stage the polycondensation proceeds by diffusion of DETA through the first layer of polymer into the capsule. The polymer produced in the oil phase swells with DETA, water and NaOH, which diffuse into the polymer and into the capsule.

When the sub layer starts to grow, small droplets appear at the organic side of the membrane, these droplets coalesce until polymer precipitation stagnates the coalescence process. Polymer will precipitate as the chain length will exceed a certain limit determined by the polymer–solvent interactions. Due to amine diffusion the polymer chains grow and precipitate. The growth rate of the polymer chains (which equals the transport rate of DETA to the reaction zone), determines the instant the polymer chains will precipitate. At slow rates it takes more time for the polymer to precipitate; at high rates this time is shorter. According to Ficks’ 1st law the rate of amine transport depends on the reciprocal value of the wall thickness. As the wall thickness increases with the maturation time of the capsules the amine transport rate decreases during the maturation. Consequently, the chain growth rate is decreased and it takes more time before the polymer will precipitate. Hence, the period of time in which small drops at the organic side of the membrane can coalesce, is increased with the maturation time. This results in larger drops after longer maturation times and in larger holes in the capsule membrane. This is verified by the photos 1-3, Fig. 3.2, which show an increase of the hole sizes in the membrane with increasing maturation times.
3.6. CONCLUSIONS

The model which is proposed for the formation of the capsule wall, describes the rate of wall formation as a function of reaction time. The rate of wall formation decreases as the reaction time proceeds. As a result the pore size of the membrane sub layer increases during maturation of the capsule wall. This is shown by photographs of cut cross sections of capsules.

The decrease of the TDC concentration is found to be proportional to $\sqrt{t}$, theoretically as well as experimentally. The rate of amine diffusion through the capsule wall determines the rate of polymer production. At slow production rates high cellular porosity is obtained, whereas at higher production rates non-cellular pores are obtained (e.g. when diamine is used in addition to the triamine).

3.7. REFERENCES

CHAPTER 4

MACRO ENCAPSULATION, THE STRUCTURE OF THE MEMBRANE
AND THE RATE OF WALL GROWTH

4.1. INTRODUCTION

Capsules are produced by interfacial polycondensation at the interface of a monodisperse oil-in-water emulsion [1]. According to the model which describes the growth of the capsule wall [2] (see chapter 3), diffusion of the amine through the wall towards the reaction zone is rate limiting. In this chapter the model presented in chapter 3 [2], will be verified by measuring the $C_{3,4\text{dc}}$ and the wall thickness as a function of the reaction time. The influence of the process conditions, which affect the properties of the membrane material and its structure, are also shown. The properties of the membrane material and the structure of the membrane affect the release characteristics of the capsules [3,4,5].

Section 4.3.4 gives the results of measurements of the rate of hydrolysis of encapsulated TDC. Both the influence of the process conditions and the rate of hydrolysis with respect to the wall formation and its properties are discussed.

4.2. EXPERIMENTS

Capsules were made by interfacial polycondensation of terephthaloyldichloride (TDC)/oil droplets in an aqueous diethylenetriamine (DETA) solution. This method to produce uniform droplets was as described in part I [2].

4.2.1. Analysis

During the process of encapsulation the capsule wall continues to grow and the TDC concentration decreases with the reaction time. In order to measure the TDC concentration as a function of the reaction time, the capsule contents were analyzed after several reaction times. A few capsules were dispersed into ethanol (96%) and subsequently broken with a rod. The non reacted TDC now reacts with ethanol to form the diethyl ester of terephthalic acid (TDE). The resulting mixture of TDE, DBP and ethanol was injected into a gas chromatograph (Packard, model 438, capillary column). The peak areas of TDE and DBP were determined by integrating the
detector signal (Infotronics, model crs 304). $C_{tdc}$ inside the capsules was proportional to the peak surface ratio ($A_{tdc}/A_{dbp}$) [6]. For the calculation of $C_{tdc}$ a calibration curve was measured. The retention indices [7] were determined for both TDE and DBP.

4.2.2. Wall-thickness

By SEM photography (JEOL JSM-35) the structure and the thickness of the wall could be determined. The capsules were dispersed in ethanol to remove the oil core; then, the capsules were dispersed in water to remove the ethanol, after which the capsule was frozen, so that, and with the aid of a microtome (Reichert-Jung, model 2700), thin slices could be cut off at -20 °C. The result was a sharp cross-section at the remaining part, by which it was possible to make SEM pictures of both the top and sub layer. The wall thickness was measured to be the distance between the inner and outer surface, when the view is perpendicular to the cutting plane.

4.2.3. Hydrolysis experiments

The rate of hydrolysis of encapsulated TDC was measured as follows. At first capsules were made as discussed before and after 4 minutes of wall maturation the capsules were washed with deionized water. Subsequently the capsules were dispersed into a solution of NaOH, so that hydrolysis of TDC with OH took place; the TDC concentration inside the capsules was measured as a function of hydrolysis time.

4.3. RESULTS

4.3.1. GC analysis

The analysis of the core content by gas chromatography shows the retention indices (I) for TDE and DBP [7] to be 1662 and 1939 respectively.

$$ I = 200 \frac{\log V_R^0(i) - \log V_R^0(nP_z)}{\log V_R^0(nP_{z+2}) - \log V_R^0(nP_z)} + 100 \, z \quad (4.1) $$

where $V_R^0(nP_z)$ $\leq V_R^0(i) \leq V_R^0(nP_{z+2})$ $V_R^0 = \text{retention volume, } nP_z = \text{n-paraffin with } z \text{ C-atoms and } z = \text{an integer. This is in agreement with results of Friocourt [6], who reports } \text{I}_{tdc} = 1650 \text{ and } \text{I}_{dbf} = 1940. \text{ Because of the small volume of the capsules, it is necessary to measure the concentration of TDC from the peak area ratio of TDC/DBP. The ratio is not influenced by the amount of the sample solution injected
in the range of 0.1-2.0 μl. The separation over a capillary column is good (see retention indices).

4.3.2. **Wall thickness as a function of time**

Fig. 4.1 shows the increase of the wall thickness as a function of √t; the thickness of the top layer is 8 - 12 μm. Due to the size of the voids in the sub layer membrane, it is difficult to obtain accurate wall thicknesses. This results in the scatter as seen in Fig. 4.1. The change of the capsule weight after drying (Fig. 4.2) shows that the amount of polymer increases during maturation.

![Graph](image)

Figure 4.1. The thickness of the capsule wall as a function of the reaction time.

- Indicates the thickness of the toplayer of the wall, which is formed in time \( t_r \).

4.3.3. **Influence of the process conditions on the wall properties**

According to the model of wall formation [2], the slope \( \left( \sqrt{a^2c} \right) \) of a plot of \( A'(t) \) versus \( \sqrt{t} \) is a function of the polymer properties \( \left( \rho_{pol}, \beta, M_u, D_{2,deta} \right) \) and the process conditions \( \left( r_t, d_c, C_{0,deta}, C_{3,t,dc} \right) \). It is related to them by:

\[
P = \sqrt[3]{\frac{72 \ r_t \ \rho_{pol} \ D_{2,deta} \ \beta}{M_u}} = \sqrt[3]{a^2c \ \frac{d_c^2}{C_{0,deta}}} \quad (4.2)
\]
Figure 4.2. The increase of the capsule weight after drying (weight of the polymer wall and the oil core) as a function of reaction time.

Figure 4.3. Polymer properties as a function of the ratio between $C_{\text{tdc}}(t = 0)$ in the organic phase and $C_{\text{deta}}(t = 0)$ in the aqueous phase.

The ratio $C_{3,\text{tdc}}/C_{0,\text{deta}}$ at $t = 0$ affects the polymer properties: $\rho_{\text{pol}}$, $M_u$ and $D_{2,\text{deta}}$. An increase of $C_{0,\text{deta}}$ relative to $C_{3,\text{tdc}}$ produces polymer with a lower degree of cross-linking, which affects the polymer properties.

Fig. 4.3 shows the dependence of $P$ on the ratio $C_{3,\text{tdc}}/C_{0,\text{deta}}$. By decreasing $C_{3,\text{tdc}}/C_{0,\text{deta}}$ polymer with less cross-links and a lower $D_{2,\text{deta}}$ was produced. This polymer is amorphous with crystalline regions [8]; a decrease of permeability
denotes an increase of the crystalline volume fraction. The polymer properties are only affected by the concentration ratio of TDC and DETA, rather than by their absolute values.

4.3.4. **Hydrolysis of TDC**

Another phenomenon in the interfacial polycondensation process is the hydrolysis of TDC, which diffuses from the organic into the aqueous phase, with \( \text{H}_2\text{O} \) and \( \text{OH}^- \):

\[
\text{TDC} + 2 \text{OH}^- \rightarrow \text{TDA} + 2 \text{Cl}^-
\]  

(a)

In the presence of enough \( \text{OH}^- \) the reaction with \( \text{H}_2\text{O} \) is negligible; measurements of the hydrolysis rate of encapsulated TDC by \( \text{H}_2\text{O} \) reveal a flux of TDC of \( 0.15 \times 10^{-2} \text{ mol/(m}^2\text{s)} \). With a concentration of \( \text{OH}^- \) of 1.0 kmol/m\(^3\) (pH = 14), the rate of hydrolysis of TDC is \( 3.87 \times 10^{-2} \text{ mol/(m}^2\text{s)} \).

As Morgan [9] states, hydrolysis of acid chloride exclusively takes place in the aqueous phase, so TDC has to transfer from the oil phase into the aqueous phase. The rate of TDC hydrolysis in the aqueous phase (reaction a) is of first order in \( c_{\text{tDC}} \) and in \( c_{\text{OH}} \) [10]:

\[
r_{\text{tDC}} = k_{\text{tDC}} c_{\text{tDC}} c_{\text{OH}}
\]  

(4.3)

For a solution with constant \( c_{\text{OH}} \), equation (4.3) becomes:

\[
r_{\text{tDC}} = k c_{\text{tDC}}
\]  

(4.4)

According to Beek [11] the flux of a substance from a disperse phase into a continuous phase with a first order reaction in the continuous phase is given by:

\[
J_{\text{03,tDC}} = \frac{D_{0,tDC} c_{\text{03,tDC}}}{\delta} \times \frac{\text{Ha} \cosh(\text{Ha}) - \text{Ha} \Gamma}{\sinh(\text{Ha})}
\]  

(4.5)

Where \( \text{Ha} \) (Hatta) and \( \Gamma \) are dimensionless variables: \( \text{Ha} = \sqrt{\frac{k \delta^2}{D_{0,tDC}}} \) and \( \Gamma = c_{0,tDC}/c_{\text{03,tDC}}; \delta = \) the transport film thickness.

For \( \text{Ha} > 3 \) equation (4.5) yields:

\[
J_{\text{03,tDC}} = \frac{D_{0,tDC} c_{\text{03,tDC}}}{\delta} \times \text{Ha}
\]  

(4.6)

As \( \text{Ha} \) is proportional to the square root of the reaction rate constant \( k \), the flux
is proportional to $\sqrt{C_{\text{OH}}}$.

After 4 minutes of polymer formation the capsules are washed with deionized water and immersed into DETA free solutions of different $C_{\text{OH}}$ without DETA. At this time enough TDC was left inside the capsules to measure TDC consumption due to hydrolysis. During this hydrolysis of TDC, no amine molecules are present to produce polymer with TDC. Consequently, the capsule wall thickness remains constant. Fig. 4.4 shows $C_{3,t_{\text{tdc}}}$ (a) as a function of time for a batch of capsules: $C_{3,t_{\text{tdc}}}$ decreases due to hydrolysis; line (b) in Fig. 4.4, which starts at $t = 4$ min., fits the data. The difference in rate of consumption of $C_{3,t_{\text{tdc}}}$ as a function of time between hydrolysis and polymerization (reaction of TDC with DETA) is illustrated by curve (a), which was calculated with the aid of:

$$A'(t) = \sqrt{a^2c \ t} \quad (4.7)$$

![Graph](image)

Figure 4.4. The concentration of TDC inside a capsule during polymerization represented by curve a due to an increase of wall thickness and during hydrolysis (represented by line b, after 4 min. of wall formation) □ indicates $C_{t_{\text{tdc}}}$ which decreases due to hydrolysis only.

The value for $\sqrt{a^2c}$ is derived from Fig. 4.3 with $C_{3,t_{\text{tdc}}} = 0.46$ kmol/m$^3$, $C_{0,\text{DETA}} = 0.68$ kmol/m$^3$ and $d_c = 4.83 \times 10^{-3}$ m. The quotient of the slope of line (b) in Fig. 4.4 and the capsule area yields the rate of hydrolysis per unit of surface area. The hydrolysis flux is a function of $C_{\text{OH}}$. Fig. 4.5 shows the relation of $\log J_{t_{\text{tdc}}}$
versus \(-\log C_{\text{OH}}\); an increase of \(C_{\text{OH}}\) results in an increase of \(J_{\text{t,deto}}\), which appears to be proportional to \(\sqrt{C_{\text{OH}}}\).

4.4. **DISCUSSION**

4.4.1. **Wall formation**

The polymerization takes place in the organic phase near the interface of the organic and water solution. High molecular weight polymer is formed by coupling an increasing number of oligomers in the organic solution near the interface [12]. In order to react, DETA molecules have to diffuse from the water into the organic phase and, when the first polymer is precipitated at the interface, also through the polymer. Because of the high reaction-rate constant, the consumption rate of TDC molecules inside a capsule is not limited by the reaction rate.

4.4.2. **Wall thickness during encapsulation**

The thickness of the capsule wall is \(d_t = d_i + d_2(t)\), which gives with the simplified relation for \(d_2(t)\) [2]:

\[
d_t = d_i + \left[ 2 \frac{D_{2,\text{deto}} C_{0,\text{deta}} M_u}{r_t \rho_{\text{pol}} B} \right] (t)
\]  

(4.8)

Fig. 4.1 shows the wall thickness as a function of \(\sqrt{t}\) (reaction time); this is in reasonable agreement with equation 4.8. Measurements of the wall thickness as a function of the reaction time for smaller sized capsules (300-1000\(\mu\)m) show very good agreement with equation 4.8 (see chapter 5). Since the thickness of the top layer is approximately 10 \(\mu\)m and the capsule diameter \(d_c\) is in the range from 4.52 to 5.04 mm, it follows that the ratio \(d_c/d_i\) is of the order of about \(4\times10^2\). Hence the produced capsule wall can be approximated as a flat sheet. From microscopy measurements it follows that the mechanism of wall formation is as follows: after the first formation of the top layer in the oil phase the polymer is swollen with the aqueous solution. Continuously DETA molecules and OH\(^-\) ions diffuse through the polymer wall towards the oil/water interface; small droplets of the aqueous phase appear at the inside of the top layer which causes the formation of voids in the membrane sub layer.

31
The effect of $C_{3,tdc}/C_{0,\text{deta}}$ on the polymer properties

The properties of the polymer which affect solute diffusion in the polymers are chain mobility and entanglement, cross-link density, equilibrium degree of swelling, crystallinity, porosity and solubility of the solute in the polymer [13]. Fuhrmann [14] describes diffusion in semi-crystalline polymers and polymer networks. The semi-crystalline polymer exists of two phases: the crystalline and the non-crystalline phases. Solute diffusion only takes place in the non-crystalline regions, so higher volume fractions of crystalline regions results in less permeable polymer. Equation (4.2) shows a relation between $P$ and $r_t$, $\rho_{\text{pol}}$, $D_{2,\text{deta}}$, $\beta$ and $M_w$. These variables are a function of the $C_{3,tdc}/C_{0,\text{deta}}$ ratio which affects the number of cross-links in the polymer. More cross-links result in less crystalline regions. Fig. 4.3 shows the relation between $P$ and $C_{3,tdc}/C_{0,\text{deta}}$. $P$ will decrease when the fraction of crystalline regions increases, which results in a decreased overall diffusion coefficient. According to Fig. 4.3, $P$ decreases and more crystalline regions are formed as the $C_{3,tdc}/C_{0,\text{deta}}$ decreases, so at lower $C_{3,tdc}/C_{0,\text{deta}}$ presumably less cross-links are formed. In this case the rate of DETA diffusion into the oil phase will increase and the possibility of the TDC molecules to react with the secondary -NH- group of polymer chains will decrease. This will result in a smaller number of cross-links in the polymer.

Figure 4.5. The rate of hydrolysis of encapsulated TDC as a function of $C_{\text{OH}}$ in the aqueous phase (O).
4.4.4. Hydrolysis of encapsulated TDC

The influence of the hydrolysis reaction for TDC is measured by Crawford [10] in a system where TDC was polymerized with piperazine. The TDC solution was dispersed into the aqueous piperazine solution. Hydrolysis of TDC took place in the aqueous phase. It appeared that the rate determining step was the first order homogeneous reaction between TDC and water in the aqueous phase at pH = 6.3. In this system no polymer was present.

The results for the rate of hydrolysis of TDC encapsulated are shown in Fig. 4.5, where \( \log(J_{tdc}) \) is plotted versus \( -\log(C_{OH}) \). The absolute value of the slope of the line in Fig. 4.5 has a value of 0.5, hence \( J_{tdc} \) is proportional to \( \sqrt{C_{OH}} \). This is in agreement with Beek [11]. Hence, the hydrolysis rate is limited by the diffusion of TDC from the organic phase into the aqueous phase.

The negative slope of curve a in Fig. 4.4 at \( t = 4 \) min., when polymer has been formed, is larger than the negative slope of line b in the absence of polymer formation. From this it follows that the reaction of TDC with DETA is faster than the reaction of TDC with OH\(^-\). Because the polycondensation takes place in the organic phase and the rate of polycondensation is higher than the rate of hydrolysis, during polymer formation no TDC diffuses from the organic into the aqueous phase and no hydrolysis of TDC takes place during capsule membrane formation.

4.5. CONCLUSIONS

Measurements of the wall thickness as a function of reaction time show a linear dependence with \( \sqrt{t} \). The influence of the concentration of TDC relative to the concentration of DETA show a decrease of the diffusion coefficient as \( C_{3,tdc}/C_{0,deita} \) at \( t = 0 \) is decreased.

Measurements of the rate of hydrolysis show that in presence of enough OH\(^-\) hydrolysis takes place only with OH\(^-\) rather than with H\(_2\)O. Because of the relation of the hydrolysis rate with \( \sqrt{C_{OH}} \) it is shown that the diffusion rate of TDC from the oil (3) into the aqueous (0) phase determines the hydrolysis rate. Consequently, during encapsulation (formation of the capsule wall) no hydrolysis of TDC takes place.
4.6. REFERENCES

CHAPTER 5

MICROENCAPSULATION; THE INFLUENCE OF PROCESS CONDITIONS ON WALL PERMEABILITY

5.1. INTRODUCTION

In the case of transfer control the capsule wall acts like a membrane which controls the release rate of the component to be released. The permeability of the capsule wall has to satisfy some criteria. To influence the permeability of the polymer membrane, one can alter both the geometrical and the morphological properties of the polymer. By reduction of the wall thickness the release rate of a component increases, just as is the case by enlarging the release surface. On the other hand, as one is restricted in capsule size and, consequently, in wall thickness, it is possible to change release properties by introducing cross-links, crystalline phases and pores in the capsule wall. In general the release rate of a component decreases with increasing cross-link density, fraction of the crystalline phase and fraction of polymer [1].

In the case of interfacial polycondensation the three parameters mentioned can be changed by changing process conditions. The addition of a diamine to the aqueous phase will result in a less cross-linked, more crystalline and more porous polymer membrane with a different porous structure. The present chapter deals with the influence of process conditions (e.g. organic solvent, concentration ratio of dichloride/triamine, concentration ratio of diamine/triamine, kind of the diamine) on the permeability properties of the membrane.

The processes to produce the capsule wall are described in two models, where the formation of macrovoids is described by 1) a constant water flux or 2) by a water flux related to the amine flux.

5.2. THEORY

In chapter 3 a model was presented which described the growth of the capsule wall and the decrease of the terephthaloyldichloride (TDC) concentration inside the capsule. Photographs proved that the wall is not homogeneous but contains macrovoids. The model accounts for these macrovoids with a constant factor (1-β,
where $\beta$ is the polymer volume fraction in the membrane. The voids are filled with the aqueous solution, which diffuses through the membrane.

In the present chapter the production of the macrovoids in the capsule wall is described by two different models; the first option is to consider the water flux to be constant, the second one is to consider the water flux to be dependent on the flux of amines into the capsules [3].

5.2.1. Models to describe the capsule wall formation

The concentration gradients across the capsule wall during capsule formation are schematically shown in Fig. 5.1. Phase 0 is the aqueous (continuous) phase, phase 1 is the membrane and phase 3 is the organic (disperse) phase.

![Concentration profile across the capsule wall.](image)

**Figure 5.1. Concentration profile across the capsule wall.**

The mass balance of TDC over a single oil drop gives the following relationship of $C_{3,\text{tdc}}$ as a function of time $t$ (where the $C_{0,\text{deta}} = C_{0,\text{deta}}$):

\[
\frac{\partial C_{3,\text{tdc}}}{\partial t} = \frac{k_{\text{deta}} \left( C_{0,\text{deta}} - C_{3,\text{deta}} \right) A_c}{r_t} \tag{5.1}
\]

where $k_{\text{deta}}$ is the mass transport coefficient (m/s), which is considered to be a linear combination of the mass transport coefficient in the voids ($D_{v,\text{deta}}/(d_t \epsilon_1)$) and in the polymer of the membrane ($D_{p,\text{deta}}/(d_t (1 - \epsilon_1))$):

\[
\frac{1}{k_{\text{deta}}} = \frac{d_t \epsilon_1}{D_{v,\text{deta}}} + \frac{d_t (1 - \epsilon_1)}{D_{p,\text{deta}}} \tag{5.2}
\]
The increase of the wall thickness with time is the sum of the 'water thickness' \( (\phi_w/\rho_w) \) and the 'polymer thickness' \( (k_{deta} M_u (C_{0,deta} - C_{3,deta})/(r_t \rho_{pol})) \):

\[
\frac{\partial d_t}{\partial t} = \phi_w \rho_w + \left[ \frac{d_t \varepsilon_t}{D_{V,deta}} + \frac{d_t (1 - \varepsilon_t)}{D_{P,deta}} \right]^{-1} \frac{M_u}{r_t \rho_{pol}} \left( C_{0,deta} - C_{3,deta} \right) \tag{5.3}
\]

5.2.1.1. Model 1: Diffusion with a constant flux of water

Since the water flux is considered to be constant, the increase of the wall thickness with time is equal to equation 5.3:

\[
\frac{\partial d_t}{\partial t} = \frac{\phi_w}{\rho_w} + \left[ \frac{d_t \varepsilon_t}{D_{V,deta}} + \frac{d_t (1 - \varepsilon_t)}{D_{P,deta}} \right]^{-1} \frac{M_u}{r_t \rho_{pol}} \left( C_{0,deta} - C_{3,deta} \right) \tag{5.4}
\]

The volume fraction of voids \( (\varepsilon_t) \) in the membrane at time \( t \) is the quotient of the volume of the water in the macrovoids and the volume of the membrane.

\[
\varepsilon_t = \frac{\phi_w t}{\rho_w d_t} \tag{5.5}
\]

Inserting equation (5.5) into equation (5.4) gives, with \( D_{V,deta} \gg D_{P,deta} \) and \( C_{3,deta} = 0 \), the following relationship for the rate of the wall growth:

\[
\frac{\partial d_t}{\partial t} = \frac{\phi_w}{\rho_w} + \frac{D_{P,deta}}{d_t - (\phi_w/\rho_w)t} \times \frac{M_u}{r_t \rho_{pol}} C_{0,deta} \tag{5.6}
\]

With \( \xi = \phi_w/\rho_w \) and \( \phi = D_{P,deta} M_u C_{0,deta}/(r_t \rho_{pol}) \) equation (5.6) can be written as:

\[
\frac{\partial d_t}{\partial t} = \xi + \frac{\phi}{d_t - \xi t} \tag{5.7}
\]

Substitution of \( Y = d_t - \xi t \) equation (5.7) becomes:

\[
Y \frac{\partial Y}{\partial t} = \left[ \xi Y + \phi \right] \frac{\partial d_t - \partial Y}{\xi} \tag{5.8}
\]
Which is equal to:

\[ \delta d_t = \left[ \frac{\varepsilon}{\phi} Y + 1 \right] \delta Y \]  
(5.9)

Integration of equation (5.9) with \( d_t = 0 \) at \( Y = 0 \) (i.e. at \( t = 0 \)) gives:

\[ d_t = \frac{\Phi_w}{\rho_w} t + \left[ \frac{2 D_{p,deta} M_u C_{0,deta} t}{\rho_{pol} \Gamma_t} \right] \]  
(5.10)

Substitution of \( k_{deta} \) (equation (5.2)), \( \varepsilon_1 \) (equation (5.5)), \( d_t \) (equation (5.10)) and \( C_{3,deta} = 0 \) into equation (5.1) gives, after integration with \( C_{3,tdc} = C_{3,tdc(0)} \) at \( t = 0 \) and \( D_{v,deta} \gg D_{p,deta} \):

\[ C_{3,tdc(0)} - C_{3,tdc(t)} = \frac{72 D_{p,deta} \rho_{pol} C_{0,deta}}{M_u \Gamma_t d_c^2} \times \sqrt{t} \]  
(5.11)

5.2.1.2. Model 2: Diffusion with a water flux depending on the amine flux

In his model Enkelmann et.al. [3] assumes that the flux of water through a membrane is dependent on the flux of the amine. The amine and water pass the membrane, the water in a hydrational form. So the water flux and the amine flux are linearly related:

\[ \Phi_w = K_1 \Phi_{deta} \]  
(5.12)

Where \( K_1 \) is the mass of the water which is transported together with one mole of DETA (kg/kmol). The flux of DETA is described by:

\[ \Phi_{deta} = k_{deta} \left( C_{0,deta} - C_{3,deta} \right) \]  
(5.13)

In combination with equation (5.2) and \( D_{v,deta} \gg D_{p,deta} \) and \( \varepsilon_1 \) replaced by \( \varepsilon_2 \), equation (5.13) becomes:

\[ \Phi_{deta} = \frac{D_{p,deta} C_{0,deta}}{d_t (1 - \varepsilon_2)} \]  
(5.14)
And equation (5.3) becomes:

$$\frac{\partial d_t}{\partial t} = \frac{D_{p,\text{dema}}}{d_t (1 - \varepsilon_2)} C_{0,\text{dema}} \left( \frac{K_1}{\rho_w} + \frac{M_u}{r_t \rho_{pol}} \right)$$  (5.15)

The volume fraction of macrovoids ($\varepsilon_2$) within the membrane is somewhat different from the fraction of voids in the first model ($\varepsilon_1$) since the water flux is not constant in this case. The volume fraction of macrovoids in a slice of the membrane at time $t$ is:

$$\varepsilon_t = \frac{\phi_w}{\rho_w} \frac{\partial t}{\partial d_t}$$  (5.16)

Combining equation (5.12) and (5.15), with $\phi_{\text{dema}} = (D_{p,\text{dema}} C_{0,\text{dema}})/(d_t (1 - \varepsilon_2))$, results into:

$$\varepsilon_t = \frac{K_1 r_t \rho_{pol}}{K_1 r_t \rho_{pol} + M_u \rho_w} = \varepsilon_2$$  (5.17)

Equation (5.17) shows that $\varepsilon_t$ is not a function of the membrane thickness ($d_t$) and constant throughout the membrane, so $\varepsilon_2 = \varepsilon_t$. SEM photographs show that the volume fraction of macrovoids increases as the membrane thickness increases; so in the real system the fraction of macrovoids is not constant (see section 5.4.3).

Equation (5.15) combined with equation (5.17) yields, after integration (with $d_t = 0$ at $t = 0$):

$$d_t = \sqrt{\frac{2 D_{p,\text{dema}} C_{0,\text{dema}} \left[ K_1 \rho_{pol} r_t + M_u \rho_w \right]^2 t}{M_u \rho_w^2 r_t \rho_{pol}}}$$  (5.18)

To obtain a relation for $C_{3,\text{tdc}}$ the mass balance as used in the model with a constant water flux can be applied (equation (5.1)). Equation (5.1) in combination with equation (5.2) (in which $\varepsilon_2$ is substituted for $\varepsilon_1$) and equation (5.18) leads to the same relationship between $C_{3,\text{tdc}}$ and time $t$ as equation (5.11).

The approaches to describe the formation of macrovoids in both models yield equal relationships for the concentration as a function of time (equation (5.11)). The relationships for the wall thickness ($d_t$) as a function of time are different for both models. The model with a constant water flux describes the wall thickness
as a quadratic function of $\sqrt{r}$, whereas the model with the water flux depending on the amine flux describes the wall thickness as a linear function of $\sqrt{r}$ only.

5.2.2. Addition of diamine to the aqueous phase

The reaction of TDC with DETA and a diamine (EDA or HMDA) is:

$$n \text{TDC} + r_t \ n \text{DETA} + r_d \ n \text{EDA} \rightarrow \text{polymer} + 2 \ n \text{HCl}$$

(a)

In this case the concentration of TDC inside a capsule decreases by reaction with DETA and EDA (or HMDA); the reaction rate is controlled by the diffusion rates of DETA and EDA (or HMDA) through the capsule wall. The right hand side of the mass balance (equation (5.1)) becomes a linear combination of the flux of DETA and EDA (or HMDA). This results in a relationship for the TDC concentration as a function of time for the model with a constant water flux:

$$C_{3,\text{tdc}}(0) - C_{3,\text{tdc}}(t) = \frac{72 \ \rho_{\text{pol}}}{M_u \ d_c^2} \left( \frac{D_{p,\text{deta}} C_{0,\text{deta}}}{r_t} + \frac{D_{p,\text{eda}} C_{0,\text{eda}}}{r_d} \right) t$$

(5.19)

The relationship for the wall thickness of the capsule becomes:

$$d_t = \frac{\phi_w}{\rho_w} t + \frac{2 \ M_u}{\rho_{\text{pol}}} \left( \frac{D_{p,\text{deta}} C_{0,\text{deta}}}{r_t} + \frac{D_{p,\text{eda}} C_{0,\text{eda}}}{r_d} \right) t$$

(5.20)

The reaction to produce polymer is limited by the diffusion of the triamine and diamine through the membrane. Both react instantaneously in the organic phase with TDC to produce polymer. The ratio between $r_t$ (the ratio of DETA reacting with TDC) and $r_d$ (the ratio of EDA reacting with TDC) equals the ratio between the fluxes of DETA and EDA:

$$\frac{r_t}{r_d} = \frac{\phi_{\text{deta}}}{\phi_{\text{eda}}} = \frac{D_{p,\text{deta}} C_{\text{deta}}(0)}{D_{p,\text{eda}} C_{\text{eda}}(0)}$$

(5.21)

Substitution equation (5.21) into equation (5.19) gives a relationship between the concentration of TDC and the diffusion coefficient of DETA:

$$C_{3,\text{tdc}}(0) - C_{3,\text{tdc}}(t) = \frac{144 \ \rho_{\text{pol}} D_{p,\text{deta}} C_{0,\text{deta}}}{M_u \ d_c^2 r_t} t$$

(5.22)
or a relationship for the concentration of TDC and the diffusion coefficient of EDA:

\[
C_{3,tdc}(0) - C_{3,tdc}(t) = \frac{144 \rho_{pol} D_{p,eda} C_{0,eda}}{M_u d_c^2 r_d} \frac{1}{t}
\]  

(5.23)

5.2.3. **Effect of crystallinity**

In general semi-crystalline polymers consist of two phases: a crystalline and a non-crystalline or amorphous phase; diffusion is assumed to take place exclusively through the amorphous phase [4]. Polymer chains are not exclusively part of the crystalline or amorphous phase, polymer segments close to the crystalline phase have reduced mobility. Therefore Fuhrmann [5] expands the two-phase model with a third phase, where the macromolecular chains have reduced mobility. In both models the amorphous phase is assumed to be swollen with solvent and penetrable for diffusing molecules whereas the crystalline phase is impenetrable. According to Lasoski [6] the diffusion coefficient in a semi-crystalline polymer is given by:

\[
D = D_a (1 - \varphi_{cr})
\]  

(5.24)

With an increasing volume fraction of crystalline phase the diffusion coefficient decreases [4-8].

Harland et.al. [4] and Siegel [9] describe the effect of tortuosity of the diffusion path on the diffusion of solvents. Because of the presence of crystallites the diffusion path for solvent molecules from one side to the other side of the membrane is increased; the overall diffusion coefficient becomes:

\[
D = D_a / \tau
\]  

(5.25)

The tortuosity \((\tau)\) increases if the size of the crystallites decreases. A relationship which describes the tortuosity as a function of the crystalline volume fraction is given by Weinkauf et.al. [8]:

\[
\tau = (1 - \varphi_{cr})^n
\]  

(5.26)

with \(1 < n < 2\); the tortuosity increases with the crystalline volume fraction.

The diffusion of solvents through the amorphous phase might be described by two models [8]: firstly the activated process:
\[ D = D_0 \exp \left( -\frac{E_0}{RT} \right) \]  

(5.27)

where \( D_0 \) is the diffusion coefficient in the bulk of the solvent, \( E_0 \) is the activation energy to create a hole large enough for the solvent molecules. Secondly the free volume theory:

\[ D = D_0 \exp \left( -\frac{B}{f} \right) \]  

(5.28)

where \( B \) is a characteristic constant for the polymer-solvent system and \( f \) is the fractional free volume.

5.2.4. Effect of cross-linking

The introduction of cross-links in an amorphous polymer produces a three-dimensional network. An increase in the degree of cross-linking (reduction of \( M_x \) = molecular weight between cross-links) results in a decrease of the solvent diffusion coefficient [10-14].

Chalykh et al. [14] describes the effect of the cross-links on the diffusion coefficient by:

\[ \ln D = \ln D_\infty - \frac{B \ a^' \ M_x^{-1}}{f \left( f - a^' \ M_x^{-1} \right)} \]  

(5.29)

Where \( B \) and \( a^' \) are constants, \( M_x \) the molecular weight between cross-links, \( f \) the fractional free volume and \( D_\infty \) the diffusion coefficient for \( M_x \rightarrow \infty \). The diffusion coefficient \( D \) increases if \( M_x \) increases (less cross-links).

In the case of a semi-crystalline polymer diffusion takes place in the amorphous phase. The incorporation of cross-links in a semi-crystalline polymer effects the diffusion through such a polymer in two ways. As the cross-link density increases, the diffusion of solvent decreases (equation (5.29)); on the other hand, the volume fraction of the crystalline phase decreases, causing the diffusion coefficient to increase (equation (5.24)). As is shown in by experiments the diffusion coefficient increases as the cross-link density increases [15, 16].

42
Figure 5.2. Apparatus to produce uniformly sized drops. Diameter range is 35 - 2000 μm. The liquid jet from the nozzle is broken by the oscillation of the loudspeaker. The jet breaks up in uniformly sized drops.

5.3. Experimental

5.3.1. Production of uniform droplets

Small droplets can be produced by breaking up a fluid jet; by applying a longitudinal oscillation to the jet droplets of uniform size are produced [17-19]. The size of the droplets is a function of the frequency and the amplitude of the oscillation, the jet diameter and the fluid velocity.

This method has been applied in Fig. 5.2 where the apparatus to produce the uniform droplets is shown [20]. It consists of a supply vessel in which a nozzle and a plunger are situated. From the nozzle (with an adjustable diameter) a fluid jet is produced. The jet breaks up due to an oscillation applied on the jet. The plunger, which is attached to the cone of a loudspeaker, supplies the oscillation. The frequency applied to the loudspeaker is controlled by an audio generator. The number of droplets is proportional to the frequency applied.
The flow rate of the organic phase was set at the lowest possible rate to produce a fluid jet from the nozzle (about 10 ml/min). The lowest possible frequency was applied (about 300 Hz) to produce uniform sized droplets. In this way the number of droplets emerging from the nozzle was minimized (about 300 capsules per second). When the flow rate is increased the oscillation frequency has to be increased also, in order to stay in the region where uniform sized droplets are produced. In this case to many droplets are produced causing droplets to coalesce in the subsequent step of micro capsule production.

5.3.2. Production of micro capsules

Small droplets (500-1000 \( \mu \text{m} \) diameter) of an organic phase are immersed into an aqueous phase. Terephthaloyldichloride is dissolved in the organic phase, a triamine, or a combination of a triamine and a diamine, and sodium hydroxide are dissolved in the aqueous phase. Polycondensation proceeds in and close to the organic side of the interface of the organic and the aqueous phases. The polymer which is produced, precipitates and forms a capsule wall. After formation of the initial layer of polymer the wall continues to grow, due to amine diffusion from the aqueous phase through the wall into the organic phase.

![Diagram of capsule production](image)

Figure 5.3. Uniform drops plunge into the soap solution and descend through the interface into the amine solution. At this point the wall starts to grow and micro capsules are produced.

44
The droplets fall down through the air into the amine solution. If the droplets are dropped into an aqueous amine solution, the first layer of polymer is produced by reaction of the chloride and the amine at the organic side of the interface instantaneously. Due to the high falling speed by which the droplets fall into the aqueous solution, the initial layer of polymer is withdrawn from the droplet surface so that a tip at the droplet tail is formed. To prevent the formation of a tail a buffer zone is introduced. Fig. 5.3 shows the vessel which contains the amine solution and the buffer zone. In the buffer zone consisting of an aqueous solution of sodiumdodecylsulfonate (NaDOS) no amine is present so that no capsule wall is produced; the droplets become spheres after falling into the buffer solution. The droplets sink with a low velocity through the buffer zone down to the amine solution. The droplets enter the amine solution where formation of the capsule wall starts. The capsules produced in this way are spherical. The interface between the buffer and the amine solution is maintained by continuously removing fluid through four pipes. Two other pipes control the flow of the amine and the buffer solution into the vessel. After a few seconds enough capsules are produced, the buffer solution is removed and samples can be taken.

5.3.3. Process conditions

Micro capsules were produced under various process conditions. The concentration ratio of terephthaloyldichloride (TDC) and diethylenetriamine (DETA) was varied between 0.2 and 1.2. The concentration of ethylenediamine (EDA) or hexamethylenediamine (HMDA) relative to the concentration of DETA was varied between 0 and 1. The concentration of NaOH in the aqueous solution was kept constant at 1.0 kmol/m³. Two organic solvents were used, dibutylphthalate (DBP) and dimethylphthalate (DMP), and several sizes of nozzle diameters were used (0.3 - 0.5 mm).

The TDC concentration of the capsules and the wall thickness as function of time were measured as described in a previous paper [2].

5.3.4. Permeability measurements

The capsules produced were subjected to permeability measurements. For that purpose the organic phase in the capsules was removed by washing them in ethanol; subsequently the ethanol was removed by washing the capsules with distilled water. The capsules, now filled with water, were immersed into solutions of 1.0 M DETA and 1.0 M NaOH so that the capsules were loaded gradually with DETA and NaOH. These capsules were immersed into a known amount of a Ni(NO₃) solution whereupon DETA
release started. The release rate was measured by measuring the concentration of the Ni(DETA)$_2$ complex spectrophotometrically at $\lambda_{max} = 850$ nm [21].

5.4. RESULTS AND DISCUSSION

5.4.1. Concentration measurements

5.4.1.1. The influence of the organic phase

Previous measurements [2] showed a linear relationship between the TDC concentration in macro capsules (2 - 4 mm diameter) and the square root of the reaction time. Fig. 5.4 shows the relation between $C_{tdc}(t = 0) - C_{tdc}(t)$ and $\sqrt{t}$ for micro capsules with a DMP core, a diameter of 1.09 mm and a ratio between $C_{tdc}$ and $C_{deta}$ at $t = 0$ of 0.82. $C_{tdc}(t = 0) - C_{tdc}(t)$ appears to be proportional to $\sqrt{t}$, it was shown that this relationship holds for the lowest diameters measured i.e. 0.54 mm.

![Graph showing concentration of TDC as a function of $\sqrt{t}$](image)

**Figure 5.4.** The concentration of TDC as a function of $\sqrt{t}$ for micro capsules with a core of dimethylphthalate (DMP) and $C_{3,tdc}/C_{0,deta} = 0.82$.

According to equation (5.11) the slope of the line in Fig. 5.4 represents a value for the properties of the membrane polymer; with known values of $C_{0,deta}$ and $d_c$ the value of $(D_p \rho_{pol})/(r_t \mu)$ can be calculated. The polymer properties change with varying initial ratio of the TDC and DETA concentration. An increase of this
ratio causes an increasing reaction of TDC with the secondary amine group of the DETA molecule. Consequently the cross-link density of the threedimensional network increases, which results in a change of the polymer properties \((D_p \rho_{pol})/(r_t M_u)\). Fig. 5.5 shows the slopes of line like that in Fig. 5.4, divided by \(C_{0, \text{deta}}\) and \(d_c^2\), which is equal to \(\sqrt{72 \frac{D_p \rho_{pol}}{r_t M_u}}\), as a function of the initial ratio of the TDC and DETA concentration \((C_{\text{tdc}}(t = 0)/C_{\text{deta}}(t = 0))\). Fig. 5.5 shows that \((D_p \rho_{pol})/(r_t M_u)\) increases with increasing initial ratio. The polymer density of polyterephthalamides varies between 1100 and 1400 kg/m\(^3\), as the reaction ratio \(r\) varies between 1 (for completely linear polymer) and 2/3 (for completely cross-linked polymer) and the molecular weight of a repeating unit, \(M_u\), varies between 199 and 233 kg/kmol. In case of a DBP core, the value for \(\rho_{pol}/(r_t M_u)\) varies between 4.72 and 10.55. According to Fig. 5.5 the value for \((72 D_p \rho_{pol})/(r_t M_u)\) is \(0.5 \times 10^{-10}\) kmol/ms at \(C_{\text{tdc}}/C_{\text{deta}} = 0.2\) and increases to \(16 \times 10^{-10}\) kmol/ms at \(C_{\text{tdc}}/C_{\text{deta}} = 1.05\).

\[
\begin{align*}
\text{kmol} & \quad \text{ms} \\
4 \times 10^{-5} & \\
3 \times 10^{-5} & \\
2 \times 10^{-5} & \\
1 \times 10^{-5} & \\
0 & \quad 0.4 \quad 0.8 \quad 1.2
\end{align*}
\]

**Figure 5.5.** The influence of \(C_{\text{tdc}}/C_{\text{deta}}\) on the permeability for DETA of microcapsules with a dibutylphthalate (DBP, ■) core or a dimethylphthalate (DMP, ○) core. Calculated from concentration measurements.

The maximum increase which can be accounted for by \(\rho_{pol}/(r_t M_u)\) is a factor 2.23, so the measured increase by a factor of 32 must be accounted for by an increase of \(D_p \rho_{pol}\) by a factor 14.3 at most. \(D_p \rho_{pol}\) changes by a combination of
changes in the crystalline volume fraction ($\varphi_{cl}$), the size of the crystallites, the
tortuosity induced by the crystalline regions and the reduced mobility of the
polymer chains in the amorphous phase close to the crystalline regions.

Fig. 5.5 also shows the same effect of the polymer properties as a function of
the ratio ($C_{tdc}/C_{deta}$) in case of a DMP core. The data of the DMP cored micro
capsules compared to the data of the DBP cored micro capsules show a higher value
for (72 $D_{p,deta} \rho_{pol})/r_{t} M_{w}$), which means that the $D_{p,deta}$ in the case of a DMP
organic phase is higher than in the case of a DBP organic phase. A higher $D_{p,deta}$
for the capsules with a DMP core indicates a higher degree of cross-linking in case
of a DMP organic phase. More cross-links are produced when the concentration ratio
of TDC and DETA increases (Fig. 5.5). Under equal conditions there is a higher
transport rate of DETA into the organic phase in case of a DMP organic phase then
in the case of a DBP organic phase, which yields a lower ratio of $C_{3,tdc}/C_{3,deta}$.
This is in contradiction with the influence of $C_{3,tdc}/C_{0,deta}$ as shown in Fig. 5.5.

\[1.5 \times 10^{-4}\]

\[1 \times 10^{-1}\]

\[5.0 \times 10^{-5}\]

\[C_{0,eda}/C_{0,deta}^{-1}\]

\[0 \quad 0.4 \quad 0.8 \quad 1.2\]

Figure 5.6. *The influence of the addition of ethylenediamine (EDA) to the amine
solution on the capsule wall permeability (capsules have a DMP core).*

*The influence of the diffusion of DETA through the capsule wall.
Calculated from concentration measurements.* $C_{3,tdc}/C_{0,deta} = 2.97 (\circ)$
and $3.58 (\circ)$.

5.4.1.2. *Influence of addition of diamines to the aqueous phase*

Micro capsules with a DMP core are produced with diamines added to the aqueous
DETA solutions. Because the diamine molecule has only two functional groups it cannot contribute to cross-linking reactions. Addition of diamines to the aqueous phase containing triamine results in a lower cross-link density of the three-dimensional network.

Fig. 5.6 shows the relationship between the slope of equation (5.22) corrected for the capsule diameter and $C_{\text{deta}}$ (i.e. $\sqrt{\frac{144}{D_{p,deta}}} \left[ \frac{\rho_{\text{pol}}}{r_t M_u} \right]$) as a function of $C_{\text{eda}}(t = 0)/C_{\text{deta}}(t = 0)$. The permeability of the capsule membrane for DETA decreases as the concentration ratio of EDA and DETA increases. Results are measured for two series of capsules, the concentration ratio of TDC and DETA being kept constant for each series of capsules. A lower permeability was measured if the $C_{\text{tdc}}/C_{\text{deta}}$ is decreased from 3.58 to 2.97; this is in agreement with the results shown in Fig. 5.5.

Fig. 5.7 shows the relationship between the slope of equation (5.23) corrected for the capsule diameter and $C_{\text{eda}}$ (i.e. $\sqrt{\frac{144}{D_{p,eda}}} \left[ \frac{\rho_{\text{pol}}}{r_d M_u} \right]$) as a function of $C_{\text{eda}}(t = 0)/C_{\text{deta}}(t = 0)$. The same change for EDA is observed; both in the case of an increase of $C_{\text{eda}}(t = 0)/C_{\text{deta}}(t = 0)$ and in the case of a decrease of $C_{\text{tdc}}/C_{\text{deta}}$. Comparison of Fig. 5.6 and Fig. 5.7 also shows a slightly higher $D_{p,eda}$ than $D_{p,deta}$.

![Figure 5.7](image.png)

**Figure 5.7.** The influence of the addition of ethylenediamine (EDA) to the amine solution on the capsule wall permeability (capsules have a DMP core). The influence of the diffusion of EDA through the capsule wall. Calculated from concentration measurements. $C_{3,tdc}/C_{0,deta} = 2.97$ (■) and 3.58 (○).
Figure 5.8. The influence of the addition of hexamethylenediamine (HMDA) to the amine solution on the capsule wall permeability (capsules have a DMP core). The influence of the diffusion of DETA through the capsule wall. Calculated from concentration measurements. \( C_{3,tdc}/C_{0,dta} = 2.87 \).

The influence of the addition of HMDA to the aqueous DETA solution is also measured; Fig. 5.8 and Fig. 5.9 show the results for \( \sqrt{144 \, D_{p,dta} \, \rho_{pol}/(r_t \, M_u)} \) and \( \sqrt{144 \, D_{p,hmda} \, \rho_{pol}/(r_d \, M_u)} \) as a function of \( C_{hmda}(t = 0)/C_{dta}(t = 0) \). The permeability also decreases with increasing concentration ratio of the diamine and the triamine. The permeability of the HMDA capsules is a factor 3 to 4 lower than that of the EDA capsules for both DETA and HMDA, for almost equal values for \( C_{tdc}/C_{dta} \). The longer \(-CH_2-\) chains in HMDA cause the production of longer linear chains, thus encouraging the formation of crystalline regions. The permeability of a polymer membrane will decrease if the fraction of crystalline regions increases.

5.4.2. Thickness measurements

5.4.2.1. The influence of the organic phase

Previous measurements [2] showed a linear relationship between the capsule wall thickness and the square root of the reaction time for macro capsules
Figure 5.9. The influence of the addition of hexamethylenediamine (HMDA) to the amine solution on the capsule wall permeability (capsules have a DMP core). The influence of the diffusion of HMDA through the capsule wall. Calculated from concentration measurements. \( \frac{C_{3,t_{dc}}}{C_{0,deta}} = 2.87 \).

Figure 5.10. The growth of the capsule wall thickness as a function of \( \sqrt{t} \). The capsule core is DMP; \( \frac{C_{3,t_{dc}}}{C_{0,deta}} = 0.233 \).
(2-4 mm). Also Fig. 5.10 shows a linear relationship between the wall thickness and the square root of \( t \), equation (5.18), which gives the wall thickness as a function of time, is equal to equation (5.10) provided 1) \( K_1 \rho_{pol} r_t \ll M_w \rho_w \) and 2) the first term in equation (5.10), i.e. the water flux term, can be neglected with respect of the second term.

From equation (5.10 or 5.18) the permeability of the polymer can be evaluated 
\( \left( \frac{D_{p, pol} M_w}{r_t \rho_{pol}} \right) \). As shown in Fig. 5.11, the permeability increases with increasing TDC/DETA concentration ratio for micro capsules with a core of DBP and DMP. The permeability of micro capsules with a DMP core is of the same order of magnitude as that of micro capsules with a DBP core.

From Fig. 5.5, \( D_{p, pol} \) as a function of \( C_{tdc}/C_{deta} \) from concentration measurements, it is shown that the \( D_{p, pol} \) is considerably higher when using a DMP core instead of a DBP core. From Fig 5.11, \( D_{p, pol} \) as a function of \( C_{tdc}/C_{deta} \) from thickness measurements, this significant difference is not clear.

![Graph](image)

**Figure 5.11.** The influence of \( C_{3,tdc}/C_{0,deta} \) on the capsule wall permeability for micro capsules with a dibutylphthalate (DBP, ■) core and a dimethylphthalate (DMP, ○) core. Calculated from thickness measurements.

### 5.4.2.2. The influence of addition of EDA to the aqueous phase

The influence of the addition of EDA to the aqueous phase was measured in the range of 0 to 1.2 of EDA/DETA concentration ratios, for two initial concentration
ratios of $C_{tdc}(t = 0)/C_{deta}(t = 0)$, being 2.97 and 3.58. The membrane permeability for DETA and EDA appears to decrease as more EDA is added to the aqueous phase (Fig. 5.12 and Fig. 5.13 respectively). Due to the addition of EDA to the aqueous phase the cross-link density decreases and the volume fraction of the crystalline phase increases causing the diffusion coefficient to decrease. Again there is no significant decrease of $D_{p, deta}$ or $D_{p, eda}$ with increasing $C_{tdc}(t = 0)/C_{deta}(t = 0)$ ratio as obtained by thickness measurements. Which is readily observed in Fig. 5.6 and Fig. 5.7 obtained by concentration measurements.

![Graph](image_url)

**Figure 5.12.** The influence of the addition of ethylenediamine (EDA) to the amine solution on the capsule wall permeability (capsules have a DMP core). The influence of the diffusion of DETA through the capsule wall. Calculated from thickness measurements. $C_{3,tdc}/C_{o, deta} = 2.97$ (■) and 3.58 (○).

5.4.3. **Assessment of both models**

Assessment of both models by the results of the concentration and the thickness experiments doesn't favor one for the other.

Concentration measurements show a concentration of TDC proportional to $\sqrt{t}$ which is in agreement with equation (5.11). This equation holds for both models.

Thickness measurements show a wall thickness proportional to $\sqrt{t}$ and an increase of the capsule wall porosity [2] as the wall grows thicker. Model 2 yields a relationship which describes the wall thickness proportional to $\sqrt{t}$ (equation
(5.17)). On the other hand, model 2 assumes that the porosity of the capsule wall \( (\epsilon_2) \) is constant. Model 1 describes the porosity \( (\epsilon_1) \) to increase with time but the relationship which describes the wall thickness is a quadratic function of \( \sqrt{t} \).

![Graph showing the influence of ethylenediamine (EDA) on capsule wall permeability.](image)

**Figure 5.13. The influence of the addition of ethylenediamine (EDA) to the amine solution on the capsule wall permeability (capsules have a DMP core). The influence of the diffusion of EDA through the capsule wall. Calculated from thickness measurements.** \( C_{j,t_{dc}}/C_{0,det} = 2.97 \) (α) and 3.58 (ο).

### 5.4.4. Permeability measurements

The release of DETA from micro capsules the following equation is given by Kondo et. al. [21]:

\[
\ln \left( \frac{C_{\text{complex}(\omega)} - C_{\text{complex}(0)}}{C_{\text{complex}(\omega)} - C_{\text{complex}(t)}} \right) = \frac{6 D_{p, deta}}{d_c d_t} t
\]

(5.30)

Where \( C_{\text{complex}(t)} \) is the concentration of the Ni(DETA)_2^+ complex concentration at \( t \). The release of DETA from capsules made with a DBP core is shown in Fig. 5.14, where the left hand side of equation (5.30) is plotted against time; a linear relationship is observed up to 700 seconds of DETA release. \( D_{p, deta} \) can be
calculated from the slope in Fig. 5.14.

Fig. 5.15 shows the calculated \( D_{p,\text{deta}} \) as a function of the capsule wall thickness for DBP core capsules for several values of \( C_{\text{tdc}}/C_{\text{deta}} \). The diffusion coefficient of DETA increases as the wall thickness increases; this indicates a change of the properties of the capsule wall during its growth. The increase of \( D_{p,\text{deta}} \) indicates an increase of cross-link density and, consequently, a decrease of crystallinity (as shown in Figs. 5.4 - 5.7), hence this in turn, indicates that the ratio \( (C_{\text{tdc}}/C_{\text{deta}}) \) is increased. One might explain these observations as follows: since the wall thickness increases with the reaction time, the flux of DETA decreases, so the ratio \( (C_{\text{tdc}}/C_{\text{deta}}) \) near the interface, where the reaction takes place, increases, resulting in the observed increase in the diffusion coefficient. In the range of \( C_{\text{tdc}}(t = 0)/C_{\text{deta}}(t = 0) \), there is no change in \( D_{p,\text{deta}} \) as calculated from permeability measurements as a function of \( C_{\text{tdc}}(t = 0)/C_{\text{deta}}(t = 0) \).

![Diagram](image)

*Figure 5.14. Permeability measurements: the release of DETA from micro capsules as a function of time, the wall thickness is 35.4 μm.*

### 5.4.5. Comparison of diffusion coefficient obtained by concentration, thickness and permeability measurements.

The diffusion coefficient of DETA through the polymer membrane \( (D_{p,\text{deta}}) \) is calculated from measurements of the TDC concentration (equation (5.11)), the capsule wall thickness (equation (5.18) with \( K_{p,\text{pol}} r_t = M_{p}\rho_{w} \)) and the permeability experiments (equation (5.30)). \( D_{p,\text{deta}} \) is calculated for \( r_t = 0.9, M_{p} = 223 \text{ kg/kmol} \) and \( \rho_{\text{pol}} = 1200 \text{ kg/m}^3 \) in case of the concentration and thickness measurements; from
permeability experiments an average of $D_{p,deta}$ is calculated.

![Graph](image)

**Figure 5.15.** The diffusion coefficient of DETA through the polymer of the capsule membrane as a function of the wall thickness. $D_{p,deta}$ is calculated from permeability measurements. $C_{3,tdc}/C_{0,deta} = 1.07$ ($\Box$), 1.03 ($\circ$), 1.03 ($\triangleright$), 0.98 ($\odot$) and 0.42 ($\Delta$).

Fig. 5.16 and Fig. 5.17 show $D_{p,deta}$ as a function of the ratio $C_{tdc}/C_{deta}$ calculated from concentration ($\odot$) and thickness ($\triangleright$) measurements: Fig. 5.16 for capsules with a DBP core, Fig. 5.17 for capsules with a DMP core. Because of the poor reproducibility of the $D_{p,deta}$ calculated from the thickness measurements there is only little agreement between the relationship of $D_{p,deta}$ and $C_{tdc}/C_{deta}$ as calculated from concentration and thickness measurements for micro capsules with a DBP and DMP core.

Fig. 5.18 shows the relationship of $D_{p,deta}$ for micro capsules with a DBP core calculated from concentration measurements ($\odot$) and thickness measurements ($\triangleright$) compared with the $D_{p,deta}$ calculated from the permeability experiments ($\ast$). Again there is poor agreement between the values for $D_{p,deta}$ calculated from the three methods of measurement.

The permeability experiments do not indicate a significant change in $D_{p,deta}$ with varying concentration ratio of TDC and DETA.
Figure 5.16. $d_{p,deta}$ calculated from concentration measurements (o) and from thickness measurements (o) ($r = 0.9, \rho_{pol} = 1200 \text{ kg/m}^3$ and a DBP core) as a function of $C_{3,tdc}/C_{0,deta}$.

5.5. CONCLUSIONS

The two models presented to account for the formation of macrovoids within the capsule membrane, result in two identical relationships for the dependence of the TDC concentration on time and in two different relationships for the wall thickness as a function of time. The relationships for the wall thickness as a function of time differ: one is quadratic in $t^2$, the other is linear in $t$. From experiments it appears that the quadratic part is negligible which leaves a square root of time dependence. In that case both equations describing the wall thickness are identical.

For micro capsules the growth of the capsule wall and the concentration of TDC inside the capsule as a function of time obey the same equations as derived previously for macro capsules [2]. Addition of diamines to the aqueous triamine solution results in the same proportionality between the TDC concentration and the wall thickness with time. Transport of amines can be well described by a linear combination of the triamine and the diamine flux.
Figure 5.17. \( D_{p,deta} \) calculated from concentration measurements (o) and from thickness measurements (o) \( (r = 0.9, \rho_{pol} = 1200 \text{ kg/m}^3 \) and a DMP core) as a function of \( C_{3,tdc/C_{0,deta}} \).

Figure 5.18. \( D_{p,deta} \) calculated from concentration measurements (o), thickness measurements (o) and permeability measurements (A) as a function of \( C_{3,tdc/C_{0,deta}} \), \( r = 0.9, \rho_{pol} = 1200 \text{ kg/m}^3 \) DBP core.
The dependence of the diffusion coefficient (calculated from concentration, thickness and permeability experiments) on the concentration ratios of TDC and DETA and on diamine and triamine agree.

5.6. REFERENCES


CHAPTER 6

MEMBRANE PERMEABILITY AND GROWTH

6.1. INTRODUCTION

At the interface of two immiscible liquids (e.g. an aqueous and an organic phase) a membrane is produced by the polycondensation reaction of e.g. terephthaloyldichloride (TDC) and diethylenetriamine (DETA). When the organic phase is immersed into the aqueous phase, small droplets are formed and the membrane produced at the interface surrounds the organic phase, thereby producing a capsule.

When the interface between the liquids is flat, a sheet of polymer is produced forming the membrane. The polymer formation is identical to the production of polymer by which capsule walls grow. In both cases the reaction proceeds near the interface of the organic and the aqueous phase. Earlier studies showed that the influence of the radius of the micro capsule on the wall thickness of the micro capsule is negligible and that the micro capsule wall can be regarded at as a sheet.

The permeability characteristic of such a membrane can be measured more accurately as in the case of a spherical membrane because the area of release is known more accurately. The first part (section 6.2) reports the permeability of sheets of membrane for NaCl for different production conditions.

Measurements of the growth of the micro capsule wall showed that the wall thickness increased proportionally to the square root of the growth time. This proportionality is related to the diffusion process of the amine through the produced polymer layer. Measurements showed that the relation holds for a growth time of 60 seconds and more (see chapter 5). The second part of this chapter (section 6.3) shows the influence of the process conditions while measuring growing membranes between two plates of glass. In the last part of this chapter (section 6.4) the absorption of light transmitted through a growing layer of polymer is reported for polymer production from 2 seconds after the time of initiation.
6.2. PERMEABILITY MEASUREMENTS

For various process conditions polymer was produced at a flat surface. This yields sheets of membrane, which were used to measure the rate of diffusion of NaCl through the membrane. The diffusion coefficient of NaCl through the membrane could be calculated from measurements of the membrane thickness (SEM), the diffusion area and the flux of NaCl through the membrane.

6.2.1. Experimental

6.2.1.1. Production of polyterephthalamide membranes

The membrane was produced by interfacial polycondensation; the reaction between terephthaloyldichloride (TDC) and diethylenetriamine (DETA) starts at contact of a solution of TDC in e.g. dibutylphthalate (DBP) and an aqueous solution of DETA. During the process HCl is released as a product of the reaction, which is neutralized by NaOH dissolved in the aqueous phase. The two solutions were brought into contact in the following way: the bottom of a glass disk was dipped into the organic phase. The thin film (approximately 20 μm) of the organic phase which sticks at the bottom of the glass disk was then brought into contact with the aqueous phase. At this moment the polycondensation starts. After 15 min. of reaction the membrane is strong enough to be rinsed with ethanol and water respectively. The membrane was then stored in water to be used for permeability measurements. During the growth of the membrane the concentration of TDC in the organic phase decreases. This is larger then the decrease of the TDC concentration of micro capsules, because of the difference in the volume/surface ratio ($2 \times 10^{-5}$ m for the membranes, $1.7 \times 10^{-4}$ m for micro capsules with $d_e = 1$ mm). However, the reaction rate of TDC and DETA is determined by the diffusion of DETA, so that the measurements of the permeability of the flat membranes are comparable to the results obtained by the micro encapsulation experiments.

In other methods to produce a sheet of polymer a layer of one of the phases without the monomers is needed, to form a flat interface. This causes a delay before both monomers meet by transport and react. Because of the rapid production of polymer (within 2 seconds after liquid–liquid contact a layer of polymer is produced, see section 6.4.2.) it is necessary that the concentration of both monomers near the interface is identical to the concentration in the bulk of the phases. That is because the concentration ratio of TDC and DETA in the bulk determines the properties of the membrane produced [3].
6.2.1.2. **Diffusion measurements**

The membranes were used to measure the rate of diffusion of NaCl through the membrane, which separated a vessel into a upper and lower part. A solution of NaCl was fed through the upper part; the NaCl diffused through the membrane into the lower part of the vessel. This part contained a conductivity cell which recorded the conductivity of the solution. The conductivity in the lower part increased with time at a decreasing rate because of the decreasing concentration difference of NaCl between the upper and lower part of the vessel. From the slope at \( t = 0 \) the flux of NaCl was calculated (kmol/(m\(^2\)s)) and with Fick's first law of \( \text{D}_{\text{NaCl}} \). The membrane surface (\( A_m \)) was \( 1.26 \times 10^{-3} \text{ m}^2 \) and the volume of the lower part (\( V_r \)) \( 80 \times 10^{-6} \text{ m}^3 \).

The permeability of the membranes towards NaCl is compared to the release of NaCl from micro capsules which have an identical membrane, viz. the capsule wall. To measure the release of NaCl micro capsules were filled with a solution of NaCl by immersing the capsules into a 1.0 kmol/m\(^3\) solution of NaCl for several days. These capsules were immersed into water with a volume \( V_{\text{ex}} \). The conductivity of the external solution increased by the release of NaCl from the micro capsules. Its conductivity was measured and from a mass balance the volume of the capsules was calculated \( (V_c) \).

6.2.1.3. **Thickness measurements**

To calculate the diffusion coefficient of NaCl through the membrane the thickness of the membrane was measured. The thickness of membranes swollen in water were measured with a micrometer. This measures the average membrane thickness of an area of 78 mm\(^2\); assuming the membrane thickness is not significantly decreased by the pressure applied during the measurement. The membrane thickness is measured at several places across the membrane, with a relative deviation of 10 %.

6.2.1.4. **Characterization of membranes by DSC, FTIR, WAXS**

The membrane material was characterized with the aid of DSC, FTIR and WAXS. For that purpose it was dried in an oven at 60 °C for 24 hours. After drying the polymer was powdered. For the FTIR measurements it was mixed with KBr and pressed to produce a tablet. FTIR was measured at a Polaris spectroscope. DSC measurements of the dried polymer were measured from 50 °C to 200 °C at a Mettler DSC 12 E.
6.2.2. Results & discussion

6.2.2.1. Influence of $C_{tdc}/C_{deta}$

From the plot of the conductivity as a function of time the slope at $t = 0$ was measured and with the aid of a calibration $\partial C_{NaCl}/\partial t$ was calculated. The diffusion coefficient of NaCl through the membrane ($D_{NaCl}$) was calculated with:

$$D_{NaCl} = \frac{\partial C_{NaCl}}{\partial t} \times \frac{V_v}{A_m} \times \frac{d_t}{C_{NaCl}}$$  \hspace{1cm} (6.1)

where $d_t$ is the thickness of the membrane.

Fig. 6.1 shows the effect of the process conditions during membrane production (i.e. $C_{tdc}/C_{deta}$ on $D_{NaCl}$). The scatter as shown in the graph is due to the variation of the membrane thickness across the area through which NaCl diffusion takes place. Despite of the scatter an increase of $D_{NaCl}$ with the $C_{tdc}/C_{deta}$ is perceptible; this is in agreement with measurements of the diffusion coefficient of amines through capsule membranes [1,2,3]. The order of the value of $D_{NaCl}$ agrees with values reported in literature [4].

![Graph showing $D_{NaCl}$ as a function of $C_{tdc}/C_{deta}$](image_url)

*Figure 6.1. $D_{NaCl}$ through TDC/DETA membranes as a function of $C_{tdc}/C_{deta}$; the organic phase is DBP.*

6.2.2.2. Addition of diamines

Addition of ethylenediamine (EDA) or hexamethylenediamine (HMDA) reduces the permeability of the capsule membrane. Fig. 6.2 shows the dependence of $D_{NaCl}$ on
\( C_{\text{eda}}/C_{\text{deta}} \) and \( C_{\text{hmda}}/C_{\text{deta}} \): The decrease of the number of cross-links, due to the increased concentration of a diamine, probably results in a polymer which has a higher volume fraction of a crystalline phase [6]. This crystalline phase largely reduces \( D_{\text{NaCl}} \). Introduction of HMDA instead of EDA increases the length of the polymer chain between cross-links, which results in a higher volume fraction of crystalline phase. This reduces the \( D_{\text{NaCl}} \) of the membrane in regard to the EDA/DETA membranes.

![Graph showing \( D_{\text{NaCl}} \) as a function of \( C_{\text{diamine}}/C_{\text{deta}} \).](image)

**Figure 6.2.** \( D_{\text{NaCl}} \) through TDC/DETA/diamine (■ EDA, + HMDA) membranes as a function of \( C_{\text{diamine}}/C_{\text{deta}} \); the organic phase is DBP.

6.2.2.3. **Characterization**

DSC measurements are performed for polymer produced from TDC and DETA with EDA \((C_{\text{tde}}/C_{\text{deta}} = 1.69 \text{ and } C_{\text{eda}}/C_{\text{deta}} = 2.67)\). It shows a broad endotherm peak at \( T = 120 \, ^{\circ}\text{C} \) in the first run, however, it has disappeared in the second run. The peak is probably due to the melting of the crystalline phase. There is no solid base to produce qualitatively values for the melting enthalpy. There is no relationship between the melting enthalpy of the crystalline phase and the amount of EDA incorporated in the membrane; as \( C_{\text{eda}}/C_{\text{deta}} \) increase the melting enthalpy fluctuates.

The diffraction pattern of small angle X-ray experiments do not show up when the same polymer is measured after being heated in an oven at 200 \(^{\circ}\text{C}\) for 24 hours. Apparently the original crystalline phase does not reappear after heating. The circle corresponds to a domain size of 1.5 nm. Mathiowitz shows that polymer
produced from EDA or HMDA with DETA and TDC is of higher crystallinity (more linear polymer) than polymer produced from DETA and TDC (more cross-links) [6].

FTIR measurements show an increase of the absorption of -CH₂- groups at 3300 cm⁻¹ when diamine is added to the aqueous phase to produce the polymer membrane. Addition of HMDA instead of EDA to the aqueous phase results in an additional increases of the absorption of the CH₂ groups.

6.2.2.4.  
**NaCl release from micro capsules**

Fig. 6.3 shows the release of NaCl from micro capsules as a function of time; it follows from a mass-balance (see [5]):

\[
\ln \left[1 - \frac{C_{ex}(t)}{C_{ex}(\infty)}\right] = -\frac{C_{in}(0) \cdot A \cdot D_{NaCl}}{V_{ex} \cdot d_{w}} \cdot t
\]  

(6.2)

where \(C_{ex}\) is the NaCl concentration in the external phase, \(C_{in}\) the concentration inside the capsules, \(n\) the number of capsules, \(A\) the surface area of one capsule, \(V_{ex}\) the volume of the external phase, \(d_{w}\) the thickness of the capsule wall and \(D_{NaCl}\) the diffusion coefficient of NaCl through the membrane. From the slope of the line in Fig. 6.3 \(D_{NaCl}\) is calculated and plotted versus \(C_{hmda}/C_{DETA}\) in Fig. 6.4. Fig. 6.4 shows that \(D_{NaCl}\) from membrane experiments and capsule release experiments are of the same order of magnitude. There is no significant decrease of \(D_{NaCl}\) with increasing concentration of HMDA relative to the concentration of DETA. Before measuring the release of NaCl the capsules are immersed into a solution of NaCl (\(C_{in}(0)\)), then, before the capsules are transferred into the external phase (\(V_{ex}\)), the outside of the capsule is rinsed quickly with water which may leave some NaCl. Furthermore discrepancies in wall thickness introduces errors in calculating \(D_{NaCl}\). This leads to the observed scatter of \(D_{NaCl}\) versus \(C_{hmda}/C_{DETA}\) in Fig. 6.4.

6.2.3.  
**Conclusions**

The diffusion of NaCl is affected by the concentration ratio of TDC and DETA in the same way as this ratio affects the diffusion of DETA during encapsulation by interfacial polycondensation [1,2,3]. Also the influence of diamines added to the aqueous phase during membrane growth is identical as can be expected from micro encapsulation experiments [3].

66
6.3. GROWTH MEASUREMENTS BY LIGHT MICROSCOPY

In micro encapsulation experiments the growth of the membrane thickness is studied by measuring the thickness of dried cut cross sections of micro capsules with SEM. Because of the amount of water which swells the membrane, an error is
introduced. Because a part of the water is incorporated in the polymer and the other part is present in macrovoids within the membrane, the actual membrane thickness can not be calculated from swelling experiments. In order to study the growth of the wall thickness a light transmission microscope is used.

6.3.1. Experimental

6.3.1.1. Growth measurements
Two glass plates were separated by a piece of tape leaving a gap of approximately 0.1 mm. At one end of the top plate a drop of the organic phase (containing TDC) was put and at the other side of the plate a drop of the aqueous phase (containing amine and NaOH) was put. Due to capillary forces both liquids spread between both glass plates making contact in the middle of the top plate. At this moment the polycondensation starts and a membrane is produced. It takes about one minute to locate the membrane and focus, before the thickness can be measured. With the aid of a microscope the direction of view is perpendicular to the plates and parallel to the membrane surface. The direction of growth is perpendicular to the direction of view. The thickness was measured with a Linkam VTD 232 video overlay device.

6.3.1.2. Process conditions
For both dibutylphthalate (DBP) and dimethylphthalate (DMP) used for the organic phase (also the core of o/w micro capsules) the growth of the membrane thickness was measured. The concentration ratio of TDC and DETA was varied between 0.5 and 4.0. For a system with \( C_{\text{tdc}}/C_{\text{deta}} = 2.0 \) diamine was added to the DETA solution. Both \( C_{\text{edta}}/C_{\text{deta}} \) and \( C_{\text{hmda}}/C_{\text{deta}} \) were varied between 0.2 and 4.0.

6.3.2. Results & discussion

6.3.2.1. Model for wall growth
After the formation of the first layer of polymer at the liquid-liquid interface, the growth rate of the membrane is determined by the diffusion of DETA through the membrane. The diffusion of DETA can be described by Ficks law (with \( D_{\text{p,deta}} < D_{\text{w,deta}} \) (see chapter 5):

\[
J_{\text{deta}} = D_{\text{p,deta}} \frac{C_{0,deta}}{d_{l}(1 - \epsilon)}
\]

(6.3)
The growth of the membrane thickness can be described by the model of a water flux which depends on the flux of amine. This gives for $d_t$ (see chapter equation 5.18):

$$d_t = \frac{2 \cdot D_{p,deta} \cdot C_0 \cdot deta \cdot [K_1 \cdot \rho_{pol} \cdot \frac{r_t}{M_u} + \frac{M_u}{\rho_w} \cdot \frac{r_t}{\rho_{pol}}]^2 \cdot t}{M_u \cdot \rho_w \cdot \frac{r_t}{\rho_{pol}}}$$ \hspace{1cm} (6.4)

![Graph showing membrane thickness as a function of time](image)

*Figure 6.5. The membrane thickness as a function of time, from light transmission experiments. (+ and ■ are duplicates).*

6.3.2.2. Growth versus time

Fig. 6.5 shows the membrane thickness as a function of time for DBP as a core liquid and $C_{tDC}/C_{deta} = 0.88$. The thickness increases proportional to $\sqrt{t}$; the deviation for $t > 300$ sec is due to expiration of TDC and/or DETA. The permeability of the membrane can be described by $\sqrt{2 \cdot D_{p,deta} \cdot M_u \cdot \frac{r_t}{\rho_{pol}}}$, which is a function of $C_{tDC}/C_{deta}$. The value of $\sqrt{2 \cdot D_{p,deta} \cdot M_u \cdot \frac{r_t}{\rho_{pol}}}$, measured from Fig. 6.5, is $5 \times 10^{-6}$ $\frac{m^5}{(kmol \cdot s)}$, whereas under identical process conditions from thickness measurements of dried micro capsule membranes this value was calculated to be $2 \times 10^{-6}$ $\frac{m^5}{(kmol \cdot s)}$ [3] (see chapter 5). The value for the dried micro capsule membrane will be larger if there is accounted for the larger thickness of the membrane when swollen. The fraction of polymer in swollen membranes was measured to be $W_d/W_s = 0.35$ at $C_{tDC}/C_{deta} = 0.88$, see Fig. 6.6. When the thickness of dried membranes is related to the weight fraction of polymer then this accounts for the difference between the membrane measurements and the micro capsule measurements.
Figure 6.6. The fraction polymer in water swollen membranes ($W_d/W_s$) as a function of the process conditions ($C_{tdc}/C_{dela}$), the organic phase is DBP. (+ and ■ are duplicates).

Figure 6.7. The permeability for DETA of TDC/DETA membranes calculated from light microscopy measurements as a function of $C_{tdc}/C_{dela}$; ■ DBP, + DMP.

6.3.2.3. Influence of $C_{tdc}/C_{dela}$

The value of $C_{tdc}/C_{dela}$ influences the number of cross-links in the membrane polymer, which in turn determines the $\sqrt{\frac{2D_{p,dela}M_u}{r_{t,\rho_{pol}}}}$. This effect is shown in Fig. 6.7 where $\sqrt{\frac{2D_{p,dela}M_u}{r_{t,\rho_{pol}}}}$ is plotted as a function of $C_{tdc}/C_{dela}$. 
with DBP and DMP used for the organic phase. There is no significant difference for membranes made in DBP or DMP; this is in agreement with measurements for micro capsules.

![Graph](image)

Figure 6.8. The permeability for DETA of TDC/DETA/diamine membranes as a function of $C_{\text{diamine}}/C_{\text{deta}}$ - EDA, + HMDA.

6.3.2.4. Addition of diamines

Fig. 6.8 shows that addition of diamine to the aqueous phase reduces $\sqrt{\frac{2}{D_{p,\text{deta}}} \frac{M_u}{(r_1 \rho_{pol})}}$. Process conditions with $C_{tdc}/C_{\text{deta}} = 2.0$ yields polymer for which this value appears to be $1.7 \times 10^{-5}$ $\text{m}^5/(\text{kmol s})$ (see Fig. 6.7); consequently the value for $\sqrt{\frac{4}{D_{p,\text{deta}}} \frac{M_u}{(r_1 \rho_{pol})}}$ is $2.4 \times 10^{-5}$ $\text{m}^5/(\text{kmol s})$ at $C_{\text{diamine}}/C_{\text{tri diamine}} = 0$. Fig. 6.9 shows the same effect for the diffusion coefficient of the diamine when diamine is added to the aqueous phase. Comparison of Figs. 6.8 and 6.9 shows that, with constant values for $M_u/(r_1 \rho_{pol})$, the diffusion coefficient for diamine is approximately twice that of DETA. Because of the secondary amine group (-NH-) in DETA it has more hydrational water than the diamine while diffusing through the polymer and/or it has more interactions with the polymer, which both result in a decrease of the diffusion coefficient of DETA compared to that of the diamine.

6.3.2.5. Influence of the organic phase

As can be seen from Fig. 6.7, there is no significant difference for the diffusion coefficient of DETA in the case of membranes made from a solution of TDC
in DBP or DMP. The method is not suitable for measuring the influence of the organic phase on the permeability of the membrane.

![Graph showing permeability as a function of concentration](image)

**Figure 6.9.** The permeability for diamine of TDC/DETA/diamine membranes as a function of \( \frac{C_{\text{diamine}}}{C_{\text{deto}}} \) ■ EDA, + HMDA.

### 6.3.3. Conclusions

The growth of the membrane thickness can be measured adequately, but it is not suitable for measuring the early stage of membrane growth. The proportionality between the thickness and \( \sqrt{t} \) is in agreement with growth measurements of micro capsules. The dependence of the diffusion coefficient of both triamine (DETA) and diamine (EDA, HMDA) on process conditions (i.e. concentration ratios) is similar to the dependency as measured for micro capsules.

### 6.4. THE EARLY STAGE OF WALL GROWTH BY LIGHT TRANSMISSION SPECTROSCOPY

The growth of the membrane thickness is determined by the diffusion of amine through the membrane. At the very first stage of membrane formation no polymer is present and consequently the growth of the membrane is not determined by diffusion of amine through the membrane. The length of this initial period of membrane formation is very short. Measurements of the membrane thickness during encapsulation or in vitro during membrane growth yields the membrane thickness as a
function of time from 30 seconds or more. Observation of the formation of the first layer of polymer shows that a layer of polymer is formed within a very short period [Morgan 1959].

By measuring the transmission of light through a growing membrane the process of membrane formation can be followed from 2 seconds and more.

6.4.1. Experimental

6.4.1.1. Experimental setup

The transmission of light was measured with a diode array spectrophotometer (Oriel instaspec) which enables us to make a spectrum of the light transmission from $\lambda = 350$ nm to $800$ nm every 5 sec. The set up to grow the membranes was identical to the membrane production used for the permeability experiments. The light source was situated above the glass disk from which a parallel light beam was emitted. The beam passed the growing membrane, after which it was led to the diode array through a glass fiber. 2 Seconds after contact between the aqueous and organic phase the transmission spectrum was measured every 5 seconds. Each spectrum was stored in a computer and after 60 spectra the membrane formation was stopped.

From each spectrum the transmission at $\lambda = 500$ nm was taken and plotted against $\sqrt{t}$ (see Fig. 6.10).

To correlate the absorbance with the thickness the growth of the membrane was stopped and the membrane thickness measured with a micrometer.

6.4.1.2. Absorbance measurements

The Lambert-Beer relationship describes the absorption of light:

$$- \log \left( \frac{I}{I_0} \right) = \left( S(\lambda) + A(\lambda) \right) \times l$$

(6.5)

where $I_0$ and $I$ are the intensities of the light before and after scattering respectively, $S(\lambda)$ the scattering coefficient of the polymer chain, $A(\lambda)$ the absorption coefficient and $l$ the path length.

In the case of membrane formation polymer chains are produced which precipitate. Light subsequently scattered by the precipitated polymer chains is not detected by the diode array. Assuming that the density of the precipitated polymer is constant throughout the process of membrane formation and the absorption coefficient is negligible to the diffraction coefficient ($S(\lambda)$) then $E$ is
proportional to the path length \( l \). Which is in turn proportional to the thickness of the membrane. The membrane thickness is proportional to \( \sqrt{l} \) (see Eq. (6.4)) so that the following relationship between \( A \) and time exists:

\[
\frac{\partial A}{\partial t} = S(\lambda) \sqrt{\frac{2 D_{p,deta} C_{deta} M_u}{\tau_l \rho_{pol}}} \tag{6.6}
\]

Absorbance was measured as a function of \( C_{tdc}/C_{deta} \) (varied between 0.3 and 3.0), as a function of \( C_{eda}/C_{deta} \) (varied between 0.5 and 2.9) and as a function of \( C_{eda}/C_{tdc} \) (varied between 0.5 and 2.9).

![Graph showing absorbance over time](image)

Figure 6.10. The absorbance of a growing TDC/DETA membrane as a function of time, the organic phase is DBP, \( C_{tdc}/C_{deta} = 2.30 \). ■ and + are duplicates.

6.4.2. Results & discussion

6.4.2.1. Growth of the membrane, absorbance versus time

Fig. 6.10 shows the relationship between the absorbance of a growing TDC/DETA membrane as a function of time with \( C_{tdc}/C_{deta} = 0.362 \) in DBP. The absorbance is already proportional to \( \sqrt{l} \) after 2 seconds of membrane formation up to 25 seconds. This means that the growth of the membrane thickness is determined by diffusion of DETA through the membrane. Within 2 seconds the top layer of the membrane determining the process of membrane growth is produced.

\( S(\lambda) \) was measured to be \( 4 \times 10^4 \) m\(^{-1}\); \( A \) and \( l \) were measured after 40 seconds and 130
seconds of membrane formation and \( S(\lambda) \) was calculated with \( S(\lambda) = \frac{A}{l} \). There is no difference between \( S(\lambda)(t = 40) \) and \( S(\lambda)(t = 120) \) despite of the appearance of larger 'bulbs' at the organic side of the membrane (see SEM photographs 1 to 3 taken after 10, 40 and 130 seconds of membrane growth respectively (Fig. 6.11)).

![SEM images of membrane formation](image1.png)

**Figure 6.11.** SEM of the organic side of a membrane, which shows the increase of the macro voids, at 10, 40 and 130 seconds respectively.

![Permeability graph](image2.png)

**Figure 6.12.** The permeability for DETA of TDC/DETA membranes as a function of \( \frac{C_{\text{tdc}}}{C_{\text{deta}}} \) measured with absorbance of the growing membrane (■) compared to measurements of the membrane thickness of micro capsules (+).
6.4.2.2. Influence of $C_{tdc}/C_{deta}$

Fig. 6.12 shows $\sqrt{2 D_{p,deta} M_u/(r_t \rho_{pol})}$ as a function of the concentration ratio of TDC and DETA ($C_{tdc}/C_{deta}$). It appears that the permeability of the membrane increases with increasing $C_{tdc}/C_{deta}$. This is probably due to the increased cross-linking and consequently decreased crystallinity of the membrane polymer. The value of $\sqrt{2 D_{p,deta} M_u/(r_t \rho_{pol})}$ measured by absorption (swollen membranes) is somewhat higher than that measured from the thickness of dried microcapsules. This is in agreement with the measurements of the thickness of membranes by light transmission microscopy (section 6.3.2.2.).

6.4.2.3. Addition of diamine

At a constant value of $C_{tdc}/C_{deta}$ of 0.75 diamine is added to the aqueous phase. The influence of EDA on the diffusion of DETA is shown in Fig. 6.13. Fig. 6.14 shows the influence of the addition of EDA to the diffusion of EDA. In both cases addition of diamine results in a strongly decreased value of the diffusion coefficient of DETA and EDA.

![Graph](image)

Figure 6.13. The permeability for DETA of TDC/DETA/EDA membranes as a function of $C_{eda}/C_{deta}$

6.4.2.4. Effect of diamine

Instead of DETA or a combination of EDA/DETA in some experiments only EDA was used in the aqueous solution. Fig. 6.15 shows the increase of the absorption with time, which appears to be proportional with $t$. The effect of the $C_{eda}/C_{tdc}$ ratio

76
on the permeability of the membrane is shown in Fig. 6.16. The membrane permeability increases with $C_{\text{eda}}/C_{\text{tdc}}$, probably due to the effect of crystallisation of the polymer.

![Graph showing permeability as a function of $C_{\text{eda}}/C_{\text{detaa}}$.](image)

**Figure 6.14.** The permeability for EDA of TDC/DETA/EDA membranes as a function of $C_{\text{eda}}/C_{\text{detaa}}$.

![Graph showing absorbance as a function of time.](image)

**Figure 6.15.** The absorbance of light transmitted through a growing TDC/EDA membrane as a function of time, $C_{\text{tdc}}/C_{\text{eda}} = 0.63$. (+ and ■ are duplicates).
6.4.3. Conclusions

The growth rate of the membrane is determined by the diffusion of amine from the aqueous phase through the membrane into the organic phase. Within 2 seconds a top layer of the membrane is formed, consequently from 2 seconds the membrane growth is determined by the diffusion of amine through the membrane. The permeability of the membranes increases with an increasing $C_{tdc}/C_{deta}$, which is in agreement with micro capsule measurements. Addition of EDA decreases the permeability of the membranes. However, an increase of EDA relative to DETA results in an increase of the diffusion coefficient of DETA through the membrane. This is in contradiction with the results obtained from micro encapsulation measurements.

![Figure 6.16. The permeability for EDA of TDC/EDA membranes as a function of $C_{eda}/C_{tdc}$.](image)

6.5. DISCUSSION MEMBRANES & MICRO CAPSULES

The influence of the process conditions on the permeability of the membrane, whether prepared to produce a capsule or a sheet of membrane, is in essence the same. The diffusion of triamine, diamine or NaCl through the membrane is reduced as the crystallinity of the polymer increases. This is a consequence of a reduced cross-link density, or/and an increase of the chain length between cross-links, due to the addition of diamines (compare Fig. 5.5 and Fig. 6.1 (reduced cross-link density) and Fig. 5.6, 5.7 with Fig. 6.2).

This is also the case from calculations of the diffusion coefficients from
thickness measurements of micro capsules (Fig. 5.11) and from calculations from
measurements of the thickness with the light transmission microscope (Fig. 6.7) and
light absorption measurements (Fig. 6.12).

This shows, that there is no difference in the mechanism of the growth of the
membrane, whether it is grown from spherical or planar geometries. This also shows,
that the assumption, which is made for the model of wall growth, holds for both
generacies.

6.6. REFERENCES

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CHAPTER 7

MICROENCAPSULATION OF A WATER-IN-OIL EMULSION

7.1. INTRODUCTION

Many applications for micro capsule systems require a core of the micro capsule which consists of an aqueous solution. The transfer release of fertilizer or pesticide which is soluble in water or the controlled release of bleach in liquid detergents require an aqueous core instead of a core with an organic solvent. To control the release rate from the core the properties of the capsule wall have to be controlled. As shown in the previous chapters the permeability of the capsule wall is determined by the reaction conditions during the interfacial polycondensation.

Micro capsules were produced by interfacial polycondensation of a dispersion of an aqueous phase in an organic phase. The influence of $C_{tdc}/C_{dela}$, the addition of EDA or HMDA to the aqueous phase and the influence of $C_{eds}/C_{tmc}$ (TMC = trimesoylchloride) are described. The model for the growth of the capsule wall and the macro voids is modified to satisfy the water-in-oil suspension.

7.2. THEORY FOR THE GROWTH OF THE CAPSULE WALL

The wall of the micro capsules is produced by the polycondensation of a diacid chloride and an amine. The rate of the polycondensation is determined by diffusion of the amine through the micro capsule wall, by which the wall is growing. From a mass balance over one micro capsule, relationships between the amine concentration inside the capsule and time and the wall thickness and time are developed. During the process of wall formation macro voids are produced within the membrane. This is described by a flux of water which is assumed to be constant, or to be depending on the flux of amine as the water is transported in a hydrial form [1].

The water-in-oil system differs from the oil-in-water system, in that in the latter the amine concentration is constant and an increase of the wall thickness only reduces the rate of diffusion. With the water-in-oil system the amine is inside the restricted volume of the micro capsules. During the growth of the capsule wall amine reacts and the concentration of the amine inside the capsules
decreases. Consequently the rate of diffusion is decreased by the decreased concentration of amine and the increased thickness of the capsule wall.

7.2.1. The growth of the capsule wall for TDC/DETA micro capsules

7.2.1.1. Model with a constant flux of water

From a mass balance over one micro capsule for DETA it follows (analogous to equation (5.1)):

\[
V_c \frac{\partial c_{3,\text{DETA}}}{\partial t} = k_{\text{DETA}} (c_{0,\text{DETA}} - c_{3,\text{DETA}}) A_c
\]  

(7.1)

where \(k_{\text{DETA}}\) is the mass transport coefficient for DETA through the membrane. DETA diffuses through the polymer matrix and the macro voids within the membrane. The resistance of the membrane to mass transfer is described by a series of the resistance of the polymer and the resistance of the macro voids. \(k_{\text{DETA}}\) is assumed to be a linear combination of two mass transport coefficients (equation (5.2)):

\[
\frac{1}{k_{\text{DETA}}} = \frac{d_t \varepsilon_1}{D_{V,\text{DETA}}} + \frac{d_t (1 - \varepsilon_1)}{D_{P,\text{DETA}}}
\]  

(7.2)

where \(d_t\) is the membrane thickness, \(\varepsilon_1\) is the fraction of macro voids, \(D_{V,\text{DETA}}\) and \(D_{P,\text{DETA}}\) are the diffusion coefficients of DETA through the voids and polymer respectively.

The growth rate of the membrane thickness can be described by the sum of the growth rate of the thickness of the macro voids (\(\dot{\phi}_m/\rho_w\)) and that of the thickness of the polymer. The growth rate of the thickness of the polymer is the product of the flux of DETA (\(k_{\text{DETA}} \times (c_{3,\text{DETA}} - c_{0,\text{DETA}})\)) and the molecular volume of the polymer unit \((M_u/r_{\text{pol}})\) (equation (5.4)).

\[
\frac{\partial d_t}{\partial t} = \frac{\phi_w}{\rho_w} + \frac{d_t \varepsilon_1}{D_{V,\text{DETA}}} + \frac{d_t (1 - \varepsilon_1)}{D_{P,\text{DETA}}} \left[ \frac{M_u}{r_{\text{pol}}} \right] \frac{(c_{3,\text{DETA}} - c_{0,\text{DETA}})}{}
\]  

(7.3)

where \(\phi_w\) is the mass flux of water (kg/m²s), \(\rho_w\) is the density of water, \(M_u\) is the molecular weight of the polymer per unit of TDC, \(\rho_{\text{pol}}\) is the density of the polymer.

The fraction of macro voids is equal to the fraction of water within the membrane, which is equal to the quotient of the total volume of water at time \(t\)
\((\phi_w t / \rho_w)\) and the membrane thickness at time \(t\) \((d_t)\) (equation (5.5)):

\[
\varepsilon_1 = \frac{\phi_w t}{\rho_w d_t}
\]  

(7.4)

A combination of equation (7.2) and equation (7.4) with equation (7.1) and equation (7.3) gives a relationship for the DETA concentration. When the resistance for mass transfer through the macro voids is negligible with respect to the resistance for mass transfer through the polymer \((D_{v,\text{DETA}} > D_{p,\text{DETA}})\), this gives:

\[
\frac{\partial C_{3,\text{DETA}}}{\partial t} = -\frac{6 D_{p,\text{DETA}}}{d_c \left( d_t - (\phi_w / \rho_w) t \right)} C_{3,\text{DETA}}
\]  

(7.5)

and a relationship for the wall thickness:

\[
\frac{\partial d_t}{\partial t} = \frac{\phi_w}{\rho_w} + \frac{D_{p,\text{DETA}}}{\left( d_t - (\phi_w / \rho_w) t \right)} \frac{M_u}{\Gamma_t \rho_{pol}} C_{3,\text{DETA}}
\]  

(7.6)

Elimination of \(d_t - (\phi_w / \rho_w) t\) by substitution of Eq. (5) into Eq. (6) and integration with at \(t = 0; d_t = 0\) and \(C_{3,\text{DETA}}(t) = C_{3,\text{DETA}}(0)\), gives:

\[
d_t = \frac{\phi_w}{\rho_w} t - \frac{d_c}{6} \frac{M_u}{\Gamma_t \rho_{pol}} \left[ C_{3,\text{DETA}}(t) - C_{3,\text{DETA}}(0) \right]
\]  

(7.7)

Equation (7.7) is substituted into equation (7.5), which gives:

\[
\frac{\partial C_{3,\text{DETA}}}{\partial t} = \frac{36 D_{p,\text{DETA}} \Gamma_t \rho_{pol}}{d_c^2 M_u} \frac{C_{3,\text{DETA}}(t)}{\left( C_{3,\text{DETA}}(t) - C_{3,\text{DETA}}(0) \right)}
\]  

(7.8)

After integration of equation (7.8) with at \(t = 0\) \(C_{3,\text{DETA}}(t) = C_{3,\text{DETA}}(0)\) this yields:

\[
\alpha - \ln(\alpha) = 1 + \frac{36 D_{p,\text{DETA}} \Gamma_t \rho_{pol}}{d_c^2 M_u C_{3,\text{DETA}}(0)} t
\]  

(7.9)

where \(\alpha = C_{3,\text{DETA}}(t)/C_{3,\text{DETA}}(0)\).

A relationship between the wall thickness \((d_t)\) and the concentration can be derived by substitution of equation (7.9) into equation (7.7), which yields:
\[
\frac{d_t}{\alpha - 1} = \frac{\phi_w d_c^2 M_u C_{3,deta}(0)}{36 \rho_w D_{p,deta} r_t \rho_{pol}} \left(1 - \frac{\ln(\alpha)}{\alpha - 1}\right) - \frac{d_c M_u C_{3,deta}(0)}{6 r_t \rho_{pol}}
\]  

(7.10)

A mass-balance gives the maximum thickness of the membrane, which given by:

\[
d_{t_{\text{max}}} = \frac{\phi_w d_c^2 M_u C_{3,deta}(0)}{36 \rho_w D_{p,deta} r_t \rho_{pol}}
\]

(7.11)

7.2.2.2. Model with a flux of water proportional to the flux of amine

According to Enkelmann [1] the amine is hydrated. This hydrated water is transported into the membrane together with the amine. The flux of water into the membrane is related to the flux of amine through the membrane:

\[
\phi_w = K_t \phi_{deta}
\]

(7.12)

The growth of the membrane becomes (with \(D_{p,deta} \ll D_{w,deta}\)):

\[
\frac{\partial d_t}{\partial t} = \frac{D_{p,deta}}{d_t (1 - e_2)} \left[\frac{K_t M_u}{\rho_w + \frac{r_t \rho_{pol}}{r_t \rho_{pol}}} \right] C_{3,deta}(t)
\]

(7.13)

The fraction of macro voids within the membrane \((e_2)\) is equal to equation (5.17) and is constant throughout the growth of the membrane. Substitution of equation (7.5) into equation (7.13) gives, after integration with at \(t = 0\), \(d_t = 0\) and \(C_{3,deta}(t) = C_{3,deta}(0)\):

\[
d_t = -\frac{d_c}{6} \left[\frac{K_t M_u}{\rho_w + \frac{r_t \rho_{pol}}{r_t \rho_{pol}}} \right] \left(C_{3,deta}(t) - C_{3,deta}(0)\right)
\]

(7.14)

To obtain a relationship which describes the wall thickness \((d_t)\) as a function of time, it is necessary to derive the relation between the DETA concentration and time. This can than be substituted into equation (7.14).

After substitution of equation (7.14) into equation (7.1) it becomes:

\[
\frac{\partial C_{3,deta}}{\partial t} = \frac{36 D_{p,deta} r_t \rho_{pol}}{d_c^2 M_u} \frac{C_{3,deta}(t)}{\left(C_{3,deta}(t) - C_{3,deta}(0)\right)}
\]

(7.15)

Which gives after integration with at \(t = 0\), \(C_{3,deta}(t) = C_{3,deta}(0)\):
\[ 1 - \alpha + \ln(\alpha) = -\frac{36 \, D_{p, \text{det}} \, r_t \, \rho_{\text{pol}}}{d_c^2 \, M_u \, C_{3, \text{det}}(0)} \]  

(7.16)

with \( \alpha = C_{3, \text{det}}(t)/C_{3, \text{det}}(0) \) (0 < \( \alpha \) ≤ 1). From equation (7.14) a relationship between \( \alpha \) and \( d_t \) can be derived, which is substituted into equation (7.16). This gives a relationship between \( d_t \) and \( t \):

\[ t = -\eta \ln \left[ 1 - \frac{d_t}{\phi} \right] - \frac{\eta}{\phi} \, d_t \]  

(7.17)

with

\[
\eta = \frac{d_c^2 \, M_u \, C_{3, \text{det}}(0)}{36 \, D_{p, \text{det}} \, r_t \, \rho_{\text{pol}}}
\]

\[
\phi = \left[ \frac{K_t + \frac{M_u}{\rho_w \, r_t \, \rho_{\text{pol}}}}{6 \, C_{3, \text{det}}(0)} \right] \frac{d_c}{d_t}
\]

\( \phi \) represents the maximum capsule wall thickness, which is the result when all DETA has reacted. With an estimation of the value of \( \phi \) one can calculate \( \ln(1 - d_t/\phi) \). A plot of \( \ln(1 - d_t/\phi) + d_t/\phi \) versus time gives a straight line. Then \( \phi \) can be varied to obtain the best coefficient of correlation; with this and the value of the slope \((\phi/\eta)\), \( \eta \) is calculated. This yields a value for the factor \( \frac{D_{p, \text{det}} r_t \rho_{\text{pol}}}{M_u} \), which is a value for the permeability of the polymer.

7.2.3. The growth of the capsule wall for TDC/DETA/EDA micro capsules

7.2.3.1. Model with a constant flux of water; EDA/DETA

A mass balance over one capsule for EDA is identical to that for DETA (equation (7.1)):

\[
\frac{\partial C_{3, \text{eda}}}{\partial t} = k_{\text{eda}} \frac{(C_{0, \text{eda}} - C_{3, \text{eda}}) \, A_c}{V_c} \]  

(7.18)

\( k_{\text{eda}} \) is the mass transport coefficient, which is defined as:
\[
\frac{1}{k_{\text{eda}}} = \frac{d_t}{D_{\text{v, deta}}} + \frac{d_t \left(1 - \epsilon_1 \right)}{D_{\text{p, eda}}}
\]  
(7.19)

The increase of the capsule wall thickness is a linear combination of the thickness of the water layer \((\phi_w/\rho_w)\) and the thickness of the polymer layer. The thickness of the polymer layer is the product of the flux of amine \((k_{\text{deta}}/r_t \times (C_{3, \text{deta}} - C_{0, \text{deta}}) + k_{\text{eda}}/r_d \times (C_{3, \text{eda}} - C_{0, \text{eda}}))\) and the molecular volume of the polymer unit \((M_u/\rho_{\text{pol}})\) produced by the polycondensation:

\[
\frac{\Delta d_t}{\Delta t} = \frac{\phi_w}{\rho_w} \left[ \frac{k_{\text{deta}} (C_{3, \text{deta}} - C_{0, \text{deta}})}{r_t} + \frac{k_{\text{eda}} (C_{3, \text{eda}} - C_{0, \text{eda}})}{r_d} \right] \frac{M_u}{\rho_{\text{pol}}}
\]  
(7.20)

A relationship for the concentration of EDA, derived similar to equation (7.5), reads:

\[
\frac{\partial C_{3, \text{eda}}}{\partial t} = \frac{6}{d_t} \frac{D_{\text{p, eda}}}{(\phi_w/\rho_w) \ t} \ C_{3, \text{eda}}
\]  
(7.21)

The relationship for the wall thickness becomes with: \(D_{\text{v, deta}} \leq D_{\text{p, deta}}, C_{0, \text{deta}} = 0\) and \(C_{0, \text{eda}} = 0\):

\[
\frac{\partial d_t}{\partial t} = \frac{\phi_w}{\rho_w} + \frac{r_t D_{\text{p, deta}} C_{3, \text{deta}} + r_t D_{\text{p, eda}} C_{3, \text{eda}}}{d_t - (\phi_w/\rho_w) \ t} \ \frac{M_u}{r_t r_d \rho_{\text{pol}}}
\]  
(7.22)

Substitution of equation (7.5) and equation (7.21) into equation (7.22) yields:

\[
\frac{\partial d_t}{\partial t} = \frac{\phi_w}{\rho_w} \left[ \frac{\partial C_{3, \text{deta}}}{\partial t} + \frac{\partial C_{3, \text{eda}}}{\partial t} \right] \frac{d_t}{6 \ r_t \ r_d \ \rho_{\text{pol}}}
\]  
(7.23)

This yields after integration with at \(t = 0, d_t = 0, C_{3, \text{deta}} = C_{3, \text{deta}}(0)\) and \(C_{3, \text{eda}} = C_{3, \text{eda}}(0)\):

\[
\frac{\phi_w}{\rho_w} t - \left[ r_d \left(C_{3, \text{deta}} - C_{3, \text{deta}}(0)\right) + r_t \left(C_{3, \text{eda}} - C_{3, \text{eda}}(0)\right) \right] \frac{d_t}{6 \ r_t \ r_d \ \rho_{\text{pol}}}
\]  
(7.24)
7.2.3.2. A model for a flux of water proportional to the flux of amine

In this case the flux of water into the membrane is a function of the flux of triamine (DETA) and the flux of diamine (EDA) through the membrane. The flux of water is:

\[ \phi_w = K_t \phi_{\text{dea}_t} + K_d \phi_{\text{eda}} \] (7.25)

In this case the growth of the wall thickness becomes:

\[ \frac{\partial d_t}{\partial t} = \frac{D_{p,\text{dea}_t}}{d_t (1 - \epsilon_2)} \left[ \frac{K_t}{\rho_w} + \frac{M_u}{r_t \rho_{pol}} \right] C_{3,\text{dea}_t}(t) + \frac{D_{p,\text{eda}}}{d_t (1 - \epsilon_2)} \left[ \frac{K_d}{\rho_w} + \frac{M_u}{r_d \rho_{pol}} \right] C_{3,\text{eda}}(t) \] (7.26)

The mass-balance for EDA becomes (analogue to equation (7.5)):

\[ \frac{\partial C_{3,\text{eda}}}{\partial t} = - \frac{6}{d_c} \frac{D_{p,\text{eda}}}{d_t (1 - \epsilon_2)} C_{3,\text{eda}} \] (7.27)

Substitution of equation (7.5) and equation (7.27) into equation (7.26) gives after integration (at \( t = 0 \), \( d_t = 0 \) and \( C_{3,\text{dea}_t}(t) = C_{3,\text{dea}_t}(0) \) and \( C_{3,\text{eda}}(t) = C_{3,\text{eda}}(0) \)):

\[ d_t = \left[ \frac{K_t}{\rho_w} + \frac{M_u}{r_t \rho_{pol}} \right] \left( C_{3,\text{dea}_t}(0) - C_{3,\text{dea}_t}(t) \right) + \left[ \frac{K_d}{\rho_w} + \frac{M_u}{r_d \rho_{pol}} \right] \left( C_{3,\text{eda}_t}(0) - C_{3,\text{eda}_t}(t) \right) \] (7.28)

From the mass-balance of DETA and EDA it follows:

\[ \ln(\alpha_{\text{eda}}) = -\frac{D_{\text{eda}}}{D_{\text{dea}}} \ln(\alpha_{\text{dea}}) \] (7.29)
7.3. EXPERIMENTAL

7.3.1. Introduction
The production of micro capsules consists of two steps: 1) the production of uniformly sized droplets of the appropriate size and 2) the formation of the wall by polycondensation surrounding the droplets to produce the micro capsules. The production of uniformly sized droplets was described in chapter 5. The droplets are produced from the aqueous solution. In this case the organic phase is the continuous phase.

7.3.2. Production of micro capsules
A beaker was filled with the organic phase in which the polycondensation proceeds, a solution of acid chloride (TDC or TMC) in dioctylphthalate (DOP) and 5 vol% SPAN 85 is added. On top of this a second organic phase (cyclohexane) forms a liquid zone (without acid chloride) in which the droplets are immersed. The droplets immerse into this zone, in which they become spherical, before entering the acidchloride solution. Once the droplets enter the acidchloride solution the polycondensation starts, the capsule wall is produced and micro capsules are formed (see Fig. 7.1.). In all cases DOP was used as a solvent for acid chloride; because of the small difference in the density of DOP and that of the micro capsules made, the micro capsules descend slowly into the organic phase, this allows a regular growth of the capsule wall (see chapter 5, Figs. 5.2 and 5.3).

Figure 7.1. The production of w/o micro capsules

87
7.3.3. **Process conditions**

Three types of experiments have been done; 1) experiments in which the aqueous solution consists of diethylenetriamine (DETA) and NaOH, and the organic phase of a solution of TDC in DOP. The concentration ratio of TDC and DETA was varied to measure its influence on the wall formation and permeability, 2) experiments in which a diamine (ethylenediamine (EDA) or hexamethylenediamine (HMDA)) is added to the aqueous phase. The concentration ratio of TDC and DETA was constant when the concentration ratio of the diamine and triamine was varied between 0 and 1.2 approximately, 3) experiments in which the aqueous phase consists of ethylenediamine (EDA) and NaOH, and the organic phase of a solution of trimesoylchloride (TMC) in DOP. The concentration ratio of EDA and TMC was varied, to measure the effect on the wall formation. In all cases 5 vol% SPAN 85 was added to the organic acidchloride solution.

7.3.4. **Thickness measurements**

To measure the thickness of the capsule wall as a function of time, the thickness of cut cross sections of the micro capsule wall were measured with SEM. During maturation a few capsules were taken out of the beaker; the organic solution was removed with ethanol and subsequently the ethanol was removed with water. The contents of the micro capsules were removed by dialyzing against water prior to preparations for cutting the micro capsules. As the capsules were cut they were dried and prepared to examine with SEM.

7.4. **RESULTS AND DISCUSSION**

7.4.1. **Concentration calculations**

It was not possible to measure the amine concentration in the micro capsules as a function of time. The rate with which the amine concentration decreases with time is described by equation (7.9). It depends on the size of the capsule (d.), and the initial amount of amine present (Camine), which are process conditions. It also depends on the density of the polymer (ρpol), the reaction ratio (r), the molecular weight per unit of polymer (Mw) and the diffusion coefficient of the amine through the polymer (Damine), which is a result of the process conditions; all these parameters are membrane properties. Calculations of αamine (i.e. Camine(t)/Camine(0)) as a function of time show little dependency on the rate of decrease of αamine with time for different values of ρpol (1050 - 1450 kg/m²), r.
Figure 7.2. Calculated $\alpha$ as a function of time for $D_{deta} = 5e-11$ (1), $1e-11$ (2), $5e-12$ (3) and $1e-12$ (4) m$^2$/s. $C_{3,deta}(0) = 1.0$ kmol/m$^3$, $d_c = 1.0$ mm, $r = 0.95$ and $\rho_{pol} = 1100$ kg/m$^3$.

Figure 7.3. Calculated $\alpha_{deta}$ and $\alpha_{eda}$ as a function of time for $D_{deta} = 1e-12$, $D_{eda} = 3e-12$ m$^2$/s.

(0.67 - 1.0) and consequently $M_u$ ($M_u = M_{tdc} + r_t M_{deta} - 2 M_{HCl}$). A significant dependency was calculated as the diffusion coefficient was varied (1x10$^{-12}$ to 5x10$^{-11}$). This is shown in Fig. 7.2., in which the $\alpha$ as a function of time was calculated with $\rho_{pol} = 1100$ kg/m$^3$, $r_t = 0.95$ and $M_u = 228$ kg/kmol and the model process conditions were $C_{3,deta}(0) = 1.0$ kmol/m$^3$ and $d_c = 1.0$ mm.
From equation (7.29) \( \alpha_{eda} \) as a function of time can be calculated. This is shown in Fig. 7.3., in which all model conditions are equal to the model conditions which were used to calculate \( \alpha_{amine} \) in Fig. 7.2.. Measurements of \( D_{deta} \) and \( D_{eda} \) show that the rate of diffusion of EDA is approximately 3 times the rate of diffusion of DETA.

![Graph showing wall thickness as a function of time](image)

*Figure 7.4. The thickness of the capsule wall as a function of time \((C_{tdc}/C_{deta} = 0.54, \square)\) and the fit of both models ('constant flux' (1), 'amine flux' (2)).*

The wall thickness can be fitted by two models, this is shown in Fig. 7.4.. The thickness of the capsule wall is, for the model with a constant flux of water, described by equation (7.7). This describes the thickness of the capsule wall as the sum of the 'water thickness' \( (\phi_w t/\rho_w) \) and the thickness of the polymer, which depends on the decrease of the amine concentration. Equation (7.9) describes the polymer thickness as a function of time. To obtain a relationship of the wall thickness \( (d_t) \) as a function of time, equation (7.9) is approximated as a 2nd order Taylor approximation. In combination with equation (7.7) this results in:

\[
d_t = \frac{\phi_w t}{\rho_w} + \sqrt{\frac{2 M_u C_{deta}(0) D_{pol,beta}}{r_t \rho_{pol}}} t \tag{30}
\]

For the model with a flux of water which depends on the flux of amine is the relationship of the wall thickness and time given by equation (7.17). The curve representing the 'constant flux' model is calculated with a fitted value for
\( (M_u D_{p, \text{deta}})/(r_t \rho_{pol}) \). With \( r_t = 0.95 \), \( M_u \) becomes 228 kg/kmol and with \( \rho_{pol} = 1100 \) kg/m\(^3\) it result in a value for \( D_{p, \text{deta}} \) of 1.64e-11 m\(^2\)/s.

For the model with a flux of water which depends on the flux of the amine equation (7.17) is fitted with a value for \( \epsilon = 0.5 \). With

\[
\epsilon = \left[ \frac{K_t}{\rho_w} \right] \times \left[ \frac{K_t}{\rho_w} + \frac{M_u}{r_t \rho_{pol}} \right]^{-1}
\]

Fitting both models for the values of the wall thickness as a function time and calculating the values for \( D_{\text{deta}} \) gives the same results for both the 'constant flux' and the 'amine flux' model. Fig. 7.5. shows the relation of \( D_{\text{deta}} \) and \( C_{\text{tdc}}/C_{\text{deta}} \) for \( C_{\text{deta}} \) at \( t = 0 \), of 1.0 and 2.0 kmol/m\(^3\). The diffusion coefficient of DETA through the membrane increases as the \( C_{\text{tdc}}/C_{\text{deta}} \) increases. There is no significant difference for the value of \( D_{\text{deta}} \) as \( C_{\text{deta}}(0) \) is changed.

![Figure 7.5. The diffusion coefficient of DETA (D_deta) as a function of C_tdc/C_deta for C_deta(0) = 1.0 (*) and 2.0 (a).](image)

7.4.2. Influence of addition of diamines to the aqueous phase

Addition of diamines to the aqueous phase greatly reduces the rate of diffusion of both DETA and EDA in case of oil-in-water micro capsules (see chapter 5). This is also the case in water-in-oil micro capsules, which is shown by Fig. (7.6). It shows the thickness of the TDC/DETA capsule wall (■) compared to the wall thickness of TDC/DETA/EDA capsules which are made under equal process conditions. It shows the wall thickness of three series of \( C_{\text{eda}}/C_{\text{deta}} \) (0.2 (+), 0.4
(*) and 1.0 (o)). The larger thickness of the TDC/DETA capsules is mainly due to the differences of the diffusion coefficient of DETA in the various systems (as was shown by Fig. (7.2)) with \( D_{\text{dela}} \) (TDC/DETA) being larger than \( D_{\text{dela}} \) (TDC/DETA/EDA) and \( D_{\text{eda}} \) (TDC/DETA/EDA).

![Figure 7.5. The wall thickness of TDC/DETA micro capsules (m) compared to the wall thickness of TDC/DETA/EDA micro capsules for equal \( C_{\text{tdc}}/C_{\text{dela}} \) and \( C_{\text{eda}}/C_{\text{dela}} \) is 0.2 (+), 0.4 (*) and 1.0 (o).](image)

Fig. 7.7. shows the thickness of the capsule wall as a function of time for TDC/DETA/EDA microcapsules. The wall is grown for all series with \( C_{\text{tdc}}/C_{\text{dela}} = 0.43 \) \( (C_{\text{dela}} = 1.25 \text{ kmol/m}^3) \). The ratio of EDA to DETA \( (C_{\text{eda}}/C_{\text{dela}}) \) ranges from 0.2 to 1.2. This did not result in significant differences in wall thicknesses as a function of time, despite the increasing concentration of EDA. The increase of the concentration of EDA should result in an increase in the driving force of diffusion and, consequently, should result in a thicker capsule wall. Since this is not the case, addition of EDA largely reduces the diffusion coefficients of both EDA and DETA in a way identical to a change of the concentration ratio of DETA to TDC.

The effect of \( C_{\text{tdc}}/C_{\text{dela}} \) on the thickness of TDC/DETA/EDA micro capsules is shown in Fig. 7.8. For \( C_{\text{eda}}/C_{\text{dela}} = 0.2 \) the wall thickness is plotted as a function of time for \( C_{\text{tdc}}/C_{\text{dela}} = 0.72 \) and 0.43 respectively. The total amine concentration for the ratio of 0.43 is 25% higher than for the ratio of 0.72, which should result in a larger wall thickness at any time. On the other hand, the permeability of the membrane is in case of TDC/DETA micro capsules reduced as the ratio of TDC to DETA decreases. So, in this case the reduction of \( C_{\text{tdc}}/C_{\text{dela}} \) from 0.72 to 0.43 yields a
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polymer membrane with a lower permeability for the amine; this compensates the larger concentration difference across the membrane.

Figure 7.7. The thickness of the capsule wall as a function of time ($C_{tdc}/C_{deta} = 0.43$) for $C_{eda}/C_{deta} = 0.2$ (■), 0.4 (+), 0.6 (*), 0.8 (○), 1.0 (×) and 1.2 (△).

Figure 7.8. The thickness of the capsule wall as a function of time ($C_{eda}/C_{deta} = 0.2$) for $C_{tdc}/C_{deta} = 0.72$ (■) and 0.43 (+).
Figure 7.9. The thickness of the capsule wall as a function of time for TDC/DETA/EDA and TDC/DETA/HMDA micro capsules ($C_{tdc}/C_{deta} = 0.43$ and $C_{diamine}/C_{deta} = 0.4$).

In chapter 5 it is shown that the addition of diamine to the aqueous phase reduces the permeability of the membrane and that this effect is enlarged when HMDA instead of EDA is added. For water-in-oil micro capsules Fig. 7.9. shows the effect of addition of HMDA instead of EDA to the aqueous phase. It compares the thickness of the capsule wall as a function of time for TDC/DETA/EDA and TDC/DETA/HMDA micro capsules, for both constant $C_{tdc}/C_{deta}$ and $C_{diamine}/C_{deta}$. The thickness of the HMDA capsule wall is smaller than the thickness of the EDA capsule wall. In both cases the concentration difference across the membrane is equal. The capsule wall thickness is lower for the HMDA capsules which results in a larger driving force for diffusion; this can compensate for the lower membrane permeability. The lower thickness of the wall is the result of a lower diffusion coefficient for the amines in case of HMDA capsules.

7.4.3. Influence of the diamine/trichloride ratio

For TDC/DETA micro capsules the trifunctional monomer, which causes cross-linking, is the amine. In chapter 4 it is shown that the ratio of TDC to DETA determines the permeability of the capsule wall to the triamine. The amount of TDC relative to the amount of DETA, or the rate of transport of TDC to the reaction zone relative to the rate of transport of DETA to the reaction zone determines if the secondary amine group reacts and, consequently, yields cross-links. Fig. 7.10.
shows the wall thickness as a function of time for TMC/EDA micro capsules. Now the trifunctional monomer (TMC) is dissolved in the organic phase. In Fig. 7.10, $C_{\text{eda}}/C_{\text{tmc}}$ is varied between 0.5 and 2.5; the wall thickness increases with increasing $C_{\text{eda}}/C_{\text{tmc}}$; this is the result of an increased concentration of EDA and/or an increased diffusion coefficient of EDA. The wall thickness can be fitted by the same equations as used for the TDC/DETA micro capsules. From the fit of both models the diffusion coefficient of EDA ($D_{\text{eda}}$) through the membrane is calculated with $r = 1.45$, $M_u = 299$ kg/kmol, $\rho_{\text{pol}} = 1100$ kg/m$^3$ and $c = 0.5$. Fig. 7.11. shows $D_{\text{eda}}$ as a function of $C_{\text{eda}}/C_{\text{tmc}}$ for both the 'constant flux' and the 'amine flux' model. The values for $D_{\text{eda}}$ calculated from the fit of the 'amine flux' model show an increase of $D_{\text{eda}}$ with the concentration ratio of the bifunctional monomer (EDA) to the trifunctional monomer (TMC). This is consistent with the results obtained from the oil-in-water micro capsules, which show the same dependency of the amine diffusion coefficient between the concentration ratio of the bifunctional monomer (TDC) and the trifunctional monomer (DETA). The results for the 'constant flux' model contradict with the 'amine flux' model, because $D_{\text{eda}}$ decreases with $C_{\text{eda}}/C_{\text{tmc}}$.

![Image](image-url)

**Figure 7.10. The thickness of the capsule wall as a function of time for different $C_{\text{eda}}/C_{\text{tmc}}$ of 0.5 ( ■ ), 1.0 (+), 1.5 ( * ), 2.0 ( □ ) and 2.5 ( × ).**

7.4.5. **Assessment of both models**

Assessment of both models by the results of the thickness measurements show that the thickness will fit to $t^{0.5}$ for both models (see Fig. 7.4.). Both models describe the growth of the capsule wall equally well. The porosity of the capsule
wall (c) increases with time; model 1 describes the porosity (ε₁) increasing with time; for model 2 the porosity (ε₂) remains constant throughout the growth of the membrane. Based upon these facts one might favor model 1 for model 2.

![Graph](image)

**Figure 7.11.** $D_{eda}$ as a function of $C_{eda}/C_{tmc}$ calculated from the 'constant flux' (■) and the 'amine flux' (□) model. Calculation parameters: $r_d = 1.45$, $M_u = 299$ kg/kmol, $\rho_{pol} = 1100$ kg/m$^3$ and $\varepsilon = 0.5$.

In modelling the growth of the capsule wall one relates the production of polymer to the diffusion of amine. This yields a relationship for the 'polymer thickness' which is proportional to $\sqrt{t}$. When the production of macro voids is also related to the diffusion of amine, this will yield a relationship for the 'macro voids' thickness also proportional to $\sqrt{t}$. Consequently, the fraction of macro voids remains constant throughout the production of the membrane. To relate the fraction of macro voids which increases throughout the production of the membrane, this shows that the production of macro voids should be proportional to $t^n$, with $n > 0.5$.

### 7.5. COMPARISON WITH O/W CAPSULES

According to Fig. 7.5 the dependency of $D_{dema}$ on $C_{tdc}/C_{dema}$ is equal to that of oil-in-water micro capsules. In both o/w and in w/o micro capsules the diffusion coefficient of the amine increases as $C_{tdc}/C_{dema}$ increases. The order of magnitude for the diffusion coefficient is also equal for both types of micro capsules (see
Addition of diamine to the aqueous phase results in both types of micro capsules into a reduction of the diffusion coefficient of the amines. The higher the amount of diamine added the lower are the diffusion coefficients for both amines (see Fig. 7.7.). This is also the case for o/w micro capsules (see Fig. 5.7).

7.6. CONCLUSIONS

The relationships which describe the concentration with time are identical for both models. In the case that diamine is added to the aqueous triamine solution, it is not possible to obtain an analytical solution for the diamine or triamine concentration with time. A relationship for the wall thickness as a function of time is derived for the 'amine flux' model if only one amine is dissolved in the aqueous phase. For the 'constant flux' model a relationship is derived for the wall thickness as a function of time and amine concentration. When the relationship for the amine concentration with time is approximated by a 2nd order Taylor polynomial, then for the 'constant flux' model a relationship between the wall thickness and time is obtained approximately.

The influences of the process conditions, i.e. $C_{tdc}/C_{deta}$, $C_{diamine}/C_{triamine}$ and $C_{eda}/C_{tmc}$, are equal to the results as measured for oil-in-water micro capsules and flat membranes. An increase of the concentration of the bifunctional monomer (TDC or EDA) relative to the concentration of the trifunctional monomer (DETA or TMC) yields polymer with an increased membrane permeability for the amine. Addition of diamine to an aqueous solution of DETA decreases the membrane permeability, which effect is larger when HMDA is added instead of EDA.

Both models yield identical relationships for the amine concentration with time, for both the o/w and w/o emulsions. The results for the permeability of the membrane produced for o/w, w/o and flat membranes show identical dependencies on the process conditions.

7.7. REFERENCES

CHAPTER 8

GENERAL CONCLUSIONS

The process of interfacial polycondensation in relation to micro encapsulation and the influence of the process conditions on the permeability of the capsule wall is studied. An introduction to this thesis is presented in chapter 1 and the theory of membrane formation by interfacial polycondensation and the production of capsules is described in chapter 2.

Chapter 3 describes the model which is proposed for the formation of the capsule wall, for o/w macro capsules. This model describes the rate of wall formation as a function of reaction time. The rate of wall formation decreases as the reaction time proceeds. As a result of the decrease of the wall growth rate the pore size of the membrane sub layer increases during maturation of the capsule wall. This is shown by photographs of cut cross sections of capsules.

In chapter 4 the macro capsule model is verified experimentally and the influence of the process conditions is measured. The decrease of the TDC concentration is found to be proportional to $\sqrt{t}$, theoretically as well as experimentally. Measurements of the wall thickness as a function of reaction time show a linear dependence with $\sqrt{t}$, as described by the model. The influence of the concentration of TDC relative to the concentration of DETA shows a decrease of the diffusion coefficient when $C_{3,TDC}/C_{0,DETA}$ at $t = 0$ is decreased. This influences the rate of amine diffusion through the capsule wall, which determines the rate of polymer production. For TDC/DETA systems high spherical cellular porosity is obtained (for o/w macro capsules), whereas for TDC/DETA/diamine systems long cellular pores are obtained.

Measurements of the rate of hydrolysis of TDC in capsules (and in absence of polymer production) show that in presence of enough OH⁻ hydrolysis takes place only with OH⁻ rather than with H₂O. It is shown that because of the correlation between the hydrolysis rate and $\sqrt{C_{OH}}$ the diffusion rate of TDC from the oil into the aqueous phase determines the hydrolysis rate. Consequently, during encapsulation (formation of the capsule wall) no hydrolysis of TDC takes place.

Chapter 5 describes the expansion of the model and the influence of the process conditions for micro capsules. For the o/w micro capsules, two models (a 'constant flux' and a 'amine flux' model) are presented to account for the
formation of macro voids within the capsule membrane, result in two identical relationships for the dependence of the TDC concentration on time and in two different relationships for the wall thickness as a function of time. The relationships for the wall thickness as a function of time are different in that: one is quadratic in $\sqrt{t}$, the other is linear in $\sqrt{t}$. From experiments it appears that the quadratic part is negligible which leaves a square root of time dependence. In that case both equations describing the wall thickness become identical. On the other hand neglecting of the quadratic part in the relationship of $d_i$ and $\sqrt{t}$ implies the presence of only a small fraction of macro voids.

For micro capsules the growth of the capsule wall and the concentration of TDC inside the capsule as a function of time obeys the same equations as derived previously for macro capsules (chapter 3). Addition of diamines to the aqueous triamine solution results in the same proportionality for the TDC concentration and the wall thickness with time. The transport of amines can be well described by a linear combination of the triamine and the diamine flux.

The dependence of the diffusion coefficient on $C_{tdc}/C_{deta}$ and on $C_{diamine}/C_{deta}$ is calculated from concentration experiments and from thickness experiments. This dependency, as calculated, agrees for both concentration and thickness experiments.

In chapter 6 the permeability and growth of flat membranes is studied. For flat membranes, the permeability as a function of the process conditions was measured with NaCl. The diffusion coefficient of NaCl is affected by the concentration ratio of TDC and DETA in the same way as this ratio affects the diffusion coefficient of DETA during encapsulation by interfacial polycondensation. Also the influence of diamines added to the aqueous phase during membrane growth is identical as can be expected from microencapsulation experiments.

The growth of the membrane thickness in vitro can be measured adequately, but it is not suitable for measuring the early stage of membrane growth. The proportionality between the thickness and $\sqrt{t}$ is in agreement with growth measurements of micro capsules. The dependence of the diffusion coefficient of both triamine (DETA) and diamine (EDA, HMDA) on process conditions (i.e. concentration ratios) is similar to the dependency as measured for micro capsules.

The growth rate of the membrane is determined by the diffusion of amine from the aqueous phase through the membrane into the organic phase. Light transmission experiments show that from less than 2 seconds the membrane growth is determined by the diffusion of amine through the membrane, consequently, within 2 seconds the top
layer of the membrane is formed. The permeability of the membranes increases with an increasing $C_{tdc}/C_{deta}$, which is in agreement with micro capsule measurements. Addition of EDA decreases the permeability of the membranes. However, an increase of EDA relative to DETA results in an increase of the diffusion coefficient of DETA through the membrane. This is in contradiction with the results obtained from microencapsulation measurements.

In chapter 7, the changes and differences, due to the w/o system, on the model relationships and on the influence of the process conditions are described. For w/o micro capsules, the relationships which describe the concentration with time are identical for both models. In the case that diamine is added to the aqueous triamine solution, it is not possible to obtain an analytical solution for the diamine or triamine concentration with time. A relationship for the wall thickness as a function of time is derived for the 'amine flux' model if only one amine is dissolved in the aqueous phase. For the 'constant flux' model a relationship is derived for the wall thickness as a function of time and the amine concentration. When the relationship for the amine concentration with time is approximated by a 2nd order Taylor polynomial, then for the 'constant flux' model a relationship between the wall thickness and time is obtained.

The influences of the process conditions, i.e. $C_{tdc}/C_{deta}$, $C_{diamine}/C_{triamine}$ and $C_{eda}/C_{tmc}$, are equal to the results as measured for oil-in-water micro capsules and flat membranes. An increase of the concentration of the bifunctional monomer (TDC or EDA) relative to the concentration of the trifunctional monomer (DETA or TMC) yields polymer with an increased membrane permeability for the amine. Addition of diamine to an aqueous solution of DETA decreases the membrane permeability, which effect is larger when HMDA is added instead of EDA.

Both models yield identical relationships for the amine concentration with time, for both the o/w and w/o emulsions. The results for the permeability of the membrane produced for o/w, w/o and flat membranes show identical dependencies on the process conditions.
SUMMARY

This thesis describes the formation of membranes in o/w, w/o micro encapsulation and of flat membranes and the influence of the process conditions on the permeability of the membranes. The membranes are produced by interfacial polycondensation of acid chlorides (terephthaloyldichloride (TDC) or trimesoylchloride (TMC)) with amines (diethylenetriamine (DETA), ethylenediamine (EDA) and hexamethylenediamine (HMDA)). The reaction takes place in the organic phase, at or near the interface. At first amine diffuses into the organic phase to react instantaneously with the acid chloride, producing oligomers. These oligomers couple as their concentration increase and the polymer formed precipitates. Thus the top layer of the membrane is produced. Amine diffuses through the layer of polymer into the organic phase. The polycondensation continues and the membrane grows. During the formation of the membrane macro voids are incorporated within the membrane. The size of the macro voids increases as the membrane thickness increases.

In chapter 3, a model, which relates the concentration of monomer inside o/w macro capsules and the wall (membrane) thickness with time, is derived. Both the model and the experimental results describe the concentration and the wall thickness to be proportional to $\sqrt{t}$. The model assumes that during the production of the micro capsule wall no hydrolysis of the acid chloride takes place. This is verified by the measurements of the concentration of TDC in previously formed capsules as a function of time, when no amine is present (so hydrolysis of TDC is the only possible reaction). The diffusion coefficient of DETA through the capsule wall increases as $C_{tdc}/C_{de}$ increases. When the amount of TDC relative to the amount of DETA increases, the probability of the secondary amine group of DETA to react and to produce cross-links also increases. As the cross-link density increases the fraction of crystalline domains decreases and consequently the diffusion coefficient of DETA increases.

In chapter 4 the influence of the process conditions on the rate of the wall growth is described. The rate of the wall growth is determined by the diffusion of the amine through the membrane. The effect of the process conditions i.e. the concentration ratios of the bifunctional to the trifunctional monomer and the effect of the addition of diamine to a solution of triamine on the growth rate of the membrane thickness are studied. The increase of the membrane thickness, in combination with the decrease of the monomer concentration inside macro capsules, relates the process conditions to the permeability of the membranes.
Chapter 5 deals with the production of uniformly sized micro capsules, which is performed in two steps: 1) production of uniformly sized droplets, 2) encapsulation of the droplets. At first a jet of the core liquid (e.g., organic phase) is broken into uniform sized droplets by applying a mechanical oscillation (by means of a loudspeaker, ca 300 Hz) at the jet. Within certain limits the jet breaks up in uniform sized droplets. Secondly the droplets are caught in a buffer solution (where no amine was present) to become spheres, after which they enter the aqueous amine solution, at which moment the polycondensation starts and produces the capsule membrane.

In chapter 5 the model is expanded to describe the formation of macro voids in o/w micro capsules, which is incorporated into the model in two ways: 1) the macro voids are the result of a constant flux of water into the membrane; 2) the macro voids are the result of a flux of water which is related to the flux of amine. Both approaches yield two identical relationships between the monomer concentration and time and two relationships for the thickness as a function of time. Both relationships derived for the micro capsules describe the monomer concentration as a function of \( \sqrt{t} \), which is the same relation as described by the relationships for macro capsules. The wall thickness as described by model 1 is a quadratic function of \( \sqrt{t} \), and as described by model 2 proportional to \( \sqrt{t} \). The effect of \( C_{t_{de}}/C_{d_{ota}} \) on the permeability for micro capsules is equal to this effect for macro capsules. The addition of diamine to the aqueous phase decreases the permeability of the membranes by 1) a decrease of the cross-link density and 2) an increase of the length of the polymer chains between cross-links. This results in a higher fraction of the crystalline phase. The measurements do not favor one model over the other, because the wall thickness measured is proportional to \( \sqrt{t} \), as described by model 2. On the other hand the porosity increases, which is best described by model 1.

Chapter 6 deals with the permeability and the early stage of the membrane formation of flat membranes. The effect of the process conditions on the permeability of flat membranes for NaCl is the same as measured for the macro and micro capsules. For micro encapsulation, the process of wall growth could be measured from 60 seconds and for dried micro capsules membranes. In this period of wall growth the rate is determined by the diffusion of amine. By measuring the light absorption through a growing membrane and relating the absorption to the membrane thickness it was possible to measure the growth of the membrane from 2 seconds and up. The absorption of light by the membrane showed to be proportional to the thickness of the membrane. From 2 seconds the absorption (i.e. the
thickness) is proportional to $\sqrt{t}$, so from this moment on the growth of the wall is determined by the rate of diffusion of the amine through the growing membrane. This verifies the model, in which we assumed that the formation and formation time of the top layer of the membrane is negligible to the growth of the sub layer of the membranes incorporating the macro voids. The absorption measurements show the same effects of the process conditions on the permeability of the membranes as has been measured for the macro en micro capsules. To study the growth of the membrane in vitro the interface of the organic and aqueous phase was created between two glass plates. With a light microscope the process of the wall growth and the formation of the macro voids was made visible. This setup also allowed to study the growth of 'wet membranes'. The results showed that the relations derived for micro capsules and applied to the 'flat membrane' growth are also valid for the wet membranes.

Chapter 7 describes the model and the influence of the process conditions for w/o micro capsules. Since the process of wall growth is determined by the diffusion of amine through the membrane in case of o/w capsules and flat membranes, the diffusion of amine is expected to be determining for the wall growth in w/o micro capsules. In the case of o/w capsules and the flat membranes the growth rate of the membrane thickness decreases because of an increase of the wall thickness. In both systems the concentration of amine remained constant during the time of measurement. Since the driving force for diffusion is the concentration gradient across the membrane there is, in w/o micro capsules an additional factor which decreases the rate of the growth of the membrane. In w/o micro capsules the concentration of amine decreases during the time of measurement, which contributes to an additional decrease of the concentration gradient and of the growth rate. Another consequence of the reverse system is, although it gives identical relationships for the concentration of amine inside the micro capsules with time, that only in the case of 'amine flux' an analytical relationship between the thickness and time is derived. In case of 'constant flux' the thickness is related to the time and the amine concentration. In both cases there is no analytical solution for the wall growth and time as diamine is added to the triamine solution. The effects of the process conditions on the membrane permeability for w/o micro capsules is the same as for o/w micro capsules.
SAMENVATTING

In deze dissertatie wordt de vorming van membranen tijdens de encapsulatie van o/w, w/o en van vlakke membranen beschreven. Tevens wordt de invloed van proces condities op de doorlatbaarheid van de membranen bekeken. De membranen worden gevormd door grensvlak polycondensatie van zuurchloriden (tereftaloyldichloride (TDC) of trimesoylchloride (TMC)) met aminen (diethyleentriamine (DETA), ethyleendiamine (EDA) en hexamethyleendiamine (HMDA)). De reactie vindt plaats in de organische fase, aan of bij het grensvlak met de waterige fase. De eerste stap in de vorming van het membraan bestaat uit de diffusie van amine naar de organische fase, waar dit momentaan reageert met het zuurchloride, onder de vorming van oligomeren. Bij een toenemende oligomeren concentratie koppelen deze en wordt polymere gevormd. Het neerslaan van het polymere vormt de top laag van het membraan. Vervolgens diffundeert amine door de top laag naar de organische fase zodat de polycondensatie continueert en het membraan groeit. Gedurende de vorming van deze sub laag worden cellulaire holtes gevormd (macro voids). De grootte van deze macro voids neemt toe naarmate de dikte van het membraan toeneemt.

In hoofdstuk 3 wordt een model afgeleid, die de monomeer concentratie in o/w macro capsules en de wand (membraan) dikte relateerd aan de groeitijd. Zowel het model als de experimentele resultaten beschrijven de concentratie en wand dikte evenredig aan $\sqrt{t}$. In het model wordt aangenomen dat tijdens de vorming van de capsule wand geen hydrolyse van het zuurchloride plaats vindt. Dit wordt geverifieerd door het meten van de TDC concentratie in capsules als een functie van tijd, wanneer geen amine aanwezig is (dan is hydrolyse de enige mogelijke reactie). De diffusie coefficient van DETA door de capsule wand neemt toe als $C_{tdc}/C_{deta}$ toeneemt. Als de hoeveelheid TDC relatief aan de hoeveelheid DETA toeneemt zal de kans dat de secundaire amine groep van DETA reageert en cross-links vormt toenemen. Indien de cross-link dichtheid toeneemt zal de fractie van crystallijne gebieden in het membraan afnemen, waardoor de diffusie coefficient van DETA toeneemt.

In hoofdstuk 4 wordt de invloed van de proces condities op de wand groeisnelheid beschreven. De snelheid waarmee de wand groeit wordt bepaald door de diffusie van amine door het membraan. Het effect van de proces condities, dwz. de verhouding van de concentraties van het bifunctionele en trifunctionele monomeer of het effect van toegevoegd diamine aan de triamine oplossing op de groeisnelheid van de membraan dikte, zijn gemeten. De toename van de wand dikte, gecombineerd met de afname van de monomeer concentratie in de capsules, relateerd de proces condities aan
de doorlaatbaarheid van het membraan.

Hoofdstuk 5 behandelde de productie van uniforme micro capsules; dit beslaat twee stappen: 1) productie van uniforme druppeltjes, 2) encapsulatie van de druppeltjes. Als eerste wordt een stroom van de kern vloeistof (bv. de organische fase) opgebroken in druppeltjes met een uniforme diameter; door, met behulp van een luidspreker, een mechanische trilling met een frequentie van circa 300 Hz op de vloeistofstroom aan te brengen. Binnen bepaalde limiteringen breekt de straal op in druppeltjes met een uniforme diameter. Ten tweede worden de uniforme druppeltjes opgevangen in een vloeibare buffer (waarin zich geen amine bevindt) zodat de druppeltjes, na hun botsing met het grensvlak van de buffer en lucht, weer bolvormig worden. Hierna zakken de druppeltjes in de amine oplossing; op dit moment start de polycondensatie en het capsule membrane gevormd wordt.

In hoofdstuk 5 wordt ook de uitbreiding van het model behandeld, die de vorming van macro voids beschrijft. Dit is op twee manieren in het model verwerkt 1) de macro voids zijn het gevolg van een constante flux van water in het membraan; 2) de macro voids zijn het gevolg van een water flux die, op zijn beurt, gerelateerd is aan de amine flux. Beide benaderingen leveren twee identieke relaties tussen de monomeer concentrate en de tijd en twee verschillende relaties voor de wand dikte als functie van de tijd. In beide relaties, die afgeleid zijn voor micro capsules, is de monomeer concentratie beschreven als een functie van \( \sqrt{t} \), deze zijn gelijk aan de relatie voor de macro capsules. De wanddikte zoals beschreven door model 1 is een kwadratische functie van \( \sqrt{t} \), en door model 2 evenredig met \( \sqrt{t} \). Het effect van de \( C_{\text{det}}/C_{\text{deta}} \) op de permeabiliteit voor micro capsules is gelijk aan dat voor macro capsules. Toevoegen van diamine aan de waterige fase verlaagd de permeabiliteit van de membranen door 1) een afname van de crosslink dichtheid, en 2) een toename van de ketenlengte tussen crosslinks. Dit resulteert in een hogere fractie kristallijnse fase. Uit de metingen blijkt geen voorkeur voor een van beide modellen, want de gemeten wanddikte is evenredig met \( \sqrt{t} \), zoals wordt beschreven door model 2. Tegenstrijdig met model 2 is de toename van de porositeit, die het best wordt beschreven door model 1.

Hoofdstuk 6 behandelt de permeabiliteit en het eerste begin van de wandvorming aan vlakke membranen. Het effect van de proces condities op de permeabiliteit van vlakke membranen voor NaCl is gelijk aan dit effect gemeten bij macro en micro capsules. Bij de micro encapsulatie kan het proces van wand groei gemeten worden vanaf 60 seconden aan gedroogde membranen. Tijdens deze periode is de wand groei bepaald door diffusie van amine. Door aan een groeiend membraan de licht
absorptie te meten en deze te relateren aan de membraan dikte is het mogelijk de membraan groei vanaf 2 seconden te meten. De licht absorptie door het membraan is evenredig met de dikte van het membraan. Het blijkt dat vanaf 2 seconden de licht absorptie (d.w.z. de membraan dikte) evenredig is met $\sqrt{t}$, vanaf dit moment is de wand groei bepaald door de diffusie van amine door het groeiende membraan. Dit ondersteund het model waarin we aannamen dat de vorming en de tijd van vorming van de top laag van het membraan verwaarloosbaar zijn ten opzichte van de groei van de sub laag.

Uit de absorptie metingen blijkt dat het effect van de proces condities op de permeabiliteit van de membranen gelijk is aan dat van de macro en micro capsules. Om de groei van membranen in vitro te meten werd een grensvlak tussen organische en waterige fase tussen twee glazen plaatjes gecreëerd. Met een licht microscoop werd het proces van de wand groei en de vorming van de macro voids zichtbaar gemaakt. Uit de resultaten bleek dat de relaties zoals afgeleid voor micro capsules en toegepast voor de groei van vlakke membranen ook gelden voor de 'natte membranen'.

In hoofdstuk 7 wordt het model en de invloed van de proces condities voor w/o capsules beschreven. Omdat de wand groei is bepaald door de diffusie van amine door het membraan in het geval van o/w capsules en vlakke membranen, wordt ook verwacht dat de diffusie van amine bepalend is voor de wand groei van w/o capsules. In het geval van o/w capsules en vlakke membranen nam de wand groeisnelheid af door een toename van de wanddikte. In beide systemen bleef de amine concentratie gedurende de meting constant. Omdat de drijvende kracht voor diffusie de concentratie gradient over het membraan is, zal bij w/o capsules een extra factor de wand groeisnelheid verlagen. Bij w/o capsules daalt de amine concentratie tijdens het experiment, dit draagt bij in een extra verlaging van de concentratie gradient en de wand groeisnelheid. Een ander gevolg van dit omgekeerde systeem is, hoewel de functies voor de amine concentratie en de tijd identiek zijn, dat voor het 'amine flux' model een analytische relatie bestaat voor de wanddikte en tijd. Voor het 'constante flux' model is de dikte een functie van de tijd en de amine concentratie. Voor beide model is geen analytische oplossing voor de wand groei en tijd relaties als diamine wordt toegevoegd aan de triamine oplossing. De effecten van de proces condities op de permeabiliteit van de membranen van w/o capsules is gelijk aan die van o/w capsules.
Symbols

\( A(t) \) \hspace{1cm} C_{\text{tdc}}(t = t_1) - C_{\text{tdc}}(t) \hspace{1cm} (\text{kmol/m}^3)

\( A'(t) \) \hspace{1cm} C_{\text{tdc}}(t = 0) - C_{\text{tdc}}(t) \hspace{1cm} (\text{kmol/m}^3)

\( A_c \) \hspace{1cm} \text{capsule area} \hspace{1cm} (m^2)

\( A_m \) \hspace{1cm} \text{area of diffusion} \hspace{1cm} (m^2)

\( A(\lambda) \) \hspace{1cm} \text{absorption coefficient} \hspace{1cm} (m^{-1})

\( a \) \hspace{1cm} \frac{6 \rho_{\text{pol}} \beta}{d_c M_u} \hspace{1cm} (\text{kmol/m}^4)

\( B \) \hspace{1cm} \text{constant characteristic of polymer–solvent system} \hspace{1cm} (-)

\( b \) \hspace{1cm} \frac{d_{2,\text{deta}}}{d_{1,\text{deta}}} \hspace{1cm} (m)

\( c \) \hspace{1cm} 2 r_t D_{2,\text{deta}} C_{0,\text{deta}} \frac{M_u}{\rho_{\text{pol}} \beta} \hspace{1cm} (m^2/s)

\( C_{\text{complex}}(t) \) \hspace{1cm} \text{concentration of Ni complex at time } t \hspace{1cm} (\text{kmol/m}^3)

\( C_j(t) \) \hspace{1cm} \text{concentration of } j \text{ at time } t \hspace{1cm} (\text{kmol/m}^3)

\( C_{\text{ex}}(t) \) \hspace{1cm} \text{concentration of NaCl in the external phase} \hspace{1cm} (\text{kmol/m}^3)

\( C_j(t_1) \) \hspace{1cm} \text{concentration of } j \text{ at time } t_1 \hspace{1cm} (\text{kmol/m}^3)

\( C_{i,j}(t) \) \hspace{1cm} \text{concentration of } j \text{ in phase } i \text{ at time } t \hspace{1cm} (\text{kmol/m}^3)

\( C_{i,k,j}(t) \) \hspace{1cm} \text{concentration of } j \text{ at interface } ik \text{ at time } t \hspace{1cm} (\text{kmol/m}^3)

\( d_c \) \hspace{1cm} \text{capsule diameter} \hspace{1cm} (m)

\( D_{\infty} \) \hspace{1cm} \text{diffusion coefficient in the complete amorphous polymer} \hspace{1cm} (m^2/s)

\( D_{i,j} \) \hspace{1cm} \text{diffusion coefficient of } j \text{ through phase } i \hspace{1cm} (m^2/s)

\( D_{p,j} \) \hspace{1cm} \text{diffusion coefficient of } j \text{ in the polymer} \hspace{1cm} (m^2/s)

\( D_{v,j} \) \hspace{1cm} \text{diffusion coefficient of } j \text{ in the voids} \hspace{1cm} (m^2/s)

\( D_a \) \hspace{1cm} \text{diffusion coefficient of the amorphous phase} \hspace{1cm} (m^2/s)

\( D_{\text{eff}} \) \hspace{1cm} \text{effective diffusion coefficient} \hspace{1cm} (m^2/s)

\( D_{iw} \) \hspace{1cm} \text{diffusion coefficient of the solute in water} \hspace{1cm} (m^2/s)

\( D_m \) \hspace{1cm} \text{diffusion coefficient in the polymer} \hspace{1cm} (m^2/s)

\( D_0 \) \hspace{1cm} \text{diffusion coefficient in the solvent} \hspace{1cm} (m^2/s)

\( d_t \) \hspace{1cm} \text{thickness of the total capsule wall} \hspace{1cm} (m)

\( d_l \) \hspace{1cm} \text{thickness of phase } i \hspace{1cm} (m)

\( d_{l}(t) \) \hspace{1cm} \text{thickness of phase } i \text{ at time } t \hspace{1cm} (m)

\( E_0 \) \hspace{1cm} \text{activation energy to create a hole} \hspace{1cm} (-)

\( f \) \hspace{1cm} \text{volume fraction of free volume} \hspace{1cm} (-)

\( H_a \) \hspace{1cm} \left(k \frac{\delta^2}{D_{0,\text{tdc}}}ight)^{0.5} \hspace{1cm} (-)
\[ I \] intensity of light after scattering

\[ I_0 \] intensity of light before scattering

\[ I_j \] retention index

\[ J_j \] rate of hydrolysis per surface unit (kmol/m²·s)

\[ k_{t_{dc}} \] hydrolysis reaction rate constant (m³·s/kmol)

\[ k_r \] reaction rate constant of polycondensation (m³·s/kmol)

\[ k_j \] mass transport coefficient (m/s)

\[ K_i \] proportional constant (kg/mol)

\[ K_p \] partition coefficient of the solute (-)

\[ l \] path length (m)

\[ M_u \] molecular weight of a polymer repeating unit (kg/kmol)

\[ M_x \] molecular weight of polymer between crosslinks (kg/kmol)

\[ \rho = \left( \frac{72 r_t \rho_{pol} D_{2,\delta_{\text{eta}}}}{M_u} \right)^{0.5} \] (kg/mol·ms)⁰.⁵

\[ r_j \] reaction rate of \( j \) (kmol/m³·s)

\[ r_p \] size of the pores in the polymer (m)

\[ r_s \] size of the solute (m)

\[ r_t \] reaction ratio TDC/DETA (-)

\[ r_d \] reaction ratio TDC/diamine (-)

\[ R \] gas constant (kJ/kmol·K)

\[ S(\lambda) \] scattering coefficient (m⁻¹)

\[ T \] temperature (K)

\[ t \] time (s)

\[ t_t \] formation time of the top layer (s)

\[ V_c \] capsule volume (m³)

\[ V_u \] volume of one mole polymer unit (m³)

\[ V_R^0 \] retention volume (m³)

\[ V_v \] volume of diffusion vessel (m³)

\[ Y \] \( X - \xi \cdot t \) (m)

\[ \alpha_j \] \( C_j(t)/C_j(t=0) \) (-)

\[ \beta \] volume fraction of polymer in the membrane (-)

\[ \delta \] transport film thickness (m)

\[ \varepsilon \] porosity of the polymer (-)

\[ \varepsilon_1 \] volume fraction of macro voids for 'constant flux' model (-)

\[ \varepsilon_2 \] volume fraction of macro voids for 'amine flux' model (-)

\[ \varepsilon_t \] fraction of macro voids of a membrane slice at \( t \) (-)
\( \lambda \) \( \frac{r_s}{r_p} \) (-)

\( \lambda_m \) characteristic time of solvent (s)

\( \theta_0 \) characteristic time of the diffusion process (s)

\( \phi_w \) flux of water (kg/m²s)

\( \phi_j \) flux of \( j \) through the capsule wall (kmol/m²s)

\( \varphi_a \) volume fraction of the amorphous phase (-)

\( \varphi_{cr} \) volume fraction of crystalline phase (-)

\( \rho_w \) density of the aqueous solution (kg/m³)

\( \rho_{pol} \) density of the polymer (kg/m³)

\( \xi \) \( \phi_w/\rho_w \) (m/s)

\( \sigma \) \( \left[ \frac{D_{p,da} M_u C_{0,da}}{T_{p, \rho_{pol}}} \right] \) (m²/s)

\( \tau \) tortuosity (-)

\( \Gamma \) \( C_{0,da}/C_{0,3,da} \) (-)

**Subscripts refer to:**

0: Continuous phase

1: Top layer of the capsule wall

2: Sub layer of the capsule wall

3: Disperse phase

\( X_{ij} \) \( i = \text{number to indicate phase} \)

\( j = \text{refers to a substance} \)

\( X = \text{quantity} \)

\( X_{ik,j} \) \( ik = \text{interface } ik \)
Curriculum Vitae

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