Impregnation of mosquito nets by means of EHDA

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Abstract

Malaria is a life threatening disease for many people, especially in Africa. It is a vector borne disease, meaning that it is spread by infected mosquitos. Malaria can be stopped by preventing mosquitos to spread. Insecticide treated nets (ITNs) are a very useful tool for this. The use of ITNs resulted already in a 20% reduction in overall child mortality in Africa.
The amount of insecticide on the ITNs gradually decreases over time. The nets therefore have to be retreated regularly. However the retreatment rate is very low (5%), reducing the effectiveness. In response to these low retreatment rates long lasting insecticidal nets, having a life time of four to five years, are being developed.

This research focusses on the development of a controlled release coating for mosquito nets, applied by means of Electro HydroDynamic Atomization, also referred to as electrospraying. EHDA produces very fine droplets from a liquid by using an electric field. The produced spray can be used to cover the mosquito nets with a coating. By adding a polymer to the liquid that is sprayed, a controlled release coating can be obtained. Poly(vinyl acetate) is used because is easily dissolvable in acetone, without having influence to the conductivity.

Too high polymer concentrations (to minimize solvent use) yielded fibres on the samples. These fibres completely clogged the net. Fibre production also occurred using a 10% emulsifiable concentrate of permethrin insecticide. Using the pure insecticides solved this problem.

Two similar insecticides were available for testing: deltamethrin and permethrin. Deltamethrin is more favourable, because of its higher activity. Determination of this insecticide with the available analytical methods was not possible. Therefore instead of deltamethrin, permethrin was used.

To prevent larger droplets to reach the net, an upwards spraying system was build. This system consists of a nozzle, a ring, 0,5 cm above the nozzle and a corona needle 2,5 cm above the nozzle. At a flow rate of 2 ml h^{-1} a stable system, in the cone-jet mode was obtained. The developed system was susceptible for dirt accumulation on both the nozzle and corona needle. Cleaning was necessary every 10 to 15 minutes.

The initial amount of permethrin on the surface of the yarn, measured via gas chromatography, was 5 mg m^{-2}. A concentration of at least 200 mg m^{-2} is necessary for the nets to be effective. Completely dissolving the coating in acetone yielded no further insecticide.
For deltamethrin a surface concentration of 20 mg m^{-2} is needed. Extrapolation of the permethrin results for deltamethrin results also in a surface concentration that is too low to be effective. However, for deltamethrin these results come much closer to the desired concentration. Other polymers could improve the release significantly.

The only explanation for the low amounts of permethrin on the mosquito net is a low spraying efficiency. Only 1.5% of the amount of insecticide sprayed is deposited on the net. Improving the efficiency can be done by giving the net an opposite charge to attract the charged droplets in the spray.

Samenvatting

Malaria is voor veel mensen, vooral in Africa, een levensbedreigende ziekte. Het wordt verspreid door geïnfecteerde muggen. De verspreiding van malaria kan worden gestopt door het voorkomen van het verspreiden van muggen. Netten die behandeld zijn met insecticide zijn een goed hulpmiddel hierbij. Het gebruik van deze netten heeft al gezorgd voor een 20% afname in kindersterfte in Afrika.
De hoeveelheid insectide op de behandelde netten daalt over verloop van tijd. Regelmatig impregneren met insecticide is noodzakelijk. Helaas wordt dit veel te weinig gedaan, slechts in 5% van de gevallen. Dit heeft een dramatisch effect op de effectiviteit. Als antwoord hierop worden er momenteel geïmpregneerde netten ontwikkeld met een levensduur van vier tot vijf jaar, zonder dat herbehandeling noodzakelijk is.

Dit onderzoek richt zich op het ontwikkelen van een coating die gereguleerd insecticide afgeeft met behulp van een techniek die electrospraying heet. Deze techniek produceert een kleine druppeltjes uit een vloeistof met behulp van een elektrisch veld. De geproduceerde nevel kan worden gebruikt om muskietennetten te coaten. Door het toevoegen van een polymeer aan de te versproeien vloeistof, wordt een gecontrolleerde afgifte van insecticide verkregen. Polyvinylacetaat is gebruikt, vanwege de oplosbaarheid in aceton, zonder invloed te hebben op de geleidbaarheid.

Te hoge polymeerconcentraties leidde tot vezelvorming op de monsters. Deze vezels verstopte de netten volledig. Dit verschijnsel deed zich ook voor bij het gebruik van een emulsie van het gebruikte insecticide, permethrin. Het gebruik van het zuivere insecticide loste het probleem op.

Twee vergelijkbare insecticides waren beschikbaar: deltametrin en permethrin. Vanwege de hogere activiteit heeft het gebruik van deltamethrin de voorkeur. Met de beschikbare analyse methodes was het detecteren van dit insecticide niet mogelijk. Om deze reden is permetrhin gebruikt in plaats van deltamethrin.

Om te voorkomen dat grote drupples het net zouden bereiken is gekozen

voor een systeem dat omhoog sproeit. Het systeem bestaat uit een nozzle, een ring, 0,5 cm boven de nozzle en een ontladingsnaald 2,5 cm boven de nozzle. Een stabiel systeem, sproeiend in de 'cone-jet mode' werd verkregen met een stromingssnelheid van 2 ml h^{-1}. Het systeem was gevoelig voor vuilophoping op zowel de nozzle als de ontladingsnaald. Deze moesten elke tien tot vijftien minuten worden schoongemaakt.

De initiële hoeveelheid permethrin op het oppervlak van de draden van de netten, was 5 mg m^{-2}, gemeten met behulp van gaschromatografie. Een concentratie van 200 mg m^{-2} is noodzakelijk om effectief te zijn. Na het compleet oplossen van de coating in aceton bleek daar verder insecticide meer in te zitten.
De benodigde oppervlakte concentratie voor deltamethrin is 20 mg m^{-2}. Het extrapoleren van de resultaten van permethrin naar deltamethrin levert ook een te lage concentratie op. Echter voor deltamethrin komt dit dichter bij de gewenste concentratie. Het gebruik van een ander polymeer zou de hoeveelheid van insecticide ruimschoots kunnen verbeteren.

De enige verklaring voor de kleine hoeveelheid permethrin op de muskietennetten is de lage sproei effeciëntie. Slecht 1,5% van de gesproeide hoeveelheid insecticide was op het net terechtgekomen. Om de effeciëntie te verbeteren kan het net tegengesteld geladen worden aan de druppels, om ze zo aan te trekken.

Contents

List of symbols

Latin symbols

a	scaling law constant	-
A	area	m^2
b	scaling law constant	-
C_i	concentration of insecticide	$g\ l^{-1}$
C_{net}	concentration insecticide on net	$mg\ m^{-2}$
d	diameter	m
D	diffusion coefficient	$m^2\ s^{-1}$
ΔH	heat of vaporization	$J\ mol^{-1}$
f_{prod}	droplet production frequency	Hz
I	current through the jet	A
I_0	reference current	A
J"	flux	$mol\ m^{-2}\ s^{-1}$
K	conductivity	$S\ m^{-1}$
L	coating thickness	m
L_{cont}	contour length of a polymer	m
l	length of a monomer unit	m
M_w	molecular weight	$g\ mol^{-1}$
n	number of monomer units	-
P	permeability	$kg\ m^{-1}\ kPa^{-1}\ s^{-1}$
q_{max}	Rayleigh limit	C
Q	flow rate	$m^3\ hr^{-1}$
Q_0	reference flow rate	$m^3\ hr^{-1}$
r	distance	m
$\langle r^2 \rangle^{\frac{1}{2}}$	root mean quare end-to-end distance	m
s	distance	m
S	solubility	$kg\ m^{-3}\ kPa^{-1}$
$\langle s^2 \rangle^{\frac{1}{2}}$	root mean square radius of gyration	m
t	time	s
T	temperature	K
V	potential	kV
V_i	molar volume of substance i	m^3

Greek symbols

δ	solubility parameter	$(\mathrm{MPa})^{1/2}$
γ	surface tension	$\mathrm{N\ m^{-1}}$
ρ	density	$\mathrm{kg\ m^{-3}}$
η	viscosity (dynamic)	$\mathrm{N\ s\ m^{-2}}$
ε	efficiency	-
χ	χ-parameter	-

Constants

k_B	Boltzmann constant	$1.38062 \cdot 10^{-23}$	$\mathrm{J\ K^{-1}}$
N_A	Avogadro's number	$6.0220453 \cdot 10^{23}$	$\mathrm{mol^{-1}}$
R	gas constant	8.3145	$\mathrm{J\ mol^{-1}\ K^{-1}}$
ϵ_0	permittivity of vacuum	$8.85419 \cdot 10^{-12}$	$\mathrm{F\ m^{-1}}$

Chapter 1

Introduction

The World Health Organization seeks, in its attempt to minimize the malaria burden in Africa, new ways of deterring and extirpating mosquitos. The first section, section 1.1, discusses the background of the malaria problem.
Technology can help organizations like the WHO in their effort to help the local people preventing malaria to spread. A technique which can help making mosquito nets that last longer is EHDA, also referred to as electrospraying. How this technique can help is the subject of this research. The goal of this research is defined in section 1.2.

1.1 Background

1.1.1 Use of mosquito nets

Malaria-carrying mosquitos usually bite at night. A safe physical barrier to mosquitos can be provided by mosquito nets. The effectiveness can be improved by impregnating the nets with insecticide. These nets are called Insecticide Treated Nets (ITNs). This insecticide repels and deters the mosquitos, which either starve from the insecticide or by a lack of blood, thus preventing further spreading of malaria.

Reduction of the mortality rate of young children by 20% can be achieved by using impregnated nets. The price of the treated nets can be a problem for poor families at risk of malaria.

Not only the costs are a problem. For the nets being effective they must be retreated with insecticide regularly. It is sometimes difficult to convince the people in Africa that this re-treatment is really necessary.

Treatment is done by submerging the nets in water with insecticide dissolved in it. After the nets have soaked up the water, the nets are dried and can be used. This treatment only lasts for approximately one year, or three subsequent washings of the net. After this period the amount of insecticide on the net is too low to be effective.

Retreatment involves the distribution of equipment and insecticide, which makes the operation complicated and expensive. Besides the practical problems, local people not always know how to retreat. This may cause problems or even harm the people retreating the nets, see section 2.4.

1.1.2 Long lasting insecticidal nets

To prevent all problems mentioned in the previous section to occur, research is being done towards long lasting insecticidal nets (LLITNs). These nets have an extended life span of approximately four to five years instead of one year and thus need no retreatment. The advantages are that the nets once given to local people don't have to be retreated. If the cost price of the nets is the same as normal ITNs, for the same amount of money more people can be provided with nets.

There are different ways to make long lasting insecticidal nets. One of the approaches is to incorporate the insecticide in the fibers of the nets. Over time the insecticide diffuses through the polymer of the net to the surface. At any time there should be enough insecticide on the surface of the nets to be effective.

Some disadvantages of this method exist. Because the insecticide is present from the moment the fibers for the nets are made, they can be a threat to people working with these nets. After making the fibers and making the nets, people have to cut them and hems have to be made. All these steps involve people touching the nets. Always some insecticide will stick to their hands and may cause harm over longer exposure times.

It is preferable that the insecticide is applied after the nets are finished for final use. In this way the nets can be safely handled during manufacturing. Another method is to use normal nets, and apply the insecticide on the net in a controlled release coating. The physical properties of the polymer used in the coating control the release rate of the repellant. Further in this report this method is explained in more detail.

1.1.3 Roll Back Malaria programme

Roll Back Malaria (RBM) is a global partnership founded in 1998 by the World Health Organization, the United Nations Development Programme, the United Nations Children's Fund and the World Bank with the goal of halving the world's malaria burden by 2010 [2]. The RBM partnership includes national governments, civil society and non-governmental organizations, research institutions, professional associations, the UN, development agencies, development banks, the private sector and the media.

RBM was founded in response to a growing concern by governments, particularly in Africa, about the continuing and increasing burden of disease and death due to malaria. RBM is being built on the shoulders of recent successful efforts in malaria-affected countries and regions to improve and support capacity to scale up action against malaria.

1.2 Aim of the project

Insecticide treated nets used at this moment do not last for longer than one year. It is the goal of this project to be able to produce nets that will last four years. This will be done by applying a controlled release coating by means of electro hydrodynamic atomization, also referred to as electrospraying.
The WHO requires that the nets are treated after they have been "assembled". This finishing means the production of ready-to-use nets from large bolts of woven nets. This procedure is very labour-intensive, and involves people handling the nets barehanded. It is therefore required that the impregnation with insecticide is applied after the nets have been finished.

1.3 Contents of this report

The method used to apply the coating in this research is electrospraying. The theory of electrospraying, as well as the relevant theoretical background of polymers is discussed in chapter 2. In chapter 3 the methods used to do the experiments with are described. The results which are obtained from the experiments are discussed in chapter 4.
Secondly a polymer must be chosen to incorporate the insecticide. This polymer must have certain properties, like being UV resistant, able to dissolve in a solvent, and have the right controlled release properties. The third goal is applying a polymer coating to mosquito nets by means of EHDA. After this the release rate has to be checked and the life span of the nets have to be verified.

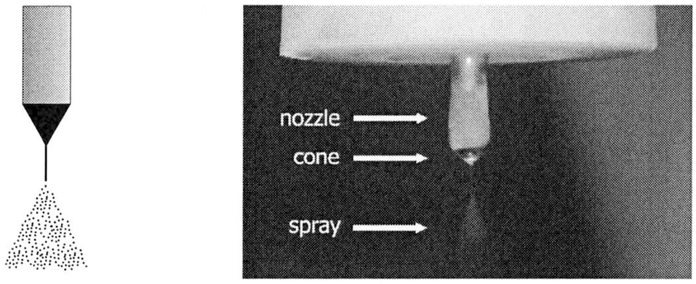
Chapter 2

Theory

2.1 Electro HydroDynamic Atomization (EHDA)

Electro HydroDynamic Atomization also referred to as electrospraying uses an electric field as the energy source to produce a spray. This electric field is generated by applying an electric potential between a nozzle and a counter electrode. A liquid is pumped through the nozzle. Due to Coulombic interaction of charges in the liquid and the applied electric field, the liquid coming out of the nozzle is accelerated. The result is the formation of a liquid jet and the disruption of this jet into droplets.

It was William Gilbert who described this phenomenon already in the sixteenth century [10]. He saw that a rubbed piece of amber attracted a water droplet, which changed into a conical shape. The break-up of a jet into fine droplets, caused by the electric field itself was defined as an electrospray in 1917 by Zeleny [24]. The formation of a cone was mathematically described by Taylor in 1964 [18], this cone first observed by Taylor was named after him. He found out that it is not the liquid meniscus that breaks up into



(a) Schematic representation (b) Actual example

Figure 2.1: Taylor cone with jet emerging, which forms a spray. Schematic representation and actual sample. Photo rotated by 180°.

droplets, but it is a charged jet emerging for the tip of cone that is responsible for the breakup. See figure 2.1 for a photograph of this phenomenon. In this photograph you can see the nozzle. The cone is visible at the tip of the nozzle. From the apex of this cone a jet is emerging, which breaks up into a mist of fine droplets. The droplets are charged and repel each other. This gives the inverse conical shape of the mist.
The break-up of the charged jet into droplets (and thus the size distribution) is influenced by numerous parameters. Two different types of parameters can be defined: operational parameters as the electric field and the liquid flow rate and physical parameters like liquid conductivity, viscosity and surface tension. The influence of these parameters will explained below.

The **electric field** is determined by the magnitude of the applied potential difference. The geometry of the nozzle (inner and outer diameter) and counter electrode also influence the electric field, and subsequently the shape of the liquid cone.
The droplet size is determined by the jet size, which on its turn is influenced by the **liquid flow rate**. If the flow is too low there will be no cone visible, because not enough liquid can be supplied to maintain a stable cone. If, on the other hand, the liquid flow rate is too high, the electric field is not able to produce a stable cone, because the cone is "overfed" with liquid.

The influence of the physical parameters is expressed in the so-called scaling laws, which are discussed below.
An overview of all the spraying modes can be found in appendix A. The most interesting mode, the cone-jet mode will be discussed here.

2.1.1 Cone-jet mode

The most interesting spraying mode is the so-called "cone-jet mode". The interest for this mode comes from the ability to produce (sub)micrometer droplets with a narrow size distribution and a high charge per droplet. There are numerous applications where electrospraying is used in the cone-jet mode. Some examples are: mass spectrometry, powder and drug particle production, thin films and in agriculture as a way of spraying pesticides.
The cone-jet mode is observed when a droplet pending on a capillary is exposed to an electric field. The droplet will be deformed to a cone, if the magnitude of the electric field is sufficiently high. In the liquid cone, ions will accelerate and will emerge from the apex of the cone as a jet. This jet breaks up into droplets by different mechanisms. With increasing potential, the varicose and the kink instability break-up respectively. The breakup of varicose instabilities occur just as in the breakup of natural jets, while kink instabilities is more disordered. The reason for this are the large lateral instabilities, resulting from the high electric forces. These two breakup

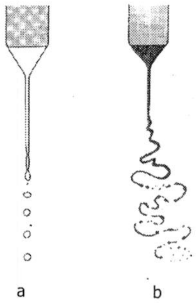


Figure 2.2: Break up mechanisms. (a) varicose instability, (b) kink instabilities, taken from [7].

mechanisms are schematically shown in figure 2.2.

Monodispersity depends on the break-up mechanism. It is found that varicose break-up is responsible for the break-up in monodispers droplets [12]. This process is a natural occurring phenomenon, just like the break-up of a water jet running from a water tap.
Hartman [12] investigated the influence of the different spraying parameters on the shape of the cone, droplet size and droplet charge. This physical model refined the work done by Fernandez de la Mora [8] and Gañán-Calvo [9].
Hartman modelled the current through a cone jet system. He found for the current in the high conductivity case:

$$\frac{I}{I_0} = b \cdot \left(\frac{Q}{Q_0}\right)^a, \tag{2.1}$$

where $I_0 = \left(\frac{\epsilon_0 \gamma^2}{\rho}\right)^{\frac{1}{2}}$, $Q_0 = \frac{\epsilon_0 \gamma}{K\rho}$, Q is the flow rate through the system, I is the current through the jet, K the conductivity of the liquid, ρ the density of the liquid, γ the surface tension of the liquid and ϵ_0 the permittivity of vacuum.
The dimensionless variables a and b are scaling constants, their values can be found in table 2.1.
From these so called *scaling laws* the droplet diameter can be calculated. For the varicose break-up regime Hartman found:

$$d_{d,varicose} = c \left(\frac{\rho \epsilon_0 Q^4}{I^2}\right)^{\frac{1}{6}} \tag{2.2}$$

The constant c was found (by fitting to experimental data) to be equal to 2.05.

Table 2.1: Values of the dimensionless scaling law parameters a and b as function of the dimensionless flow rate $\frac{Q}{Q_0}$, taken from [12].

$\frac{Q}{Q_0}$ [-]	a [-]	b [-]
< 50	0.493	2.215
50 - 250	0.518	1.931
> 250	0.427	3.203

The diameter of the droplets generated by kink instability was found to be:

$$d_{d,kink} = \left(0.8 \cdot \frac{288\epsilon_0 \gamma Q^2}{I^2}\right)^{\frac{1}{3}} \tag{2.3}$$

The kink instability regime is entered when the droplet size calculated by equation 2.2 is larger than the one calculation from equation 2.3. If this is the case equation 2.3 should be used to calculate the droplet size.

2.1.2 Droplet charge

The droplets produced by means of EHDA are highly charged. A charged droplet will disintegrate when the outward pressure produced by the electric field at the surface overcomes the inward pressure produced by the surface tension, γ. If the charge on a the surface of a droplet is too high the droplet is disrupted, lowering the charge per surface area ratio. The Rayleigh limit is the maximum charge possible on a droplet, where the radial surface stress and electric stress are equal.
The maximum charge of a droplet q_{max} is given by:

$$q_{max} = \pi\sqrt{8\epsilon_0 \gamma (d_{droplet})^3} \tag{2.4}$$

where ϵ_0 is the permittivity of vacuum, γ is the surface tension and $d_{droplet}$ is the droplet diameter.
Evaporation of the liquid causes the charge per unit surface area to increase, because the volume and subsequently the surface area decrease. It is thus necessary to prevent the accumulation of charge by either preventing evaporation or to discharge the droplets. The latter is usually the only option, because evaporation of the solvent is desired. An overview of techniques to discharge droplets is described by Cloupeau [6].
One of the options described by Cloupeau is discharging by using a corona needle. The needle is oppositely placed of the spraying nozzle. At sufficient high electric field the needle starts to produce ions oppositely charged as the droplets.

2.2 Polymer properties for controlled release

To control the release rate of the active agent from the coating, the polymer that incorporates the active agent is the most important parameter. The degree of cross-linking and the molecular weight are two important parameters to control the diffusion coefficient, as will be explained in section 2.2.1. Another important parameter is the glass transition temperature, described in section 2.2.2.

2.2.1 Controlled release

The mass transfer of active agent from the polymer to the surface is described by three coefficients: diffusion, solubility and permeability.
Diffusion can occur on a macroscopic scale through pores in the polymer matrix. On a molecular level by passing between polymer chains, e.g. a polymer and active agent have been mixed to form a homogeneous system, also referred to as a matrix system. Diffusion is the process of molecules travelling from the polymer matrix, where there is a high concentration into the external environment, where the concentration is low. As the release continues, its rate normally decreases with this type of system. The active agent closer to the surface of the coating already had moved to the surface. The molecules from the core of the coating must travel progressively longer distances, therefore requires a longer diffusion time to release.
The active agent moves from the center (high concentration) to the surface (low concentration). The diffusion depends on size, shape and polarity of the active agent as well on the polymer-chain motion. The latter is influenced by inter chain attractive forces like van der Waals' interactions, hydrogen bonding, crystallinity and degree of cross-linking. Diffusion is driven by a concentration gradient between the core and the surface of the coating. According to Fick's law:

$$J" = -D \cdot \frac{C_{surface} - C_{core}}{L} \tag{2.5}$$

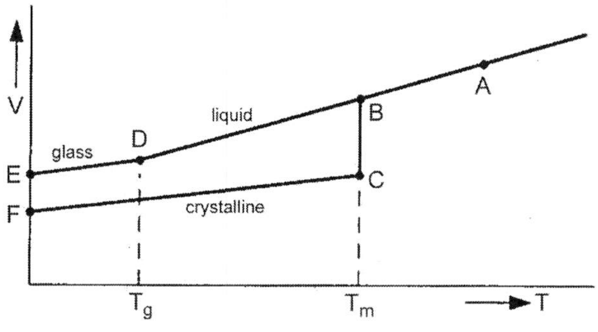
Where $J"$ is the flux through the coating, D is the diffusion coefficient and L is the thickness of the coating. This equation show that the flux through the coating decreases with decreasing concentration in the core of the coating.
Permeability is the rate of transport of a molecule through a polymer as a result the combined effects of diffusion and solubility. The permeability coefficient determines the amount of molecules passing through per unit of time, per area and per unit pressure. The permeability coefficient (P) is the product of the diffusion coefficient (D) and the solubility coefficient (S):

$$P = S \times D \tag{2.6}$$

Rubbery materials, having a large free volume, are for small molecules easy to diffuse through. Because of the rubbery phase in semi crystalline materials above T_g (see section 2.2.2) the diffusion rate is higher than in the glass phase. Deviations from this rule can be attributed to the solubility parameter. The permeability can be influenced by adding additives to the polymer.

2.2.2 Glass transition temperature

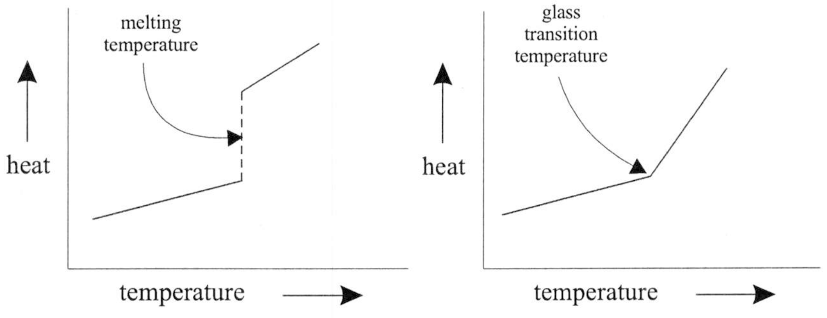
The glass transition temperature (T_g) is the temperature below which the polymer becomes hard and brittle, like glass. Some polymers are used above their glass transition temperatures, and some are used below. Hard plastics like polystyrene and poly(methyl methacrylate), are used below their glass transition temperatures; that is in their glassy state. Their T_g's are well above room temperature, both at around 100 °C. Rubber elastomers like polyisoprene and polyisobutylene, are used above their T_g's, that is, in the rubbery state, where they are soft and flexible. The glass transition temperature is, however, not the same as the melting point. Melting only occurs to crystalline polymers. The polymer chains brake lose from the crystalline structure and become a (disordered) liquid. The glass transition is a transition which happens in an amorphous polymer. Also crystalline polymers will have some amorphous portion, about 40 to 70% of the sample. A sample of polymer thus can have both a glass transition temperature as well as a melting temperature. But only the amorphous phase undergoes the glass transition and the crystalline phase the melting. The volume as a function of the temperature is also different for crystalline and amorphous polymers, this can be seen in figure 2.3.



(a)

Figure 2.3: A volume versus temperature plot, adapted from [19]

The glass transition temperature can be lowered by adding a *plasticiser* to the polymer. These small molecules increase the free volume, making more room for the polymer molecules to move around. This process lowers the temperature at which the molecules can move. By increasing the free volume, also the diffusion of plasticisers and active agent increases.



(a) Crystalline polymer (b) Amorphous polymer

Figure 2.4: A heat versus temperature plot, showing the difference between (a) first order and (b) second order transition.

When a crystalline polymer melts it adsorbs energy without increasing in temperature. This is a first order transition, see figure 2.4 (a). In a amorphous polymer only a change in heat capacity can be observed, therefore this transition is a second order transition, see figure 2.4 (b).

The glass transition temperature is determined by the flexibility of the polymer backbone. The more flexible the backbone is the lower the glass transition temeprature is. Large side groups hinder the movement of the polymer molecule, resulting in a higher glass transition temperature.

2.2.3 Molecular weight

The molecular weight of the polymers is very important for its properties. For example the viscosity of polymers is dependent on the molecular weight according to:

$$\eta \propto {M_w}^{3.4} \tag{2.7}$$

The high value of the exponent reflects the large influence of the chain length on the viscosity. With increasing viscosity it is more difficult to dissolve the polymer. For each polymer there will be a maximum molecular weight above which the polymer will not be able to dissolve, it then only absorbs the solvent.

With increasing molecular weight, the chain of the polymer will also be longer. If the length of the chain is larger than the droplet diameter, fibres can be formed in stead of nice spherical droplets.

The contour length of a polymer is simply the length of a monomer (l) times the number of monomer units (n):

$$L_{cont} = n \times l. \tag{2.8}$$

But because polymer are flexible (especially is solutions) it is more realistic to consider the distance between the chain ends, i.e. the *end-to-end distance*

r [23].
An isolated polymer is flexible and r changes continuously. The root mean square (RMS) end-to-end distance, $\langle r^2\rangle^{\frac{1}{2}}$ is more representable, $\langle\ \rangle$ indicating the average over time.
It is found, assuming freely-jointed chains and using random-walk calculations that:

$$\langle r^2\rangle_f^{\frac{1}{2}} = n^{\frac{1}{2}} \times l \tag{2.9}$$

where the subscript $_f$ indicates that a freely jointed chain is assumed. Properties of dilute polymer solutions which are dependant on chain size are controlled by the radius of gyration, rather than the end-to-end distance. This radius of gyration is the average distance of a chain segment from the center of mass of the molecule. The radius of gyration, $\langle s^2\rangle^{1/2}$ is related to $\langle r^2\rangle^{1/2}$ (for linear Gaussian chains) by:

$$\langle s^2\rangle^{\frac{1}{2}} = \frac{\langle r^2\rangle^{\frac{1}{2}}}{6^{\frac{1}{2}}} \tag{2.10}$$

This means that for droplet to be generated that $\langle \mathrm{s}^2\rangle^{\frac{1}{2}} < \mathrm{d}_{\mathrm{droplet}}$. If the polymer diameter is larger than the droplet diameter, it means that the polymer does not 'fit' in the droplet, and unwanted side effects can occur.

2.3 Spraying the polymer or its monomers

To make a coating of a polymer on a mosquito net one can choose between two alternatives, being spraying reactive monomers or a dissolved polymer. Both options will be explained below.

A solution can be made with exists of solvent, reactive monomer(s) and reaction initiators. This solution than can be sprayed on the nets using electrospray. The monomer(s) react and form a cross-linked polymer coating on the net. When the stock solution also contains any active agent, this agent will be incorporated in the polymer coating on the net.
This method enables the use of cross-linked polymers for the controlled release coating. The release rate of the active agent can be controlled by the degree of cross-linking of the polymer. However, because of the reactivity of the monomers the stock solution must be refreshed often. This is not very practical. A possibility is the use of monomers that only react when exposed to air of water, like some polyurethanes. These polymers only polymerize when there is water(vapour) present. The reaction thus only starts after the spraying and extends the shelf life of the spraying solution.
The monomer(s) used for polymerization are often highly reactive and therefore hazardous. This raises the need for special precautions and safety measures, like closed environments and air filtering.

To control this process of spraying and polymerization a lot of parameters are involved. This makes the process for this research needlessly complicated.

Anther option is to spray a polymer solution on the net. The solvent evaporates and the remaining polymer forms a coating on the substrate. This process is easier to use than the previous one, because no reactions are involved. The only requirement is that the polymer must be soluble. It is preferred that cheap and unharmful solvents will do. A polymer can be dissolved if the solubility parameter of the polymer and solvent are similar. The solubility parameters of some common solvents can be found in table 2.2

Table 2.2: Some solvents for polymeric systems

solvent	δ (MPa)$^{1/2}$	taken from
xylene	18.2	[5]
toluene	18.2	[4]
ethyl acetate	18.6	[4]
acetone	20.3	[14]
1,4-dioxane	20.5	[14]
ethanol	26.2	[5]
water	48.0	[5]

2.3.1 Solubility parameter

The solubility parameter expresses the interaction between a polymer and a solvent. The solubility parameter δ_i of substance i is defined as:

$$\delta \equiv \sqrt{\frac{\Delta H - RT}{V_m}} \tag{2.11}$$

where ΔH is the heat of vaporization, R is the gas constant, T is the temperature and V_m is the molar volume. Thermodynamics on the binary mixture gives the χ parameter expressed by the solubility parameters:

$$\chi = \frac{V_S}{N_A k_B T} (\delta_S - \delta_P)^2 + 0.34 \tag{2.12}$$

where subscript S and P stand for solvent and polymer, respectively. Equation 2.12 illustrates that the polymer and the solvent mix when their solubility parameters are close and do not when they differ a lot. Further more equation 2.12 is always positive. It fails to describe specific interactions that may make χ negative such as the hydrogen bonding.

Cross linked polymers are in general not soluble in any solvent. This means that these cannot be used as reacted polymer. Only the monomers can be sprayed with all the difficulties explained above.
For the polymer to dissolve there is a maximum to the molecular weight of the polymer. Higher molecular weight means longer molecules, which are more difficult to dissolve. If the molecular weight is too high it is even impossible to dissolve this polymer. It is important to select a polymer with a correct molecular weight. If the molecules are too short this means that the release rate will be higher (see section 2.2.1).

2.4 Safety and environment

This section reviews the toxicity and hazards of different insecticides and methods used for the impregnation of mosquito nets. It also provides recommendations on their save use and operation.

2.4.1 Insecticide dangers

Insecticides are dangerous chemicals. They are developed to repel and kill insects, but can also harm people who get in contact with these chemicals. Acute toxicity may occur through treatment and handling of insecticides for treatment of mosquito nets. Most at risk are people directly involved in dipping large numbers of nets. Adverse effects reported include, eye pain and irritation, swelling of the face, headache and dizziness. The use of rubber gloves is necessary and the use of mouth and nose mask is recommended for people dipping large numbers of nets.

Table 2.3: Dosage for different insecticides. Taken from [1].

insecticide	formulation[1] and concentration	dosage[2]
Permethrin	EC: 20%, 25%, 50%	200-500
Deltamethrin	SC: 2.5% and WT 25%[3]	15-25
Lambdacyhalothrin	CS	10-20
Alpha-cypermethrin	SC	20-40
Cyfluthrin	EW 5%	50
Etofenprox	EW 10%[3]	200

[1] EC: emulsifiable concentrate, SC: suspension concentrate, WT: water dispersible tablet, CS: microencapsulated, EW: emulsion, oil in water.
[2] Milligrams of active ingredient per square meter of netting.
[3] WHO specifications under development.

The insecticide products used for impregnation mosquito nets are shown in table 2.3. All listed products successfully passed the WHO Pesticide Evaluation Scheme (WHOPES) [3]). They are all pyrethroid insecticides, the only group of insecticides presently recommended for this use. The reason for this is their high knock down effect, repellency, irritancy and efficacy at low dosages for mosquitos while still being safe for humans. Pyrethroids are toxic due their affinity for and intrinsic effect on receptor or targets within the sodium channels essential for nerve conduction.

The acute toxicity of a mixture of two isomers depends on the ratio of the amounts of the two isomers in the formulation. For example, the acute oral LD_{50}[1] of permethrin for female rats increases from 224 milligrams of the pyrethroid per kilogram of body weight (mg kg^{-1}) to 6000 mg kg^{-1} as the proportion of the trans-isomer increases from 20 percent to 80 percent [15]. Most commercial formulations have a fixed isomeric ratio. Formulations made of a single isomer (deltamethrin, for example) are likely to be much more toxic than those with four to eight isomers.

Table 2.4: LD_{50}: acute oral and dermal toxicity of insecticides[1], adapted from [20].

insecticide	oral toxicity[2]	dermal toxicity[2]
Alpha-cypermethrin SC 10%	4,932	2,000
Cyfluthrin EW 5%	2,100	>5,000
Deltamethrin SC 1%	>10,000	>10,000
Deltamethrin WT 25%	1,965	>2,000 (rabbit)
Etofenprox EW 10%	>5,000[3]	>5,000
Permethrin EC: 10%	5,000-6,000	4,000-10,000

[1] As reported by manufacturers in the Material Safety Data Sheets of the products. The material safety data sheets of 3 major manufacturers have been consulted for provision of data related to permethrin EC10%.

[2] In milligram of insecticide per kilogram bodyweight in rats.

[3] The exact figure for the acute oral toxicity of etofenprox EW 10%, a non-ester pyrethroid, is not available. However, by extrapolation from the figures for active ingredient, it would give a figure of >400,000 mg kg^{-1} bodyweight.

Synthetic pyrethroids have a wide variety of cute oral toxicity to mammals. Compared to organophosphates, carbamate, and organochlorine pesticides they are in general less acutely toxic. Third generation pyrethroids, like deltamethrin and cyhalothrin, containing a cynano-group ($-C \equiv N$) are an exception to this rule. Studies have shown that the main effects are neurotoxicity at high doses and liver enlargement. The changes are reversible,

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[1] The LD_{50} is the dose of a chemical which kills 50 percent of a sample population.

this is an unique characteristic of pyrethroid poisoning in mammals.
In table 2.4 the LD_{50} values in rats are shown, both for oral as well as dermal administration.

2.4.2 Insecticide aerosols

Aerosols can be hazardous to humans. An aerosols is a suspension of solid or liquid particles in a gas [13]. This combination of gas and particles can be inhaled by humans. The particles in the gas can be deposited in the human respiratory system. The place of deposition depends on the particle size, while the toxicity depends on chemical composition and where the particles are deposited. There are several mechanisms for deposition of particles (in the lungs).
The most important deposition mechanisms in the respiratory system are: interception, inertial impaction, diffusion, gravitational settling and electrostatic attraction. Inhaled particles can also be exhaled. From figure 2.5 it can be seen that droplets smaller than 0.1 μm deposit in the alveoli (the deepest parts of the lung), where they can taken up by the blood directly. When spraying insecticides one has to be very careful to prevent inhaling the aerosolized mixture of polymer, solvent, and insecticide. Usage of a closed environment is recommended.

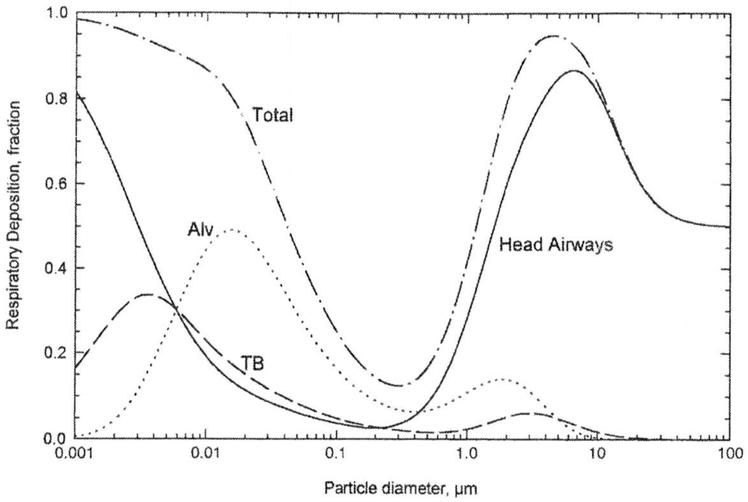


Figure 2.5: Predicted total and regional deposition for light exercise based on ICRP deposition model. Average data for males and females. Taken from [13].

During the coating process a lot of solvent will evaporate. Both for economic and environmental reasons the solvent should be reused. For the solvent to be reused it is necessary that the spraying is done in a closed environment. The 'exhaust' gas should be scrubbed, which requires a lot of additional equipment. The solvent used should therefore be unharmful. There always be spills of solvent and a full recovery will not be possible, so it it also necessary to use a cheap solvent. If the spraying is done locally the solvent also must be stored under tropical conditions. A not inflammable solvent is therefore preferred, but practically this will be not possible, because the insecticides dissolve only in organic solvents.

Chapter 3

Experimental

The experiments that were conducted will be described in this chapter. Several configurations have been tested and their set-up will be described in section 3.1. Section 3.2 is about the droplets formed by spraying the polymer solution. The coating is made with the configuration that was best suitable, this procedure is described in section 3.3. When the coating is finally applied to the substrate, the release rate have to be tested. The procedure measuring the release rate can be found in section 3.4.

3.1 EHDA Configuration

An EHDA setup consists of several parts. A syringe pump is used to generate a liquid flow through the system. A syringe pump is used because it is capable of generating a very stable flow at low flow rates. The syringe pump used in the experiment is an Aitecs, model SEP-10S.
To generate droplets, the liquid has to be pumped through a nozzle. This nozzle is normally made from metal. To this metallic nozzle a high voltage is applied. This high voltage is generated in a high voltage supply, the one used is a Heinzinger, model 20000-05 pos. This power supply is capable of generating a voltage of 20.000 V (20 kV).
An important factor to create a stable system is the type of counter electrode used. There are three different types of counter electrodes:

- plate
- ring
- corona needle

Every combination of counter electrode and nozzle generates a different electric field. The electric field influences the spray and is responsible of getting the right spraying mode. The counter electrode is therefore an important factor in the set-up.

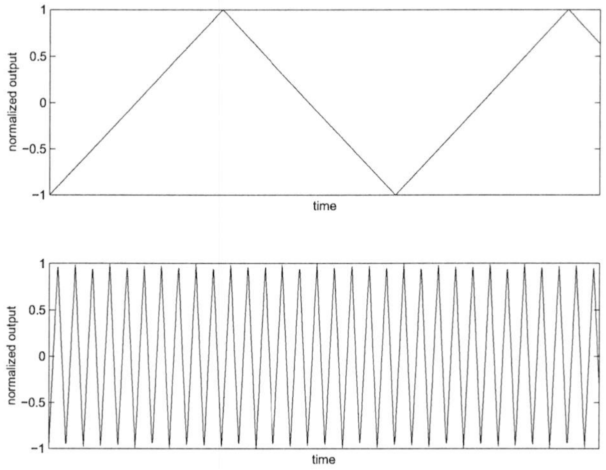


Figure 3.1: Qualitative signal of the signal generators as function of time (top: HP, bottom: Philips)

To be able to cover larger areas with a single spraying nozzle, the net is moved between the nozzle and the counter electrode. This done by means of a modified XY-recorder (Philips PM8131). The X and Y inputs are connected to two function generators (Hewlett Packard 3310B and Philips PM5131). These are set to a sawtooth output. The output of the signal generators can be found in figure 3.1. It can be seen that the frequencies are different. This is done to prevent spraying only on a diagonal line, which would occur if $f_1 = f_2$. Combining the signals in a xy-plot results in coverage of the whole net as can be seen in figure 3.2. The lines do not have to touch each other, because the spray will be broader than the lines shown in the figure. Because of this, also some overlap will occur if the net moves

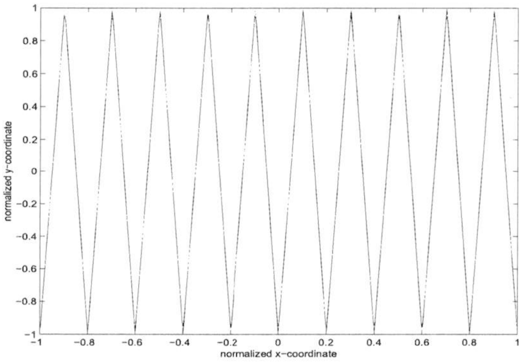


Figure 3.2: Normalized path of the XY recorder (obtained by combining the two output signals from figure 3.1)

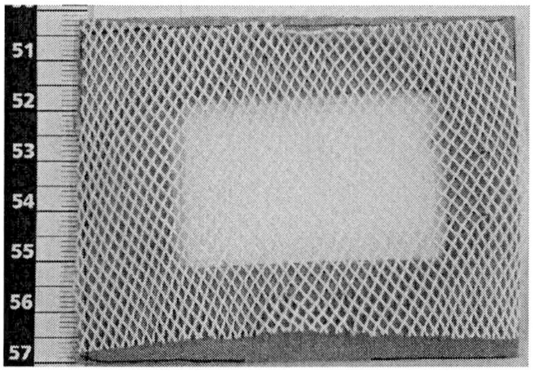


Figure 3.3: Small sample holder used for test spraying

over the nozzle.

The speed of the movement of the net relative to the nozzle is controlled by the frequency. The amplitude of the signal generators corresponds with the area that is covered. To spray the insecticide (supplied by 'Melspring International', The Netherlands) on samples of the mosquito nets (supplied by 'A to Z Textile Mills Limited', Tanzania), a sample holder was made of cardboard. Staples are used to fix the net to the sample holder. A small one (8.5 by 6.0 cm) was used for small samples, see figure 3.3. For larger samples a holder of 20 by 23 cm was used. The net is connected via the staples to the holder. The staples itself are connected via a wire to ground, so that there are many connections between the net and ground, to lower the resistance. The sample holder is attached to the XY-recorder via a clamp. This clamp is connected to the slit which normally would move the recorder pen. Figure 3.4 shows the construction.

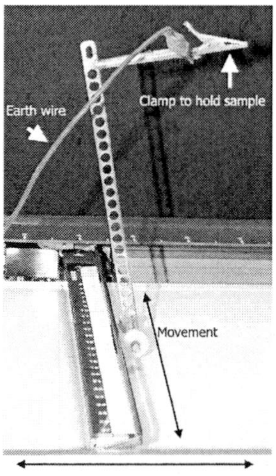


Figure 3.4: Detail of the XY recorder with arm to attach samples

3.2 Droplet formation

Measurements of the droplet size were used to check if the spraying was stable. A stable system should be in the cone-jet mode. The varicose or kink instability breakup should yield a highly monodispers aerosol. It is also used to check if equations 2.2 and 2.3 can be used for spraying of polymer solutions.

The droplets are deposited on a microscope slide. This glass plate was put in the spray for a couple of seconds to deposit enough droplets. Analysis under the microscope yields pictures from which the size can be obtained.

To be able to obtain the size, the microscope should be calibrated. This is done with a standard calibration slide. This slide has an etched scale division of 0.01 mm (10 μm).

3.3 Coating experiments

The coating applied to the nets must have a minimum amount of active agent, see table 2.3 for values. To coat a certain area of net, one has to know how long to spray this area, when the flow rate and insecticide concentration in the stock solution are known. To calculate the total spraying time the following equation is derived via dimension analysis:

$$t = \frac{A \cdot C_{net}}{Q \cdot C_{insecticide} \cdot \varepsilon} \tag{3.1}$$

where A is the spraying area, C_{net} is the desired dose of insecticide on the net, Q is the flow rate of the EHDA set-up, $C_{insecticide}$ is the insecticide concentration in the stock solution and ε is the spraying efficiency. The spraying efficiency is defined as the ratio of amount of insecticide on the net over the amount of insecticide that was sprayed. To calculated the minimum spraying time an estimated efficiency of 10% is used. This is chosen to be sure that enough insecticide will be incorporated in the coating. For the calculation of the spraying time see appendix C.3.

For different commonly used insecticides the required dosage is shown in table 2.3. Insecticides requiring a low dosage are favorable, because they will have less influence on the liquid properties of the liquid that is sprayed. Therefore deltamethrin is favorite to do the experiments with, but has some disadvantages concerning the analytic method used, as will be explained in the next section. Therefore permethrin is used. The chemical and physical properties of both insecticides can be found in appendix D.

3.4 Release rate experiments

The melting point of deltamethrin is 98 to 101°C, and decomposes at temperatures over 300°C. This makes this chemical not suitable for analysis via gas chromatography, it would not move through the column and it also would damage it. For the analysis it is better to use chemicals with a lower boiling point, therefore permethrin was chosen over deltamethrin. The latter is more active, so less is needed, but for the experiments permethrin was used with the specificated surface concentration of deltamethrin (25 mg m^{-2}, see table 2.3)

Once the coating is applied to the mosquito nets, the release rate has to be measured. Long Lasting Insecticidal Nets are a new development, so no standards exists for nets treated by means of EHDA with deltamethrin. There is an interim specification [21] for permethrin-incorporated mosquito nets. These nets consist of mono-filament fibres instead of multi-filament fibres. The permethrin is removed from the surface of the yarn by means of rinsing for 1 minute with acetone. The initial surface concentration is determined from the obtained solution. The nets prepared by means of EHDA cannot be rinsed with acetone, because the polymer used for the coating dissolves in acetone. The polymer must not be present in the samples that will be analyzed, because it would damage the chromatographic column. An other solvent must be used, in which permethrin will dissolve, while the polymer does not. The solubility of the insecticide in the solvent must be good. Ethanol is chosen, because its capacity to dissolve permethrin (see table D.2), but not the polymer because of the large difference in solubility parameters (see table 2.2).

For the analysis a gas chromatograph is used. The chromatographic column used in the WHO interim specification for permethrin incorporated nets has a stationery phase which consists of 50% diphenyl- and 50% dimethylpolysiloxane. This column is not available in the university so another type is used. The column (type: Varian CP-Sil 5 CB) used is a capillary column, 50 m × 0.53 mm with a 1 μm film thickness of a 100% dimethylpolysiloxane stationary phase, see figure 3.5. Separations on this column are almost entirely based on boiling points. In the samples that will be analyzed the only components present are the insecticide and the solvent, so this should be no problem. The chromatograph is operated at a constant temperature of 250°C, while the detector was operated at 280°C. A volume of 1 μl is

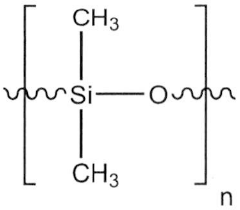


Figure 3.5: Molecular formula of the stationary phase, dimethylpolysiloxane.

injected.

To quantify the results analytical standards, with different concentrations, are made. The area underneath the peak corresponding with permethrin represents the quantity of insecticide present in the sample.

The detector of the gas chromatograph is a flame ionization detector. This detector is a little hydrogen flame. Around the flame a collector is present, having a negative potential with respect to the burner. A small current will flow through the electrode in the case only the carrier gas comes out of the column. If an organic component will come out, it will burn in the flame, producing a large amount of ions. The result is a large increase in the current. this current is proportional to the amount of component. The output of the detector is analyzed by a computer, which also calculates the peak area and retention time (the time needed by a component to elute from the column).

Chapter 4

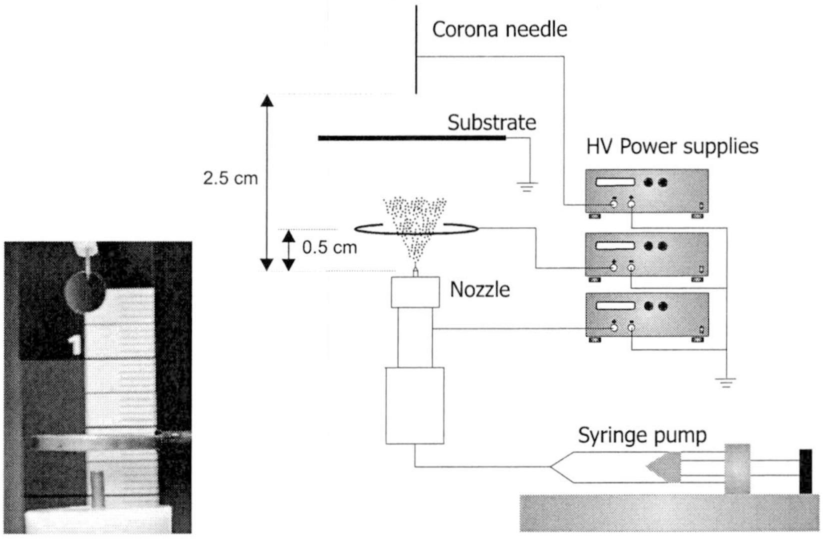
Results and discussion

This research towards a coating for mosquito nets applied by means of EHDA is not only focussed on the coating itself, but also on the development of a practical setup. In section 4.1 the results of the design of the setup are presented. During the design of the setup some tests with different polymers are done. The results of these preliminary tests are discussed in section 4.2. The selection of the polymer used for the release experiments is explained in section 4.3. Section 4.4 is about optimizing the spraying conditions for the selected polymer. Under optimal conditions the electrospray produces a monodispers aerosol. Section 4.5 deals with this subject.
Finally the mosquito nets itself are sprayed with the polymer/insecticide solution. Samples are sprayed and tested for the release of insecticide. The results of these test are presented in section 4.6. Section 4.7 deals with the tests done to measure the efficiency of the setup.

4.1 The (optimal) EHDA setup

For the design of an electrospray setup there are (still) no design rules. This means that by trial-and-error the setup had to be optimized. The considerations to the final setup are presented here.
The first approach was to get a simple setup as possible. Therefore only a nozzle and counter electrode were used. An electrospray setup is normally used to spray downwards, so that gravity helps to pull the droplets down. It was found that when the spray is not 100 percent stable sometimes large drops fall of the nozzle. To prevent these large drops to reach the net, the whole setup is turned upside down. You see this flipped over setup in figure 4.1.

During the first experiments a grounded metal plate was used as counter electrode. However, the droplets leaving the nozzle are charged. These charged droplets, once deposited on the substrate repel all next droplets.



(a) Detail photo of nozzle, ring and needle. Scale in mm.

(b) Schematic drawing of the setup

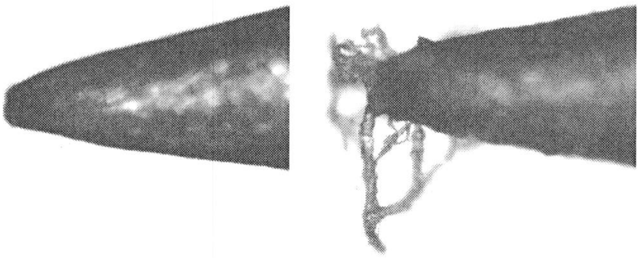
Figure 4.1: EHDA setup used for the coating experiments.

This has dramatic effect on the efficiency of the process. In section 4.7 more can be found on this topic.
For the nets to attract and neutralize the droplet it has to have an opposite charge. It was tried to electrostatically charge the nets. Because of a too high conductivity the charge was already lost the moment spraying started, so this method could not be used, with polyester net nets.
The counter electrode is therefore replaced by a corona needle. Corona needles have the property of releasing oppositely charged ions, if the applied electric field is high enough. These ions neutralize the charged droplets, presumable resulting in higher efficiencies.
Different nozzle were tested for their ability to produce a stable cone and spray. The nozzle and the result are shown in table 4.1. One nozzle (number 1 from table 4.1) was used to spray all the sample. This nozzle produced a spray with a diameter of about 2.5 to 3 cm. This is not sufficient for

Table 4.1: Nozzle properties used for impregnating

nozzle number	outer diameter	inner diameter	stable spray
1	2 mm	0.4 mm	++
2	3 mm	0.5 mm	+/–
3	5 mm	0.4 mm	– –

spraying the complete samples. For this purpose either the nozzle or the net had to be moved. Moving the nozzle is quite cumbersome, because of the weight of the nozzle and counter electrode. Also longer feeding line and electrical wiring is necessary. To overcome all these difficulties the net is moved between the nozzle and counter electrode, by means of a xy-recorder. The movement of the nets between the nozzle and the needle had to be quite accurate. It often happened that the net got entangled in either the nozzle or the needle. This could be solved to stretch the net in the holder. This problem will be more difficult to solve when finished nets will be sprayed. The only option is to have a larger distance between the nozzle and counter electrode, or using the net itself as counter electrode.
Another problem with the nozzle and the corona needle was the accumulation of polymer on their surfaces over time. When polymer started to accumulate on the corona needle, the potential between the nozzle en needle had to be increased for the spraying system to stay in the stable cone-jet mode. After further accumulation, increasing the potential did not help anymore. This point was reached after about 10 minutes. The spraying had to be stopped and the needle cleaned. An example of a clean and dirty needle can be found in figure 4.2.



(a) Clean needle (b) Dirty needle

Figure 4.2: Microscope photos of a clean and dirty needle.

4.2 Preliminary experimental results with different polymers

Before the experiments with PVAc were started, some other polymers were tried. First polystyrene (PS) was used. This polymer dissolves easily in acetone (technical grade was used for all the experiments) and was easy to spray. But because of the unknown origin and the high glass transition temperature (see table 4.2) this one could not be used. Secondly a polyurethane was tested. Polyurethanes are used in foams and also in coatings. The monomers for polyurethanes are di- or tri-isocyanates. If triisocyanates are

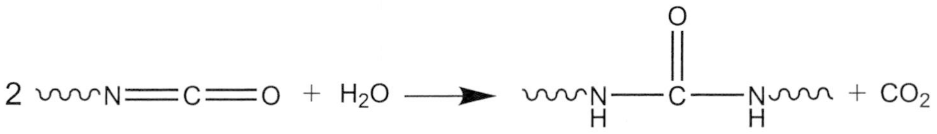


Figure 4.3: Polymerization of isocyanates to polyurethane.

used a cross-linked polymeric network is obtained. In this case only the monomers can be sprayed. The monomers polymerize in the presence of water, as can be seen from the reaction scheme which is shown in figure 4.3. The un-reacted monomers were put directly in the solvent, which was again acetone. The solution is water free, so polymerization only start as the solvent is evaporated. The polyurethane droplets that were deposited on a glass plate can be seen in figure 4.4.

The isocyanate monomers used are highly reactive (they are used in fast drying glues) and thereforr one must be very careful to avoid inhaling this aerosol. This solution could also be sprayed. The obtained coating after spraying is, due to the stiff cross-linked polymer, difficult to bend. This means that cracks will start to break up the coating if the mosquito nets are folded.

Because of the precautions that have to be taken this polymer is not further used.

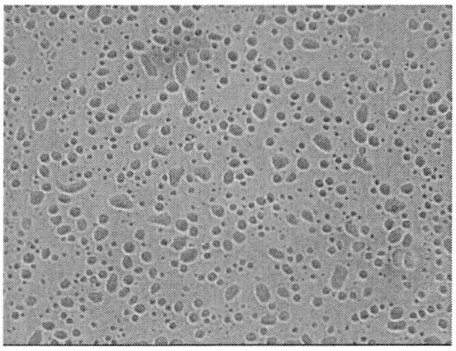


Figure 4.4: Polyurethane droplets on a glass plate

4.3 Polymer selection

The polymer properties are the most important parameter for the right properties of the coating. The requirements to the polymer are:

- Soluble in cheap and unharmful solvent;
- UV Resistance;

Table 4.2: Some polymers with their physical properties

polymer	short	T_g (°C)	use
poly(vinyl acetate)	PVAc	25	latex paints
poly(methyl methacrylate)	PMMA	110	perspex
polystyrene	PS	95	disposable coffee cups
polyethylene	PE	-120	foil, plastic bags

- Water and detergent resistance;
- Compatible with polyester (where most nets are made off)

Another important property is the glass transition temperature, T_g. The polymer should be used above the T_g, to have free volume to incorporate the insecticide. All these constraints narrowed down the amount off possible candidates, of which some are shown in table 4.2. For all the experiments the polymer poly(vinyl acetate), or PVAc is used. The molecular structure of PVAc can be found in figure 4.5. The n denotes the number of monomer units.

PVAc is soluble in a lot of solvents, as can be seen in table 2.2. Solvents with a solubility parameter near the solubility parameter of PVAc (19.2 MPa$^{1/2}$) are suitable. Acetone was chosen for its availability, price and safety.

For the experiments polymer with a molecular weight of 500,000 and 140,000 was obtained. The first was not soluble in acetone, while the latter was. The polymer with the molecular weight of 140,000 was thus used for all the experiments.

4.4 Spraying conditions

The concentration of polymer in the stock solution is important for the spray. It influences the conductivity and surface tension. This influence

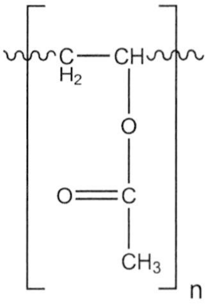
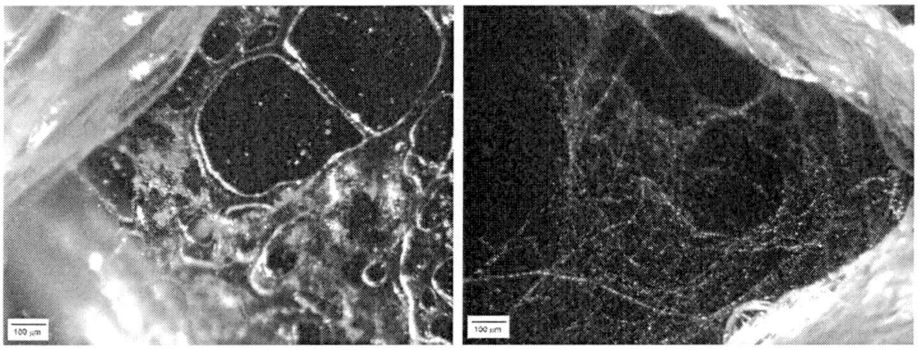


Figure 4.5: Molecular formula of poly(vinyl acetate), PVAc.

increases with concentration.
The solubility of poly(vinyl acetate) in acetone is at least 50 g l^{-1}. It was observed that with increasing the amount of polymer to dissolve, the time needed for the polymer to dissolve also increased. A high polymer concentration is wanted both for economic and environmental reasons. The solvent evaporates and (in the end) has to be recycled, so as little as possible should be used. A saturated solution could be sprayed, but yielded not only droplets but also many fibres, which clogged the nets. For an example of a net with fibres, due to too high polymer concentrations see figure 4.6(a). A concentration of 20 g l^{-1} turned out to be good. It was easy to spray and yielded no fibres.

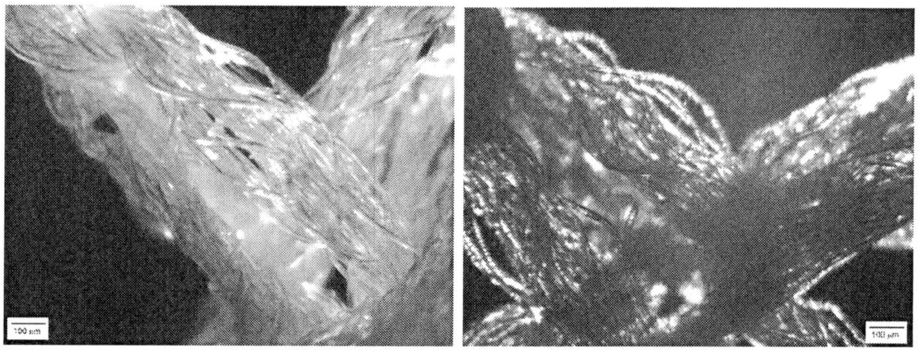


(a) Fibres due to too high polymer concentration (b) Fibres due to insecticide formulation

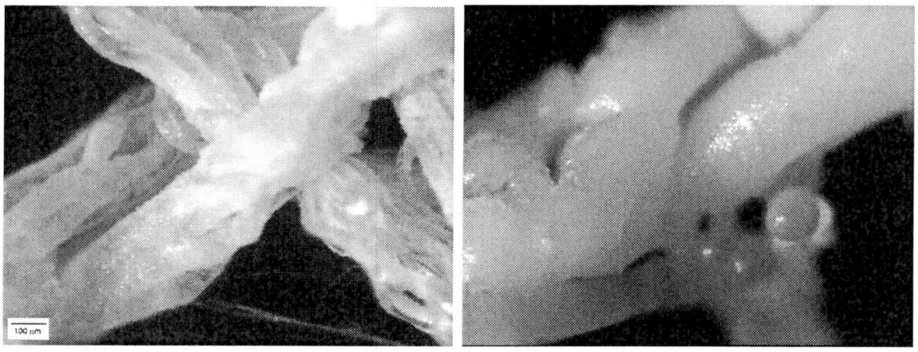
Figure 4.6: Fibre formation on mosquito nets.

If too long is sprayed on the same place, the amount of coating is locally very high. In the end it will be so high that the fibres of the net are not even visible anymore. The process from a clean net to complete coverage can be found in figure 4.7. The first picture shows a clean net. No droplets can be observed. The second photo shows a net that has been sprayed for 15 minutes. Droplets of polymer are clearly visible on the surface of the filaments. The droplets appear as sparkling light dots on the photo. If spraying continues all the filaments are covered with polymer, but still can be recognized as filaments. After more than 15 minutes spraying at the same position a thick layer of polymer is formed around the fibres, completely filling the space between the filaments. These are not separately recognizable anymore.

After all the test without the insecticide (for safety reasons), the insecticide could be added to the polymer solution. For the same reason as with the polymer, the insecticide concentration also has to be high. Also to keep the spraying time limited this is wanted.



(a) Clean net. (b) Moving net sprayed for 15 minutes



(c) Net sprayed for 10 minutes at the same place (d) Net sprayed for 15 minutes at the same place

Figure 4.7: Microscope pictures of the progress of the spraying process of mosquito nets

Available for testing were a 10% EC[1] permethrin concentrate and a 1% SC[2] deltamethrin concentrate. The use of deltamethrin was favorable, because of its higher activity. This insecticide turned out to be unusable, because of its inability to mix with the polymer mixture. Therefore the permethrin concentrate was used. It was mixed with the polymer solution to a 10 g l^{-1} (based on pure insecticide) mixture. This mixture also could be sprayed easily. However an unwanted effect occurred. Already after short times (about 30 seconds) of spraying the nets fibre formation was observed, not only on the nets but already in the air. For this type of fibre formation see figure 4.6(b).
The only way to solve this problem was to use pure formulations of the insecticides. Melspring International was so kind to get pure formulations from Jordan. They supplied a 93% technical pure formulation of permethrin and a 98% technical grade deltamethrin. Both were tested in a 10 g l^{-1} poly-

---

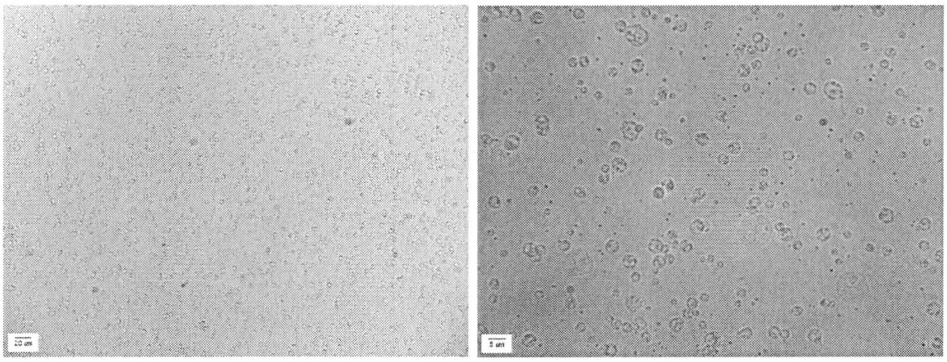
[1] Emulsifiable concentrate

[2] Suspension concentrate

mer solution, with a polymer concentration of 20 g l^{-1}. The nets sprayed with this pure insecticide/polymer solution did not show any fibre formation. The source of the fibre formation must be attributed to the additives, like emulsifiers, in the different formulations.

4.5 Droplet size

The droplet size is measured by putting a microscope glass slide in the electrospray. This slide is then put under a microscope to make pictures via a camera. The size is determined by comparing the photo's with a calibration standard. In figure 4.8 the result of spraying for a couple of seconds on a glass plate is shown. The applied voltage to the nozzle was +10.0 kV, to the ring +5.5 kV and to the corona needle -2.0 kV. The flow rate was 2.0 ml hr^{-1}. The particle size of the particles in this figure is about 5 μm. This sample is representative for other samples as well. It can be seen from figure 4.8 that small satellite droplets are produced. The size of these smaller droplets is in the order of 1 μm.
There is a large difference between the droplet size determined from figure 4.8 and the one calculated from the scaling laws in appendix C.1 (19 μm). This can be explained with the evaporation of the solvent. If this is taken into account the calculated droplet size will be 6 μm. This corresponds reasonably well with the results from the figures.



(a) magnification 10×

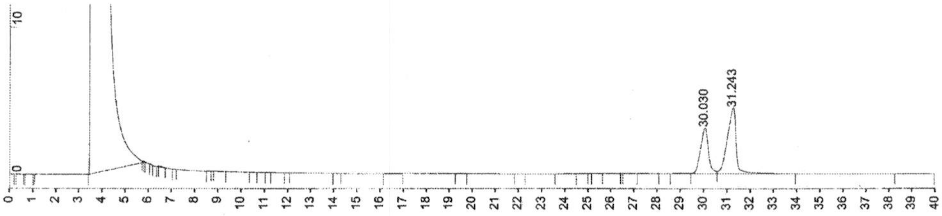
(b) magnification 50×

Figure 4.8: Microscope picture of droplets deposited on a glass plate.

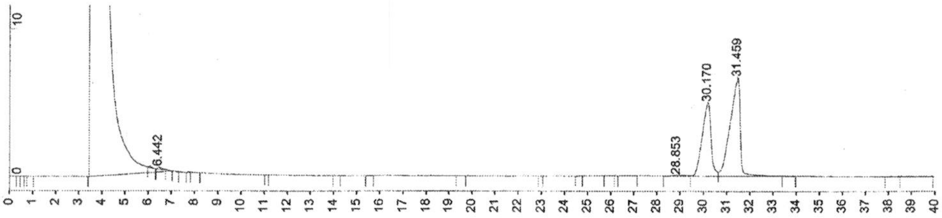
4.6 Controlled release experiments

4.6.1 Permethrin standards

For the quantification of insecticide on the mosquito net samples, permethrin standards are needed. Two standards are made. For these standards 79,28 and 140,44 mg of permethrin are weighted into two 25 ml volumetric flasks. The permethrin is dissolved and diluted to volume with analytical grade ethanol (Baker, analytical grade). Two calibration solutions are obtained with a concentration of 3.17 g l^{-1} and 5.62 g l^{-1} respectively.
These two standards are analyzed with the gas chromatograph. The chromatograms of the two standards are shown in figure 4.9. Three peaks can be observed. The first large peak (at t=4 min) is the injection peak, resulting from the ethanol. The next two peaks are the permethrin isomers, respectively the cis- and trans-isomer.



(a) Permethrin standard, 3.17 $g\ l^{-1}$



(b) Permethrin standard, 5.62 $g\ l^{-1}$

Figure 4.9: Gas chromatogram with clear separation of cis- (at 30 min.) and trans-permethrin (at 31 min.).

4.6.2 Analysis of sprayed mosquito net samples

The sample nets are sprayed with the insecticide/polymer mixture, described in section 4.4. After spraying the nets are cut to a size of 15 × 13 cm, because not all of the surface is sprayed.
The piece of net is put in a 250 ml Erlenmeyer flask. About 50 ml of ethanol (Baker, analytical grade) is added. The flask (with cap) is shaken vigorously for 2 minutes, after which the net is removed and put on a clean beaker glass to dry to the air.

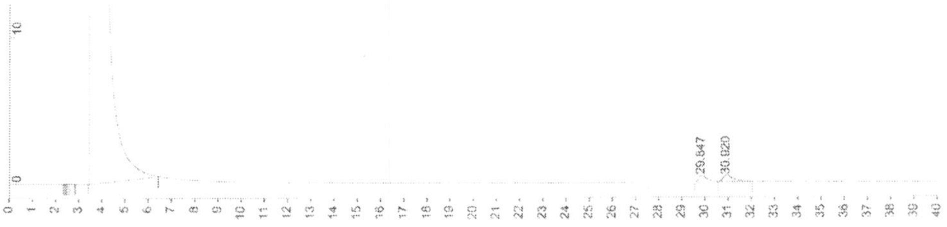
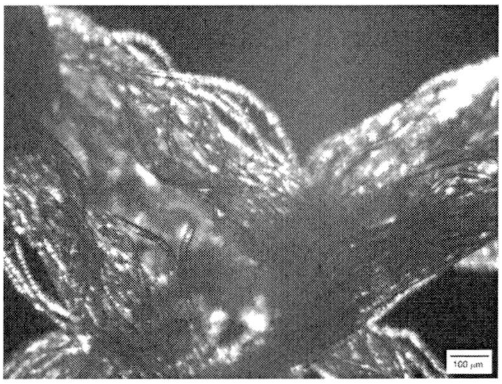


Figure 4.10: Gas chromatogram of a sprayed net

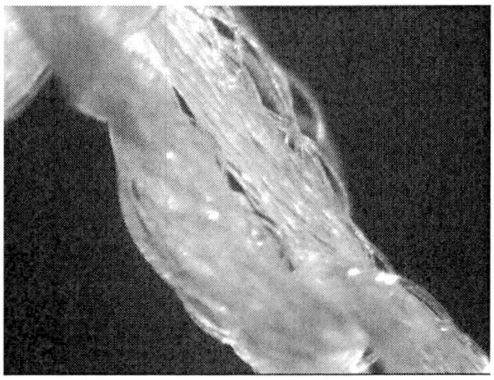
The ethanol extract is evaporated to dryness on a hot plate. After cooling down 3,00 ml ethanol is added by pipette. This is the sample solution, which is analyzed with the gas liquid chromatograph. In figure 4.10 it can be seen that indeed permethrin is present in the sample, and thus on the sprayed mosquito net. By calculating the area underneath the peaks and comparing them with the area and known amount in the permethrin standards, it was calculated that 0.1 mg of permethrin was present on the piece of sample net. With an area of 13 × 15 cm, this leads to a surface concentration of 5.2 mg m^{-2}. This too low for the nets to be effective. After this first measurement, the sample is put in an oven at 70 °C to accelerate diffusion of remaining insecticide to the surface. After two hours the sample is removed from the oven and cooled down to room temperature. The insecticide is extracted from the net and analyzed as described above. The resulting chromatogram did not show any peak, from which can be concluded that no more insecticide was present in the coating. The coating itself was still present on the net as can be seen in figure 4.11.

4.7 Spraying efficiency

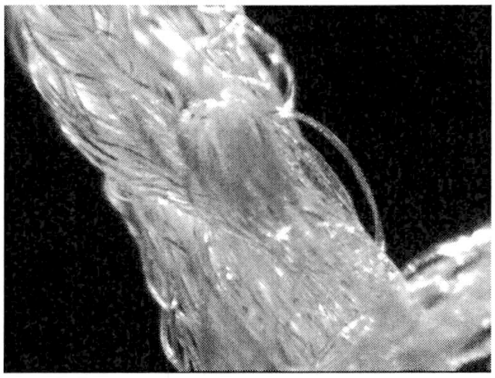
For the measurements of the spraying efficiency a solution of a fluorescent dye was electrosprayed. To be able to quantify the amount of fluorescent material, also the droplets sprayed through the net were collected on a plate. This plate was put behind the sample. By comparing the amount of fluorescence from the net and from the plate the efficiency could be calculated. The florescence of the samples are tested in a dark chamber (UVP Epi Chemi II Darkroom), with ultra violet light. A camera connected to a computer could quantify to amount of florescence from the samples. There was however a problem: the nets itself are fluorescent (at wavelengths of 365 and 254 nm, available in the UV-darkroom), so no distinction could be made between the net and the fluorescent material on the nets. Different fluorescent materials (see table 4.3) were tested, but with none of them a distinction between the fluorescence of the net and of the dye could be made. Trials with different filters between the sample and camera also led to no success. An other option to obtain the spraying efficiency was to compare the amount



(a) Net after spraying



(b) Net after one time rinsing with ethanol



(c) Net after two times rinsing with ethanol

Figure 4.11: Microscope pictures of mosquito nets at different stages of analysis

Table 4.3: Fluorescent materials tested

Fluorescent material	Max. absorbed wavelength	Excitation wavelength
Rhodamine	530 nm	556 nm
Fluorescein	490 nm	514 nm

of insecticide on the net via the gas chromatograms and compare this to the amount of insecticide sprayed. The amount of insecticide on the surface is known. Also the spraying time, liquid flow rate and concentration of insecticide in the spraying solution are known, the amount of insecticide sprayed can thus be calculated.

The sample, of which the gas chromatogram is shown in figure 4.10, is sprayed for 20 minutes. The amount of insecticide sprayed in this this is equal to the time multiplied with the concentration and flow rate. This amount for the sample mentioned is 6.7 mg. The amount measured on the net is 0.1 mg. The spraying efficiency is thus 1.5%, which is very low.

This result can be justified with the observations. When spraying the samples it was seen that a large part of the spray went through the net. This part is thus deposited. It can be expected that the efficiency then should be proportional to the amount of area covered by the fibers of the net. This area is larger than 1.5%. This means that the net repels the spray, resulting in a very low spraying efficiency.

Chapter 5

Conclusions

In this study, applying a controlled release coating to mosquito nets by means of electro hydrodynamic atomization has been investigated. A setup to produce coated samples was also designed.

Electrospraying different polymers dissolved in acetone was shown to be possible. For the application of controlled release coatings poly(vinyl acetate) was tested. This polymer was dissolved in acetone together with the insecticide permethrin and sprayed on polyester mosquito nets.

To produce a stable electrospray and a nice coating, a system was used that sprays upwards. This in order to prevent large droplets from reaching the net. These large droplets are mainly produced when the system was not in the cone-jet mode.
Having a stable spraying system for longer times was not possible because of accumulation of polymer on both the nozzle and the corona needle. Spraying one sample required cleaning the system two or three times.
To be able to coat the mosquito nets, the samples had to lead through the setup perfectly horizontal. With small pieces of net (up to 20 × 25 cm) this was possible, but with larger nets, that are irregularly shaped, this will be more complicated, due to the small distance between the nozzle and the corona needle.

Obtaining nice coatings with a 10% emulsifiable concentrate of permethrin turned out to be nearly impossible. Fibre formation occurred and could only be prevented by using pure insecticides (both deltamethrin and permethrin) for the preparation of the spraying solution.

The presence of insecticide on the treated mosquito nets has been proved by means of extraction with ethanol and analysis via gas chromatography. The initial surface concentration of the insecticide on the coated net was found to be 5 mg m^{-2}. This concentration is not high enough to create treated nets with the desired effectiveness. This small amount of insecticide on the nets is the results of a very low spraying efficiency, being only 1.5%. To increase the spraying efficiency, one could consider using oppositely charged nets.

The conductivity of the used polyester mosquito nets is too low to conduct the charge from the deposited droplets to ground. On the other hand, it was too high to electrostatically pre-charge the nets to attract the oppositely charged droplets.

Chapter 6

Recommendations

The amount of insecticide present in the coating made in this project was too low to be effective with the selected insecticides. To increase the insecticide concentration on the mosquito nets, the insecticide concentration in the spraying solution could be increased.
Larger amounts of insecticide on the nets will be obtained if the spraying efficiency is increased. The reason for the low efficiency is the repulsion of the droplets by the net. If this can be prevented, by either pre-charging the net or faster removing the charge from the net, the efficiency will increase. Both options require the use of different nets instead of polyester nets.

It is recommended to use pure formulations of insecticide, because this report shows that using emulsified concentrates with poly(vinyl acetate) yields the formation of fibres instead of an aerosol. Further testing with insecticide should be done with deltamethrin, which is more active than the other insecticides currently recommended by the WHO. To be able to detect the presence of deltamethrin on the nets, another analytical method should be used.
All the insecticide is removed from the net after rinsing once. The controlled release coating is thus not good in controlling the release. It is therefore necessary to do research to other polymers, which have better release properties.

The stability of the spraying system was reduced as the nozzle and needle became more covered with polymer. Therefore further research has to be done to solve this. Especially when scaling up the system this can be a problem. In order to coat full-size mosquito nets, it is necessary to scale-up the process. Multiple nozzles should be used to cover larger surfaces. Also the distance between the nozzle and corona needle should be increased. Another option is to use the net as counter electrode. However the conductivity of the net should be increased for this to work.

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Appendix A

EHDA modes

For constant liquid properties and flow rate, the system moves through different spray modes, as the applied voltage is increased. Figure A.1 presents a flow chart describing the modes as function of the applied potential. It is not valid for all liquids under all conditions. The figure gives a general description of the mode progression.

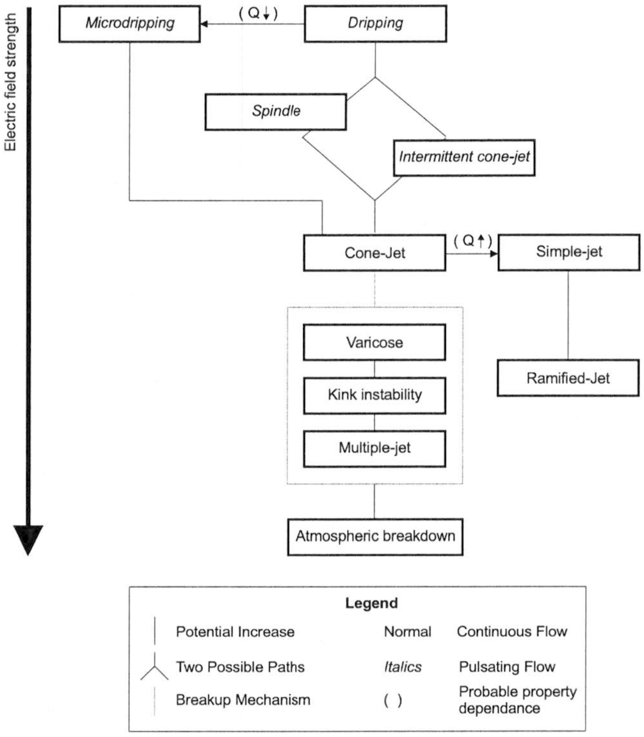

Figure A.1: Different modes of EHDA as function of the applied potential. Taken from [11]

In the following part all the modes from figure A.1 will subsequently be described.
In the **dripping mode** large droplets are produced. The diameter is usually larger than the capillary diameter as can be seen in figure A.3. There is no formation of satellite drops, so a monodisperse spray is created. Reduction of the nozzle diameter may result in an significantly increased maximum emission frequency. Normally the frequency of droplet production is low (about 500 Hz). The diameter and the frequency are functions of the applied potential:

$$\mathrm{f}_{\mathrm{prod}} \propto V \tag{A.1}$$

and

$$\frac{1}{d_{droplet}} \propto V \tag{A.2}$$

In figure A.2 the relation between these two can be seen.

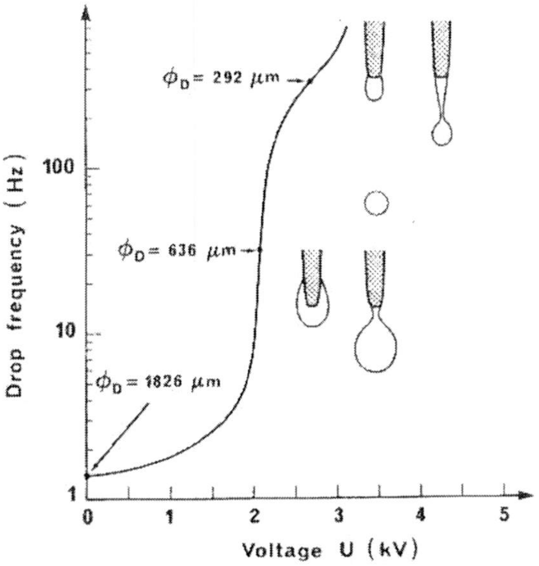

Figure A.2: Dripping mode. Droplet frequency versus applied voltage. ϕ_D is the droplet diameter. Taken from [7].

This phenomenon has a twofold cause:

1. attraction of liquid towards the counter electrode due to the action of the electric field on the charges located at the end of the hanging drop [16, 17];
2. a reduction in the surface tension of the liquid due to the fact that electric charges on the surface create an electrostatic pressure opposite to the capillary pressure [6].

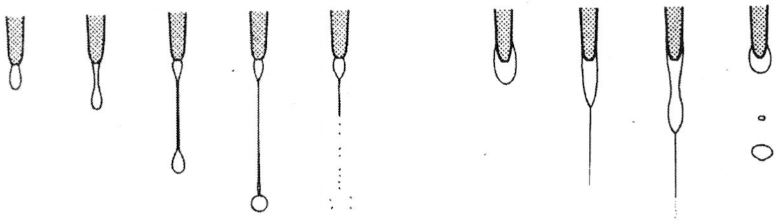

Figure A.3: Dripping mode without jet (left) and with jet (right). Taken from [7].

Figure A.3 (left) shows the dripping mode of a somewhat viscous liquid ($\mu = 68$ mPa·s). This higher viscosity results in a the breaking up of a long thin filament. When the main drops detaches also a large number of smaller droplets are formed. The electric field acting on the end of the pendant droplet is sometimes high enough to create a jet, as can be seen in A.3 on the right side. It follows the same process as for the cone-jet mode, which is described below. The difference between the dripping and **microdripping**

Figure A.4: Microdripping mode; different stages of drop formation. Taken from [7].

mode is that the latter emits droplets from the apex of the cone in stead of a jet that breaks up. An example of droplet emission in the microdripping mode is given in figure A.4. This mode occurs at low flow rates and the droplet production frequency is about two order of magnitude higher than the dripping mode.
From figure A.5 it can be concluded that the microdripping mode and the cone-jet mode can occur under the same experimental conditions. In the transition zone, one spraying mode may replace the other, each being maintained fort a rather long period. The microdripping is however more difficult to obtain than the cone-jet mode. The reason is the smaller diversity of the conditions. The microdripping mode is observed only for small flow rates. It depends, more than other modes, highly on details as shape and degree of wettability of the nozzle.

A special case of dipping mode is the **spindle mode**. Two types of droplet formation occur in this mode, generating two distinct droplet sizes. A large primary droplet is produced together with several small satellite, as can be seen in figure A.6. A jet extends from the meniscus and collapses into the

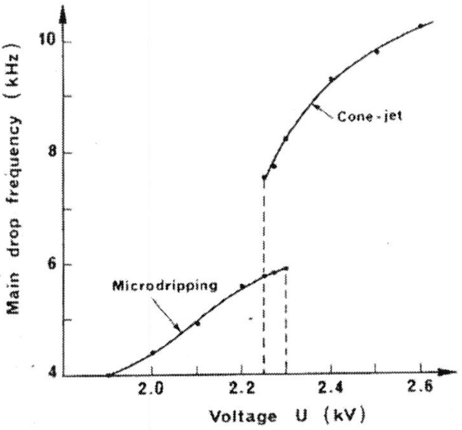

Figure A.5: Example of transition from microdripping to cone-jet mode: droplet frequency versus applied voltage. Taken from [7].

primary and satellite droplets.
An unstable jet is, as the name suggest, produced in the **intermittent cone-jet mode**. After the cone-jet has occurred the meniscus collapses to the capillary and several large droplets may be emitted (see figure A.7).

The **cone-jet mode** is one of the most interesting functioning modes. It can be obtained for many liquids having a high variety of conductivities. The produced aerosol can have a very large range of average droplet diameters, and the aerosols are sometimes monodispers. The most distinct characteristic of the cone-jet mode is the stable cone, and the emerging jet form the apex of this cone. This phenomenon was first observed by Zeleny (1915) [24], but Taylor (1964) [18] was the first to describe the phenomenon mathematically. He calculated for the ideal case (straight generatrix and no hydrostatic pressure) the half angle of the cone to be equal to 49.3°. This

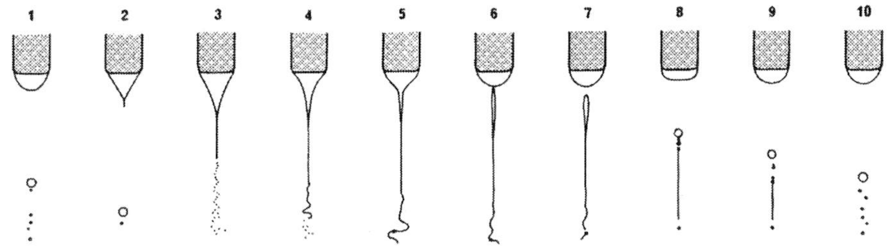

Figure A.6: Spindle mode; different stages of drop formation. Taken from [7].

Figure A.7: Intermittent cone-jet mode. Taken from [7].

result can only be obtained for a single value of the applied potential. Experience shows however that there are stable conical menisci for a certain range of of variation in the hydrostatic pressure and applied potential. In addition, the value of the angle at the apex is variable and the generatrix of the cone may either be concave or convex.

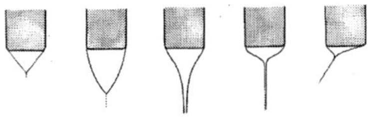

Figure A.8: Different forms of meniscus in cone-jet mode. Taken from [7].

The shape of the cone is different for liquids with different conductivities. This can be seen in figure A.8. The left two pictures shows the menisci of liquids with relatively high conductivities. The jet formation zone is limited to the apex of the cone. The third and fourth pictures shows the form of the meniscus for liquids with lower conductivities. The acceleration zone extends further towards the base of the cone. In the limit, it begins at the outlet of capillary. The length of the jet increases with the viscosity, the resistivity and the flow rate of the liquid. The size of the jet determines the average droplet size. This diameter depends mainly on the conductivity and the flow rate. For a given liquid the cone-jet mode only appears within a limited range of flow rates. The flow rate has to decrease with increasing conductivity.

Breaking up of the jet emerging from the apex of the cone can occur by three mechanisms as a function of increasing potential:

1. Varicose break up (figure A.9(a))
   This mechanisms is the same as the breakup into droplets of a neutral jet.
2. Kink instabilities (figure A.9(b))
   When the electrostatic pressure is high enough the charge of the largest droplets, just after separation, exceeds the Rayleigh limit. This causes the droplet to break up into smaller droplets. For slightly higher voltages, lateral kink-type instabilities appear. The jet stretches out into disordered winding threads and a polydisperse aerosol is obtained.

3. Multi-jet mode (figure A.9c)
   In the highest voltage range the multi-jet mode is obtained. On the rim of the nozzle multiple jets occur. The number of jets increase with increasing potential.

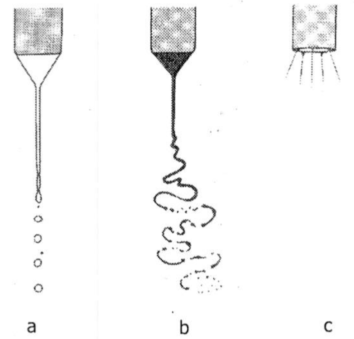

Figure A.9: Break up mechanisms. (a) varicose instability, (b) kink instabilities, (c) multiple jets. Taken from [7].

A jet can also be formed in the absence of an electric field. If the kinetic energy of the liquid flow is sufficiently high enough to overcome the surface energy, the **simple-jet mode** is obtained. This can be seen in Figure A.10a, b and c. The jet can be charged and accelerated by only a small potential. In this case the **ramified-jet mode** can occur. The surface charges increase with increasing potential, resulting in secondary jets emerging from the primary jet, as can be seen in Figure A.10d and e.

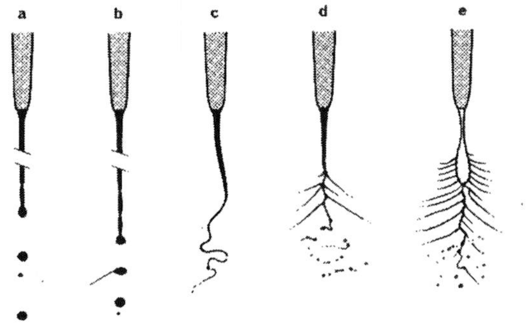

Figure A.10: Simple jet (a, b, c); ramified jet (d, e). Taken from [7].

Appendix B

Cone-jet model

In 1964 Taylor [18] described the cone (however without jet) analytically. The cone is therefore called *Taylor cone.* Relations for the droplet size and current as function of flow rate and liquid properties were derived by Fernandez de la Morra [8] and Cañán-Calvo [9]. These relations are referred to as scaling laws.

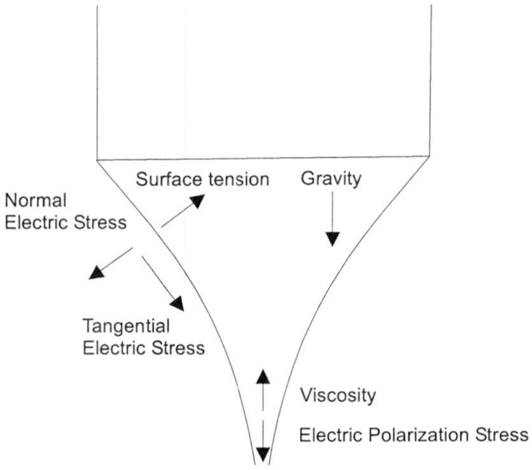

Figure B.1: Forces acting on the Taylor-cone. Taken from [12].

A physical numerical model based on mechanical first principals are developed by Hartman [12]. He was the first to take the jet emerging from the apex of the cone into account. The model predict the shape of the liquid cone and jet, the electric field in and outside the cone, and the surface charge density at the liquid surface. The liquid velocity at the cone surface is also estimated by the model.

In the case of high conductivity, Hartman found for the current:

$$\frac{I}{I_0} = b \cdot \left(\frac{Q}{Q_0}\right)^a \tag{2.1}$$

where $I_0 = \left(\frac{\epsilon_0 \gamma^2}{\rho}\right)^{\frac{1}{2}}$ and $Q_0 = \frac{\epsilon_0 \gamma}{K \rho}$.

The droplet size is dependant on the break-up mechanism. For low stress ratios, break-up occurs due to varicose instabilities:

$$d_{d,varicose} = c \left(\frac{\rho \epsilon_0 Q^4}{I^2}\right)^{\frac{1}{6}} \tag{2.2}$$

For higher stress ratios break-up the following is equation is found for the kink instability mechanism:

$$d_{d,kink} = \left(0.8 \cdot \frac{288 \epsilon_0 \gamma Q^2}{I^2}\right)^{\frac{1}{3}} \tag{2.3}$$

Appendix C

Calculations

C.1 Droplet size

The values for the equations:

symbol	value	unit	value	unit in SI
c			2.05	[-]
ρ			800	[kg m^{-3}]
Q	2.0	[ml h^{-1}]	5.56 $\cdot 10^{-10}$	[m^3 s^{-1}]
γ	22.8	[mN m^{-1}]	2.28 $\cdot 10^{-2}$	[N m^{-1}]
K	20	[μS m^{-1}]	2.0 $\cdot 10^{-5}$	[S m^{-1}]
ϵ_0			8.85 $\cdot 10^{-12}$	[C^2 J^{-1} m^{-1}]

$$\mathrm{Q}_0 = \frac{8.85 \cdot 10^{-12} \times 2.28 \cdot 10^{-2}}{2.0 \cdot 10^{-5} \times 800} = 1.26 \cdot 10^{-11}\ [\mathrm{m}^3\ \mathrm{s}^{-1}]$$

$$\mathrm{I}_0 = \left(\frac{8.85 \cdot 10^{-12} \times (2.28 \cdot 10^{-2})^2}{0.8}\right)^{\frac{1}{2}} = 7.58 \cdot 10^{-8}\ [\mathrm{A}]$$

$$\frac{\mathrm{Q}}{\mathrm{Q}_0} = \frac{5.56 \cdot 10^{-10}}{1.26 \cdot 10^{-11}} = 44\ [-]$$

$$\mathrm{I} = 7.58 \cdot 10^{-8} \times 2.215 \times (44)^{0.493} = 3.4 \cdot 10^{-8}\ [A]$$

$$\mathrm{d}_{\mathrm{varicose}} = 2.05 \times \left(\frac{800 \times 8.85 \cdot 10^{-12} \times (5.56 \cdot 10^{-10})^4}{3.4 \cdot 10^{-8}}\right)^{\frac{1}{6}} = 19\ [\mu\mathrm{m}]$$

$$\mathrm{d}_{\mathrm{kink}} = \left(0.8 \times \frac{288 \times 8.85 \cdot 10^{-12} \times 2.28 \cdot 10^{-2} \times (5.56 \cdot 10^{-10})^2}{(3.4 \cdot 10^{-8})^2}\right)^{\frac{1}{3}} = 23\ [\mu\mathrm{m}]$$

Because $\mathrm{d}_{\mathrm{varicose}} < \mathrm{d}_{\mathrm{kink}}$, $\mathrm{d}_{\mathrm{varicose}}$ should be used. The droplets consist of 96 % acetone, and 4 % polymer and insecticide. The acetone evaporates, leaving smaller droplets than calculated above. The diameter of the droplets without acetone is:

$$\begin{aligned}
\mathrm{V} &= \frac{1}{6} \times \pi \times \mathrm{d}^3_{\mathrm{varicose}} = 3.6 \cdot 10^{-15}\ [\mathrm{m}^3] \\
\mathrm{m} &= \mathrm{V} \times \rho = 3.6 \cdot 10^{-15} \times 800 = 2.9 \cdot 10^{-12}\ [\mathrm{kg}] \\
4\ \%\ \text{of}\ 2.9 \cdot 10^{-12} &= 1.1 \cdot 10^{-13}\ [\mathrm{kg}] \\
\frac{1.1 \cdot 10^{-13}}{600} &= 1.9 \cdot 10^{-16}\ [\mathrm{m}^3] \\
\text{droplet size} &= \sqrt[3]{\frac{1.9 \cdot 10^{-16}}{\frac{1}{6} \times \pi}} = 6\ [\mu\mathrm{m}]
\end{aligned}$$

C.2 Polymer chain size

The average molecular weight of the poly(vinyl acetate) used is 140.000. Every monomer unit has a mass of 86.09. This means that every polymer molecule consists of 1626 units (on average).
With equation 2.9 it is calculated that:

$$\langle s^2 \rangle_f^{\frac{1}{2}} = \frac{\sqrt{1626} \times 153}{\sqrt{6}} = 2.5\ nm$$

This much smaller than the calculated and measured droplet size.

C.3 Spraying time

Sample nets are produced with a size of 12 x 15 cm, being 0.018 m^2. A minimum concentration of 20 $\mathrm{mg} \cdot \mathrm{m}^{-2}$ is required, see table 2.3.
The total minimum amount of insecticide needed on the samples is:
0.018 $\mathrm{m}^2 \times 20\ \mathrm{mg\ m}^{-2} = 0.36$ mg.

The concentration of insecticide in the stock solution is 10 $\mathrm{mg} \cdot \mathrm{ml}^{-1}$.

The total amount of liquid needed is thus: $\frac{0.36\ \mathrm{mg}}{10\ \mathrm{mg\ ml}^{-1}} = 0.036$ ml.

The liquid flow rate is 2 ml hr^{-1}, so the spraying time is: $\frac{0.036\ \mathrm{ml}}{2\ \mathrm{ml\ hr}^{-1}} = 1.3$ min.

The spraying is not 100% effective, so the efficiency should also be taking into account. This efficiency is very hard to measure, so a estimation is made. A major part of the total number of droplets is sprayed through the net. A efficiency of 10% is therefore used. This means that one needs to spray 10 times longer than calculated. This means that spraying the samples over a time of 13 minutes should yield the desired insecticide concentration.

The general equation for calculating the spraying time is:

$$t = \frac{A \cdot C_{net}}{C_i \cdot Q \cdot \varepsilon} \tag{C.1}$$

Appendix D

Properties of insecticides

Table D.1: Chemical and physical properties of deltamethrin and permethrin

property	deltamethrin	permetrhin
Molecular formula	$C_{22}H_{19}Br_2NO_3$	$C_{21}H_{20}Cl_2O_3$
CAS registry number	52918-63-5	52645-53-1
Physical state	crystalline powder	viscous liquid
Color	colorless	yellow brown
Odor	odorless	
Relative density	0.5	1.214
Relative molecular mass	505.25	391.31
Melting point	$98-101\,^\circ\mathrm{C}$	$34-39\,^\circ\mathrm{C}$
Boiling point	decomposes $> 300\,^\circ\mathrm{C}$	$220\,^\circ\mathrm{C}$ (0.05 mmHg)
Water solubility ($20\,^\circ\mathrm{C}$)	<0.002 mg l^{-1}	0.2 mg l^{-1}
Vapor pressure ($25\,^\circ\mathrm{C}$)	2.0 μPa	1.3 μPa

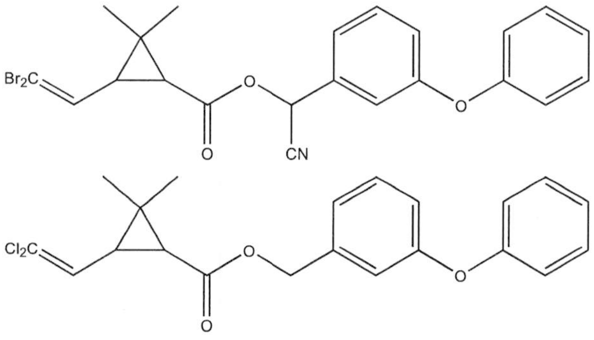

Figure D.1: Chemical structure of deltamethrin (top) and permethrin (bottom)

Table D.2: Solubility in different solvents. Taken from [22].

solvent	deltamethrin*	permethrin*
acetone	500 g l^{-1}	450 g l^{-1}
ethanol	15 g l^{-1}	>450 g l^{-1}
cyclohexanone	750 g l^{-1}	>450 g l^{-1}
dioxane	900 g l^{-1}	
xylene	250 g l^{-1}	$>$ 1 kg kg^{-1}
hexane		$>$ 1 kg kg^{-1}
methanol		258 g kg^{-1}
chloroform		>450 g l^{-1}

* Not all values are in the same units!

Acknowledgement

After nearly eight years it is almost over. No more frustrations about my setup that worked one day, but did not work the other day under the same circumstances. After a slow start and a very busy end, the moment of leaving Delft is almost there! But leaving without saying 'goodbye' and 'thank you' is rude. Even for a Delft student, from whom it is said that rudeness is a trademark for them. Therefore in random order:

First I like to thank Jan Marijnissen whose course "Particle Technology II" introduced me into the world of electrospray. His never ending enthusiasm got me enthusiastic for the "mosquito net" project. Also many thanks for giving me the opportunity to go to the aerosol conference in Madrid. It was a very nice experience for me.

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The person with whom I spent most of the time during this project is Jan van Erven. From the moment you moved to Ypenburg you started exercising again by biking every day to Delft with me. I hope you will be able to continue on your own, although it probably will be somewhat later. Success with your Ph.D. in Delft, and hopefully your laserlab project will be finished soon, so you can start concentrating on gathering data.

Ajay you and me shared our office for almost a year. It really became our home after the redecoration I should have done much earlier. Funny how the size of the room doubled only by rearranging the desks and even put an extra table in. Good luck with finishing your TWaio course, and with your Ph.D. you will start in September.

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The lunch group expanded from five people to an astonishing amount of ten people who joined lunch on an almost daily basis. Jan, Bas, Sjaak, Mike, Ineke, Ajay, Christian, Nikhil and Maria thank you very much for all the lunches we had together. But don't forget: no boats!

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