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Applying Polypyrrole on Plastics for the Electrodeposition of Copper


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Roger van den Schoor
oktober 2000
Applying Polypyrrole on Plastics for the Electrodeposition of Copper
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Applying Polypyrrole on Plastics for the Electrodeposition of Copper

Proefschrift

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Contents

1 General Introduction 1

Part A The in-situ Polymerisation of Pyrrole on a Non-Conducting Substrate

2 Introduction 7

3 Applying a Smooth Polypyrrole Layer 17

4 Effect of the Processing Time and the Temperature of the Oxidant Solution on the Properties of the Polypyrrole Layer 35

5 Influence of the Fe(ClO₄)₃ and HClO₄ Concentrations in the Oxidant Solution on the Properties of the Polypyrrole Layer 43

Part B The Electrochemical Deposition of Copper on a Polypyrrole Layer

6 Introduction 67

7 Increasing the Front Velocity 71

8 Influence of Thiourea on the Growth of Copper Crystals: an Electrochemical Atomic Force Microscopy Study 89

9 The Non-Uniformity and Other Properties of the Copper Layer 103

Summary and Conclusions 115

Samenvatting 119

Curriculum Vitae 123

Dankwoord 125
Chapter 1

General Introduction
1.1 Applications of metallized plastics

By the metallization of plastics the different properties of the metals and the plastics are combined. Polymers are generally used because of the low weight, the electrically insulating properties, and the ease of processing. The latter gives designers a larger freedom in shaping products. Metals are used because of the appearance and the good thermal and electrical conductivity. These properties of the metals divide the field of applications in a decorative group and a functional group.

In the decorative group, products are made in all kinds of shapes, which are light, and have a metallic appearance. These products are widely used. Examples are for instance a showerhead in the sanitary industry and the small logo on the bonnet in the automotive industry [1].

In the functional group the electrical properties of the metallic layer are important. For safety reasons some precious electronic parts in aeroplanes and cars have to be protected against electromagnetic interference. This can be achieved by metallizing the interior of e.g. a computer housing with copper or nickel [2,3].

Another important application is in the printed circuit boards (PCB’s). In PCB’s a smooth copper layer is applied on a plastic substrate, usually an epoxy resin. Required patterns are obtained by shielding with a coating on the copper layer during further metallization. After etching the patterns are realised.

1.2 Applying a metallic layer on a plastic substrate

There are several techniques to apply a metal on a non-conducting substrate. In general, prior to the metallization process the plastic is cleaned and optionally oxidatively pre-treated. Subsequently the metal can be applied directly or in several steps on the substrate, see figure 1.1. The direct methods, line 1 in figure 1.1, can be divided in four groups, viz. conducting paints, metal foils, thermal spraying, and vacuum techniques.

The conducting paints contain a binder with a conducting filler, like carbon black, nickel, and copper, and are usually applied with a spray gun. For good adhesion the paint must be adjusted to the plastic.

A self-adhering metal foil, e.g. aluminium, can be applied. However, this method is labour-intensive and thus can not be used for large series. Metal foils can also be laminated on a polymer, for instance copper foils in PCB’s. Because of the high temperature this technique is restricted to a limited number of polymers.

During thermal spraying a metal wire is molten with either a flame or an electrical arc discharge, and subsequently sprayed on the substrate with compressed air. Because of the temperature this technique is also restricted to a limited number of plastics.

There are two vacuum techniques, viz. chemical vapour deposition (CVD) and physical vapour deposition (PVD). During CVD a metallic precursor is brought in the vapour phase [4]. By increasing the temperature of the substrate the precursor decomposes
and a metallic layer is deposited on the sample. This decomposition process can be accelerated by the use of a laser. With PVD two different techniques are used to make metal particles, viz. evaporation and sputtering. During evaporation a metal is brought in the vapour phase by heating. The vapour condensates on the colder substrate and a metallic layer is formed. During sputtering metal particles are formed by sputtering of e.g. argon on the metal and subsequently these particles deposit on the substrate. An important drawback of these methods is the use of the expensive vacuum techniques. Moreover the adhesion between the metal and the substrate is depending on the substrate and metal used. Furthermore, for CVD a high temperature stable substrate is needed restricting the substrates which can be used.

A three-step method, line 2 in figure 1.1, is based on seeding layers [5]. In this process first a seeding layer of palladium is deposited on the substrate. Subsequently a metallic layer, e.g. nickel, is electroless deposited on the sample. Finally, a metallic layer can be applied on the nickel layer with a galvanic deposition process. The drawbacks of this process are the use of environmental-unfriendly chemicals such as formaldehyde and the use of expensive precious metal catalysts.

The last method discussed here is relative new one based on the use of intrinsically conducting polymers (ICP’s) as a primer for electrochemical deposition [6], line 3 in figure 1.1. A conductive layer containing an ICP is applied on the substrate. The conductive layer is applied either by using a paint, which contains the ICP, or by in-situ polymerisation of the monomer on the substrate. Subsequently a metallic layer can be electrochemically deposited onto this layer.

An advantage of this last method above the other methods is that it can be applied on almost all substrates. Moreover, when a high electrically conducting layer can be applied this method can also be used for patterned deposition. After the patterned deposition the ICP can

---

![Diagram](image_url)

**Figure 1.1** Different methods for applying a metal on a plastic substrate.
be made non-conducting and hence this method can also be used for the fabrication of PCB’s. This method is the subject of this thesis.

1.3 Outline of this thesis

This thesis is divided into two parts.

In part A the process used for the in-situ polymerisation of pyrrole on an epoxy substrate and the influence of the different process steps on the properties of the formed polypyrrole layer are discussed. Chapter 3 presents the effect of the pre-treatments, the oxidative cerium treatment and the corona treatment, and the composition of the monomer solution on the roughness, adhesion, and sheet resistance of the polypyrrole layer. More insight is obtained in the factors, which are important for applying a smooth, well-adhering polypyrrole layer. The process parameters of the (oxidising) polymerisation solution are important for the electrical properties of the polypyrrole layer. Chapter 4 focuses on two important process parameters, the time the substrate spent in the oxidant solution, and the temperature of this solution during oxidation. In chapter 5 the influence of the Fe(ClO₄)₃ and HClO₄ concentrations in this solution on the sheet resistance of the polypyrrole layer and on the rate of the polymerisation reaction are discussed. More knowledge about the influence of HClO₄ on the polymerisation reaction is provided. Furthermore, the electrochemical characterisation of the polypyrrole layer is presented in this chapter.

In part B the electrochemical deposition of copper on a polypyrrole layer on polyether-imide is discussed. The copper deposition starts at the ohmic contact and propagates laterally during deposition. In chapter 7 the investigations on the effect of the deposition potential and different organic additives in the copper solution on the lateral deposition velocity (or front velocity) of copper are described. The results give more insight in the lateral deposition of copper. Chapter 8 presents an in-situ electrochemical atomic force microscopy (EC-AFM) study on the growth of copper crystals on polypyrrole and the effect of thiourea on this growth. The deposition potential and additives also influence the non-uniformity, toughness, roughness, and appearance of the copper layer, which is described in chapter 9.

References

The *in-situ* Polymerisation of Pyrrole on a Non-Conducting Substrate
Chapter 2

Introduction
2.1 Intrinsically conducting polymers

In 1961 Hatano and co-workers [1] found that the conjugated polymer polyacetylene has a low conductivity. These polymers attracted more attention when the groups of Shirakawa, MacDiarmid and Heeger [2] obtained much higher conductivities by exposing polyacetylene films to strongly oxidising and reducing agents. During this process free charge carriers are formed on the polymer, this is called doping in analogy with conventional inorganic semiconductors like silicon. To compensate the charges on the polymer counterions (anions or cations) are incorporated. These counterions are often denoted as dopants. Because the electrical conductivity occurs through the polymer and not through a conducting filler in the polymer these polymers are called intrinsically conducting polymers (ICP’s).

The major drawback of polyacetylene is the decrease of the conductivity on exposure to air. Hence for commercial applications more environmentally stable ICP’s have been developed. The most important ones are polypyrrole (PPy) [3], polyaniline (PANI) [4], poly(1,3-ethylene dioxythiophene) (PEDT) [5], and polyphenylene vinylene [6], see figure 2.1.

![Figure 2.1 Intrinsically conducting polymers: a) polyacetylene, b) polypyrrole (PPy), c) polyaniline (PANI), d) poly(1,3-ethylene dioxythiophene) (PEDT), and e) polyphenylene vinylene.](image)

There are already some commercial applications of ICP’s. In capacitors ICP’s function as conducting electrode [7-9]. Another application is an ICP as emitting polymer in light-emitting diodes [10,11]. In the photographic industry transparent anti-static coatings based on PEDT are used [12,13]. For the through-hole plating in PCB’s in the beginning PPy was applied, nowadays PEDT is used [13,14].

2.2 Conductivity in intrinsically conducting polymers

Intrinsically conducting polymers (ICP’s) become conductive during the doping process because free charge carriers are formed on the polymer chain. To understand the formation of charge carriers in conjugated polymers the structure of the ICP’s has to be discussed. The general structure of a conjugated polymer consists of an alternating sequence
of single and double bonds. Except polyacetylene all ICP's consist of aromatic rings and hence here only ICP's with aromatic rings will be considered. The ground state of such a polymer, e.g. polypyrrole, consists of long bonds between the rings and an aromatic structure within the ring. This polymer can also be presented in a so-called quinoid structure characterised by shortened bonds between the rings and quinoid rings, see figure 2.2. The quinoid geometry can be considered as an excited state configuration of the aromatic structure, which is higher in energy.

![Aromatic and quinoid structure](image)

**Figure 2.2** Two senses of bond alternation for polypyrrole: aromatic and quinoid structure.

Charge carriers in conjugated polymers can be generated by oxidative or reductive doping in which electrons are transferred away from or to the polymer chains, respectively. Because polypyrrole is doped by an oxidation reaction we will here consider the oxidative doping. Reductive doping, which is rarely used, can be described in a similar way.

Oxidation of the ground state of polypyrrole leads to a radical cation on the polymer. The positive charge and the unpaired electron can not move independently because of higher energy of the quinoid structure between the positive charge and the unpaired electron, see figure 2.3. This self-localised structural deformation is mobile along the chain and is called a polaron in condensed-matter physics.

Upon further oxidation of polypyrrole two things can happen, either a second electron is removed from a different chain creating a new polaron, or the unpaired electron of the previously formed polaron is removed. The latter results in a dication confined to a single lattice deformation on the chain, which is called bipolaron. Bipolarons can also be formed from two polarons in which their unpaired electrons form a bond on a doubly oxidised polymer chain.
These polarons and bipolarons are considered to be responsible for the conduction on a polymer chain. To explain the conductive behaviour of bulk materials beside these intrachain mechanisms interchain mechanisms such as hopping must occur. Although a range of charge transport mechanisms have been suggested to describe the charge migration process in conducting polymers, the mechanism is not well understood yet. In all cases the conductivity ($\sigma$) can be written as

$$\sigma = en\mu$$  \hspace{1cm} (2.1)

where $e$ is the elementary charge, $n$ the density of the mobile charge carriers and $\mu$ the mobility of the charge carriers. The charge carriers can either be free electrons, holes or charged defects in the polymer structure. Because of the counterions the charge carriers in conducting polymers are more or less bonded to their position on the polymer chain. This of course will have a large influence on the mobility of the charge carriers. Even if free motion
along a chain occurs, the microheterogeneous nature of most polymers and chain-to-chain transfer of the charges will have a large influence on the bulk conductivity. By doping the number of mobile charge carriers is enlarged. The number of charge carriers or doping level can be estimated by measuring the number of counterions in the polymer. In ICP’s the highest conductivities are found at doping levels of several tens of percents.

2.3 Measuring the sheet resistance

The electrical property of a material is usually given by either the resistivity or the conductivity. The resistivity is given in Ω m, however for ICP’s usually Ω cm is used. The conductivity for ICP’s is normally given in Ω⁻¹ cm⁻¹ or Siemens per centimetre (S/cm).

The measured resistance depends on the geometry of the sample and is not a material property. The relation between the measured resistance \( R \) and the resistivity \( \rho \) of a material is given by

\[
R = \rho \frac{l}{bd} \tag{2.2}
\]

where \( l \) is the length, \( b \) is the width, and \( d \) is the thickness of the sample, see figure 2.4.

For some applications, like anti-static films and galvanic deposition, not the electrical properties of the applied material are of importance, but the electrical properties of the applied layers along the surface are essential. A thick layer with a low conductivity can be just as effective as a thin layer with a high conductivity. A measure for the electrical resistance of a layer is the sheet resistance. The unit of the sheet resistance is Ohm (Ω), but for clarity usually Ohm per square (Ω/□) is used. The sheet resistance \( (R_\text{s}) \) of a layer is the resistance measured when the width \( (b) \) of the electrodes is equal to the length \( (l) \) of the

![Figure 2.4](image)

**Figure 2.4** Schematic representation of a four-point resistance measurement with parallel electrodes.
sample. So

\[ R_a = \frac{P}{d} = R \frac{b}{l} \quad (2.3) \]

The sheet resistance is independent of the lateral dimensions of the sample but is depending on the thickness of the layer.

The sheet resistance of a layer with a high resistivity can not be determined accurately with a two-point method. The sheet resistance can then be determined with a four-point resistance measurement with parallel electrodes, see figure 2.4. The current is applied on the outer electrodes. Subsequently the voltage can be measured on the inner electrodes with a small current and hence with negligible contact resistance. The sheet resistance of the conducting layer can be calculated with equation 2.3 provided that i) the thickness \(d\) of the conducting layer is much smaller than the length \(l\) between the electrodes, ii) the sample underneath the conducting layer is non-conductive, and iii) the width \(b\) of the conducting layer is equal to or smaller than the width of the electrodes.

### 2.4 Applying an intrinsically conducting polymer on a non-conducting substrate

Before intrinsically conducting polymers (ICP’s) are applied on non-conducting substrates the substrate is often pre-treated to improve the adhesion between the conductive polymers and the substrate. Besides the more or less common pre-treatments like corona and plasma activation, and different chemical etching techniques, other methods were used. To improve the adhesion on glass a silane, which contains a pyrrole unit, was applied before applying the ICP. Polymers, like polyethylene and polystyrene, were sulphonated before the polymerisation of pyrrole \([15,16]\). Finally, the copolymer tetrafluoroethylene-hexafluoropropylene was grafted with acrylic acid or styrene by \(\gamma\)-irradiation prior to the polymerisation of pyrrole \([17,18]\).

ICP’s have been applied on various non-conducting substrates in numerous ways. Rubner and co-workers \([19-23]\) applied diverse ICP’s by dipping substrates successively in a diluted aqueous solution containing the desired conducting polymer and in a diluted aqueous solution containing a polyanion, e.g. sulphonated polystyrene. Romelow et al. \([24]\) applied polypyrrole films by casting from a chloroform solution containing the polymer. Jonas et al. \([12,13]\) developed an anti-static coating which contains the conducting polymer PEDT.

Applying an ICP by \textit{in-situ} polymerisation has been investigated intensively. During \textit{in-situ} polymerisation a monomer, e.g. pyrrole, is polymerised with an oxidant, like \(\text{Fe}^{3+}\) and \(\text{S}_2\text{O}_8^{2-}\), in the presence of the substrate, resulting in the deposition of a thin conducting polymer layer on the substrate. The substrate, monomer, and oxidant are brought together either in one step, see e.g. \([8,25-30]\), or by first applying the monomer on the substrate and subsequently the oxidant, see e.g. \([14,31-33]\), or vice versa, see e.g. \([14,34,35]\).

Porous materials, like textiles, paper, and membranes, can either be saturated with a solution containing the oxidant and subsequently exposed to the monomer \([35,36]\) or vice
versa [30,33]. On some substrates a porous polymer layer is applied, which can absorb either the oxidant [34] or the monomer [31].

The ICP's polypyrrole, polyaniline, and PEDT have been used for the electrochemical deposition of copper. The copper deposition on PANI was not successful in high acidic copper solutions because the equilibrium potential of PANI increases with increasing acid concentration [37]. PEDT is already used in a commercial process for through-hole plating of printed circuit boards [13]. However, this polymer is very expensive and hence not commercially interesting for the use on large areas. Therefore for this project polypyrrole is chosen as ICP for the electrochemical deposition of copper.

The polypyrrole layer can be applied by dipping the substrate first in a solution containing the oxidant and subsequently immersing the substrate in a solution containing the monomer pyrrole. A disadvantage of this method is that after dipping in the monomer solution this solution gets polluted and cannot be used a second time. Therefore we dipped the substrate first in a solution containing the monomer pyrrole and subsequently immersed the substrate in a solution containing the oxidant.

A common used substrate in PCB's is a glass fibre-reinforced epoxy resin. Hence, we used these substrates for the application of polypyrrole layers.

For the polymerisation of pyrrole on the epoxy resin the following method was chosen for further optimisation. The substrate was cleaned with acetone. After drying, the substrate (75 x 10 x 1 mm$^3$) was pre-treated by immersion in a solution containing 10 g of Ce(SO$_4$)$_2$*4H$_2$O (0.12 M), 2.7 ml of H$_2$SO$_4$ (0.25 M) and 200 ml demiwater for 5 minutes. Subsequently, the substrate was dipped in the monomer bath containing a solution of pyrrole in 2-propanol (20 % v/v), to apply a layer of pyrrole. Finally the substrate was immersed in an oxidant solution containing 20.65 g of Fe(ClO$_4$)$_3$*9H$_2$O (0.20 M), 12.2 ml of 60% HClO$_4$ (0.56 M) and 200 ml demiwater at 0°C for 5 minutes. After polymerisation the substrate was rinsed with demiwater and dried at room temperature.

2.5 Special demands for the conducting layer

The deposition of metals starts at the ohmic contact and propagates laterally during deposition because of the relative high resistance of the conducting layer. The metallization process and hence the velocity of the lateral deposition must be as fast as possible for a commercial application. De Leeuw et al. [38] demonstrated that this lateral deposition velocity is inverse proportional to the square root of the sheet resistance. The velocity increases with decreasing sheet resistance. So for a fast metallization process the sheet resistance must be as low as possible.

For patterned layers, e.g. PCB, the contact between the diverse areas where the metal must be deposited is provided by the conducting layer. To avoid a large difference in the structure and properties of the metal layers deposited on the diverse areas a potential drop over the conducting layer of about 200 mV has shown to be acceptable at more negative deposition potentials. Moreover, for the deposition of a metal on a certain area at a certain
potential a minimal current is needed. The resistance between the areas is depending on the
gyometry between the areas and the sheet resistance of the conducting layer. For simplicity
we assume a square geometry of 1 by 1 cm and a sheet resistance of 1 Ω/□. Hence the
resistance between the layers is 1 Ω, see equation 2.3. This results in a maximal deposition
current of 200 mA without exceeding this potential drop. If the sheet resistance is 100 times
larger then the current decreases a factor 100, and only a very small area can be deposited
with copper without exceeding the potential drop, which is acceptable. From these
calculations we concluded that the sheet resistance of the conducting layer must at least lie
under 10 Ω/□ for patterned deposition.

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Chapter 3

Applying a Smooth Polypyrrole Layer

Abstract

For the metallization process, a smooth adhering polypyrrole layer is required. The polypyrrole layer was applied by first dipping the substrate in a bath containing the monomer pyrrole and subsequently immersing the substrate in an aqueous solution containing an oxidant. In this chapter the influence of the cerium and the corona treatment of the epoxy resin and the influence of the pyrrole concentration in the monomer bath on the properties of the polypyrrole layer are described.

In an aqueous solution pure pyrrole spreads on the untreated epoxy substrate and forms droplets on the treated epoxy substrates as is demonstrated with calculations and measurements of the interfacial tensions. The measurements with a profilometer and an AFM showed that the epoxy substrates are roughened by corona treatment, while the cerium treatment has no such an effect.

The polymerisation of pyrrole occurs in the water phase and the formed polypyrrole partly deposits on the epoxy substrate. The Fe^{3+} in the polymerisation solution can react with the epoxy resin and form reactive groups. These groups can react with the polypyrrole and in this way the polypyrrole can be chemically bonded to the epoxy resin. The polypyrrole formed on the pyrrole can not be chemically attached to the epoxy substrate underneath.

On the untreated epoxy substrate pure pyrrole spreads resulting in a poor adhesion between the deposited polypyrrole and the substrate. Consequently after rinsing only a small amount of polypyrrole remained anywhere no pyrrole was present on the substrate, causing a higher overall sheet resistance. On the treated epoxy resin a grey polypyrrole layer with black spots remained after rinsing. The black spots are caused by the pyrrole droplets formed on the treated epoxy resin. No chemical bonding is formed between the polypyrrole deposited on the pyrrole droplet and the epoxy resin underneath, explaining the poor adhesion of the black spots.

The amount of pyrrole remaining on the substrate after dipping in the monomer bath increases with the pyrrole concentration in the monomer solution. At increasing pyrrole concentration the polymerisation rate increases and hence more polypyrrole is formed and deposited on the substrate in the same synthesis time, resulting in a lower sheet resistance of the polypyrrole layer. At pyrrole concentrations of 50 vol% and lower in the monomer bath the monomer solution dissolves in water and hence no droplets are formed on the epoxy substrate. This results in a smooth adhering polypyrrole layer on the epoxy substrate.

3.1 Introduction

To apply a smooth copper layer, a smooth adhering polypyrrole layer on the substrate is required. To achieve this the epoxy resin is normally treated with the oxidant cerium(IV) before the pyrrole is applied on the substrate [1]. However, the influence of this pre-treatment on the surface is not known, it is assumed that this pre-treatment etches, oxidises, activates, conditions and cleans the surface. Another method to oxidise the surface of a polymer is corona treatment. During corona treatment chemical structures like carbonyls,
carboxyls, hydroxyls, ozonides, peroxides and amides are formed on the surface [2,3]. In general, more oxygen than nitrogen containing structures are formed. These structures improve the surface properties, like wettability and adhesion.

The way the monomer is added can also change the properties of the polypyrrole layer. The monomer was added to the oxidant solution separately [4-8] or by applying it on the substrate prior to immersing in the oxidant solution [1,9-11]. For porous materials the substrate is often impregnated with a solution containing the monomer [9,10]. Yoshikawa et al. [11] coated poly(ethylene terephthalate) (PET) with poly(methyl methacrylate) (PMMA) and found that pyrrole dissolved in the PMMA after dipping in pure pyrrole. Hupe et al. [1] dipped their substrates in an aqueous solution containing pyrrole prior to immersing in the oxidant solution. They added a water-miscible organic solvent like methanol, ethanol, 2-propanol (IPA), and ketones to promote the solubility of pyrrole in this aqueous solution. Their monomer solutions contained 20 vol% pyrrole.

In this chapter the influence of the pre-treatment and the influence of the pyrrole concentration in the monomer bath on the properties of the polypyrrole layer are discussed.

### 3.2 Experimental

Non-conducting substrates were made out of FR4-Duraver-E-prepregs 7628 (a raw material for glass fibre-reinforced epoxy resins) obtained from Isola Benelux S.A. (B). The prepregs were cured at 180°C in 2 hours and subsequently cut into pieces of 1.0 x 7.5 cm². Pyrrole (Acros Organics) was distilled and stored cool and dark prior to use. Ce(SO₄)₂·4H₂O (Acros Organics), H₂SO₄ (Fluka Chemika), Fe(ClO₄)₃·9H₂O (Fluka Chemika), 60% HClO₄ (Fluka Chemika), and 2-propanol (Merck) were all used as received.

For the polymerisation of pyrrole on the epoxy resin, the substrate was first cleaned with acetone. After drying, the substrate (75 x 10 x 1 mm³) was pre-treated by immersion in a solution containing 10 g of Ce(SO₄)₂·4H₂O (0.12 M), 2.7 ml of H₂SO₄ (0.25 M) and 200 ml demiwater for 5 minutes. Subsequently, the substrate was dipped in the monomer bath containing either pure pyrrole or a solution of pyrrole in 2-propanol, to apply a layer of pyrrole. Finally the substrate was immersed in an oxidant solution containing 20.65 g of Fe(ClO₄)₃·9H₂O (0.20 M), 12.2 ml of 60% HClO₄ (0.56 M) and 200 ml demiwater at 0°C for 5 minutes. After polymerisation the substrate was rinsed with demiwater and dried at room temperature.

Besides a cerium treatment of the epoxy resin also a corona treatment was used. For corona treatment a high voltage (~20 kV) with a high frequency (~25 kHz) was applied between a grounded plate and an electrode in ambient air, see figure 3.1. By carefully turning, both sides of the substrate were corona treated with a solid-state Tantec Model HV 05-2 generator at about 90 W and about 25 kHz for 10 seconds. The air gap between the electrode and the grounded plate was 3.5 mm.

Sheet resistances reported here are the average values obtained by four-probe resistance measurements on at least three samples at room temperature.
A Krüss contact angle measurement system G10 was used to determine the contact angles and the interfacial tensions between two liquids by the pendant drop method at room temperature. The surface tensions of the liquids were measured with a Krüss K8600 Du Nouy tensiometer. To determine the interfacial tensions different methods [12-14] can be used. In practice, however, the differences between the two methods are small. We used the method from Owens, Wendt, Rabel and Kaelble [12,13].

Roughness measurements were performed at room temperature on an UBM microfocus profilometer with a point density of 500 points/mm and 100 points/mm in the x and y direction, respectively. The surfaces (5.6 x 0.8 mm²) were analysed using a cut off of 0.8 mm and DIN 4768.

Atomic Force Microscopy (AFM) measurements were conducted with a Digital Instruments Nanoscope III scanning force microscope at room temperature. All experiments were conducted in the contact mode with standard Si₃N₄ tips. After flattening of the surface the roughness parameters were determined. Beside the roughness parameters, Rₐ (arithmetic average) and Rₛ (root mean square value), also the ratio of the actual to the projected area, Rₛ, was determined. This surface area ratio is 1 for a flat surface and is (a few percent) larger for a rough surface.

3.3 Pyrrole droplet

3.3.1 Determination of the contact angles

Whether a solvent forms droplets or spreads over a substrate can be predicted with the spreading coefficient, S. For the spreading of pyrrole on a substrate in water, S is defined as

\[ S_{SP} = \gamma_{SW} - \gamma_{WP} - \gamma_{SP} \]  

(3.1)

where \( \gamma_{SW} \) is the interfacial tension between the substrate and aqueous solution, \( \gamma_{SP} \) is the interfacial tension between the substrate and pyrrole, and \( \gamma_{WP} \) is the interfacial tension between the water and pyrrole.
between the aqueous solution and pyrrole. If the spreading coefficient is positive the liquid will spread over the substrate, and if this value is negative the liquid will form a droplet on the substrate.

When droplets are formed on the substrate, the contact angle can be estimated with the Young equation. The Young equation for a pyrrole droplet on a substrate in an aqueous solution is given by

\[ \gamma_{SW} = \gamma_{SP} + \gamma_{WP} \cos \Theta \]  

(3.2)

where \( \Theta \) is the contact angle, see also figure 3.2.

In our case the aqueous solution contains 0.20 M Fe(ClO\textsubscript{4})\textsubscript{3} and 1.0 M HClO\textsubscript{4}. However, Fe\textsuperscript{3+} and pyrrole react with each other and hence it is not possible to determine the contact angle of pyrrole in the Fe\textsuperscript{3+} solution directly. Instead the diverse contact angles and tensions were determined for water.

For the calculation of the spreading coefficients and the contact angles the surface tensions and the interfacial tensions have to be determined. When the contact angle is too small the interfacial tension can not be determined with Young’s equation. Then according to Owens, Wendt, Rabel and Kaelble [12,13] the interfacial tensions, \( \gamma_{12} \), between two materials can be determined with

\[ \gamma_{12} = \gamma_1 + \gamma_2 - 2 \left( \left( \gamma_1 \gamma_2 \right)^{1/2} + \left( \gamma_1 \gamma_2 \right)^{1/2} \right) \]  

(3.3)

where \( \gamma_1 \) and \( \gamma_2 \) are the polar and disperse part of the surface tension, \( \gamma \)

\[ \gamma = \gamma^d + \gamma^p \]  

(3.4)

The surface tension, including both the disperse and the polar part, of the liquids and substrates are required input parameters to calculate the interfacial tension. For a solid substrate the surface tension can be determined with the Owens, Wendt, Rabel, and

\[ \gamma_{SW} \]

\[ \gamma_{SP} \]

\[ \gamma_{WP} \]

\[ \Theta \]

Figure 3.2  Schematic representation of the formation of a pyrrole droplet on a substrate in water.
Kaelble method [12,13]. The disperse and polar parts of the surface tension of a liquid can be determined by measuring the contact angle of the liquid on a non-polar solid, like Teflon. After combining Young’s equation with equation 3.3 and taking into account that for any apolar surface, \( \gamma^p = 0 \), we can write for the disperse part of the liquid, \( \gamma^d \),

\[
\gamma^d_i = \frac{\gamma_i^2}{4\gamma} \left(1 + \cos \Theta \right)^2
\]  

(3.5)

The disperse and polar part of the surface tension of any specific liquid can be obtained by measuring the overall surface tension of the specific liquid, determining the surface energy of Teflon, and measuring the contact angle between this liquid and the Teflon surface.

The surface tension thus obtained for the diverse liquids and substrates are given in table 3.1. The surface tensions found for Teflon and IPA are in good agreement with what was found by others, [15] and [16] respectively. For both pre-treatments the polar part of the surface tension was increased. After corona treatment the disperse part of the surface tension was also increased.

The interfacial tension between water and pyrrole was determined with the pendant drop method, see table 3.2. The interfacial tension between the \( \text{Fe}^{3+} \) solution and pyrrole was determined with equation 3.3 because \( \text{Fe}^{3+} \) and pyrrole react with each other. Because of the low contact angles the interfacial tensions between the corona treated epoxy resin and pyrrole, and between the diverse epoxy substrates and IPA were also determined with equation 3.3. This equation was also used to determine the interfacial tensions between the solids. The remaining interfacial tensions could be determined with the Young equation.

The values in table 3.1 and 3.2 were used for the calculations of the spreading coefficients and contact angles of pyrrole on the epoxy substrate in pure water or in the \( \text{Fe}^{3+} \) solution. The values are listed in table 3.3.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \gamma ) (mN/m)</th>
<th>( \gamma^d ) (mN/m)</th>
<th>( \gamma^p ) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>solids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teflon</td>
<td>18.2</td>
<td>18.2</td>
<td>0</td>
</tr>
<tr>
<td>epoxy</td>
<td>37.6</td>
<td>37.0</td>
<td>0.6</td>
</tr>
<tr>
<td>epoxy cerium</td>
<td>47.8</td>
<td>35.1</td>
<td>12.7</td>
</tr>
<tr>
<td>epoxy corona</td>
<td>69.2</td>
<td>46.2</td>
<td>23.0</td>
</tr>
<tr>
<td>polypyrrole</td>
<td>58.7</td>
<td>47.5</td>
<td>11.2</td>
</tr>
<tr>
<td><strong>liquids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>72.8</td>
<td>26.0 [17]</td>
<td>46.8 [17]</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} ) solution</td>
<td>66.7</td>
<td>25.7</td>
<td>41.0</td>
</tr>
<tr>
<td>pyrrole</td>
<td>30.9</td>
<td>22.1</td>
<td>8.8</td>
</tr>
<tr>
<td>IPA</td>
<td>21.8</td>
<td>21.8</td>
<td>0</td>
</tr>
</tbody>
</table>
### Table 3.2  Calculated interfacial tensions and measured contact angles between diverse materials.

<table>
<thead>
<tr>
<th></th>
<th>( \gamma ) (mN/m)</th>
<th>( \theta ) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>solid/liquid</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>epoxy/Fe(^{3+}) solution</td>
<td>32.5</td>
<td>86</td>
</tr>
<tr>
<td>epoxy cerium/Fe(^{3+}) solution</td>
<td>14.5</td>
<td>60</td>
</tr>
<tr>
<td>epoxy corona/Fe(^{3+}) solution</td>
<td>17.4</td>
<td>39</td>
</tr>
<tr>
<td>epoxy/water</td>
<td>32.1</td>
<td>86</td>
</tr>
<tr>
<td>epoxy cerium/water</td>
<td>22.9</td>
<td>70</td>
</tr>
<tr>
<td>epoxy corona/water</td>
<td>12.5</td>
<td>39</td>
</tr>
<tr>
<td>epoxy/pyrrole</td>
<td>12.0</td>
<td>34</td>
</tr>
<tr>
<td>epoxy cerium/pyrrole</td>
<td>19.7</td>
<td>25</td>
</tr>
<tr>
<td>epoxy corona/pyrrole</td>
<td>7.7(^a)</td>
<td>– (^b)</td>
</tr>
<tr>
<td>epoxy/IPA</td>
<td>2.6(^a)</td>
<td>– (^b)</td>
</tr>
<tr>
<td>epoxy cerium/IPA</td>
<td>14.3(^a)</td>
<td>– (^b)</td>
</tr>
<tr>
<td>epoxy corona/IPA</td>
<td>27.5(^a)</td>
<td>–</td>
</tr>
<tr>
<td><strong>liquid/liquid</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{3+}) solution/pyrrole</td>
<td>11.9(^a)</td>
<td></td>
</tr>
<tr>
<td>water/pyrrole</td>
<td>6.2(^c)</td>
<td></td>
</tr>
<tr>
<td><strong>solid/solid</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>epoxy/polyaniline</td>
<td>7.3(^a)</td>
<td></td>
</tr>
<tr>
<td>epoxy cerium/polyaniline</td>
<td>1.0(^a)</td>
<td></td>
</tr>
<tr>
<td>epoxy corona/polyaniline</td>
<td>2.1(^a)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Determined with Owens, Wendt, Rabel and Kaelble, equation 3.3.

\(^b\) Very small angle could not be determined.

\(^c\) Determined with pendant drop method.

### Table 3.3  Calculated spreading coefficients, \( S \), and calculated contact angles, \( \Theta \), of pyrrole on the epoxy resin in the Fe\(^{3+}\) solution or in pure water and measured contact angles of pyrrole on the epoxy substrate in pure water, \( \Theta_{\text{wm}} \).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( S ) (mN/m)</th>
<th>( \Theta_{Te} ) (°)</th>
<th>( S ) (mN/m)</th>
<th>( \Theta_{W} ) (°)</th>
<th>( \Theta_{\text{wm}} ) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>epoxy</td>
<td>9</td>
<td>–</td>
<td>14</td>
<td>–</td>
<td>40</td>
</tr>
<tr>
<td>epoxy cerium</td>
<td>-17</td>
<td>115</td>
<td>-3</td>
<td>60</td>
<td>115</td>
</tr>
<tr>
<td>epoxy corona</td>
<td>-2</td>
<td>35</td>
<td>-1</td>
<td>40</td>
<td>75</td>
</tr>
</tbody>
</table>
3.3.2 Validation

To validate the calculations the contact angles of pyrrole on the substrate in water were measured, see table 3.3. Moreover, for the reversed situation where a water droplet is formed on the substrate in pyrrole, the spreading coefficients and contact angles were also calculated and measured, see table 3.4.

The measured contact angles were in all cases larger than the calculated ones, see table 3.3 and 3.4. The difference in the calculated and the measured contact angle is caused by the buoyancy force, which pyrrole experiences in water and vice versa. This force pushes the droplet upward and therefore the contact angle could not be determined correctly.

Only for pyrrole on the untreated epoxy substrate in water it was calculated that the pyrrole would spread over the surface, in all other cases a droplet would be formed, see table 3.3 and 3.4. Only for the former it was found that during the measurements when the pyrrole droplet was put on the surface the pyrrole was attracted by the surface and immediately spread over the untreated surface. In all other cases it was more difficult to get the droplet from the syringe to the substrate.

Although for a water droplet on the untreated epoxy substrate in pyrrole the spreading coefficient is negative, the contact angle could not be calculated. This indicates that a water droplet can not adhere to the untreated substrate in pyrrole. During the measurements it was found that a water droplet drifted from the untreated surface and hence no contact angle could be determined.

These examples show that the calculated spreading coefficients and contact angles can be used qualitatively for the study of droplet behaviour on a substrate.

<table>
<thead>
<tr>
<th>substrate</th>
<th>$S_{Py}$ (mN/m)</th>
<th>$\Theta_{Py}$ ($^\circ$)</th>
<th>$\Theta_{Py_m}$ ($^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>epoxy</td>
<td>-26</td>
<td>-*</td>
<td>-*</td>
</tr>
<tr>
<td>epoxy cerium</td>
<td>-9</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>epoxy corona</td>
<td>-11</td>
<td>140</td>
<td>160</td>
</tr>
</tbody>
</table>

* Could not be calculated.
# Could not be measured.

3.3.3 Surface roughness

After the cerium and the corona treatment the surface tension of the epoxy substrate was increased, see table 3.1. When a solid surface is rough [18], Young's equation can be rewritten as
Figure 3.3  *AFM images of an epoxy resin before (left) and after (right) cerium treatment.*

Figure 3.4  *AFM images of an epoxy resin before (left) and after (right) corona treatment.*

An increase in the surface roughness is not reflected in the $R_a$ or $R_q$ values because the used scale is not representative for the total surface. The small differences in $R_a$ and $R_q$ before and after treatment are probably due to the fact that the images were not taken at exactly the same position. The increase in the roughness on this scale can be seen in the surface area ratio, $R_a$. After corona treatment this ratio increased with 1%, which is due to the increase of the surface roughness. This increase in roughness is not seen with the profilometer because the sampling distance is larger, about 2 µm. For cerium treated epoxy substrate there is also no significant difference in the roughness parameters on this scale, indicating that the cerium treatment has no influence on the surface roughness of an epoxy resin.

The large increase in the surface tension after pre-treatment can not be explained by the surface roughness. Therefore the increase of the surface tension of the corona and the cerium treated epoxy resin must be caused by the incorporation of oxygen and or nitrogen atoms in the surface.
3.3.4 Conclusions

The addition of Fe(ClO₄)₂ and HClO₄ to water does not have a large influence on the disperse and polar part of the surface tension, see table 3.1. Hence, the interfacial tensions between the diverse materials and pure water or the Fe³⁺ solution do not differ much, as can be seen in table 3.2. Consequently, the calculated contact angles and spreading coefficients of pyrrole on the substrate in pure water or in the Fe³⁺ solution are comparable, see table 3.3. Therefore pure water can be used as model for the Fe³⁺ solution.

It was found that the total substrate was covered with pyrrole after dipping in the monomer bath independent of the pre-treatment and the composition of the monomer bath. This is in agreement with the low contact angles between pyrrole and the diverse epoxy substrates and between IPA and the diverse epoxy substrates, see table 3.2.

Calculations and measurements of the interfacial tensions showed that pyrrole spreads on the untreated epoxy substrates in the oxidant bath, see table 3.3. After the cerium and the corona treatment of the epoxy substrate the surface tensions increases, causing the formation of pyrrole droplets on epoxy substrates in the oxidant bath.

3.4 Solubility of the monomer solution

Whether a pyrrole droplet is formed on a substrate also depends on the solubility of the monomer solution in water. Hence, the phase diagram of our system must be considered. Our system contained the following liquid phases: the solvent IPA, the non-solvent water, and the monomer pyrrole. Furthermore, there is the oxidant, Fe³⁺, in the water phase.

When the substrate is dipped into the polymerisation solution two processes occur simultaneously. The three liquid phases are mixed, and pyrrole is polymerised by the Fe³⁺. The polymerisation reaction starts slowly [19], and therefore the polymerisation reaction and formed products do hardly interfere with the mixing of the phases.

At a constant temperature, in our case 0°C, the system is homogeneous for a certain range of compositions. Phase separation occurs in the hatched region in figure 3.5. In our

![Figure 3.5](image)

**Figure 3.5** Schematic representation of the phase diagram between pyrrole, water and 2-propanol (IPA). The hatched area is the composition of the solution where the solutions do not mix.
system IPA mixes well with both pyrrole and water. However, the solubility of pyrrole in water is poor [16]. Therefore the liquids do not mix well when the pyrrole or water concentration is too high. In our system only the pyrrole concentration in the monomer bath can be changed. At a pyrrole concentration of e.g. 20 vol%, the composition of the system lies on the lower dotted line in figure 3.5, and hence the pyrrole solution dissolves in water. At a pyrrole concentration in the monomer bath of e.g. 80 vol% the composition comes in the hatched area and thus droplets are formed on the epoxy resin, see phase diagram.

### 3.5 Polymerisation and adhesion

To predict whether or not a layer will adhere to a substrate, the work of adhesion $W$ is used

$$W_{SPy} = \gamma_S + \gamma_{PP} - \gamma_{SPP},$$  \hspace{1cm} (3.7)

The work of adhesion is a measure for the physical adhesion between two materials. If this value is negative the layer will probably release, and if this value is positive the layer will adhere to the substrate.

The work of adhesion of polypyrrole on the pre-treated and untreated epoxy substrates were calculated from the values in table 3.1 and 3.2 and are about 110 mN/m. Because the work of adhesion is positive the polypyrrole layer adhered to the substrate when the substrate was removed from the oxidant solution. During rinsing with water the polypyrrole, which was only physically bonded, was rinsed off. The small difference in the work of adhesion of the untreated and treated epoxy substrates can not explain the large difference in adhesion.

The polymerisation of pyrrole occurs in the water phase [20-22]. During the polymerisation pyrrole forms first oligomers. These pyrrole oligomers grow until the oligomers become insoluble and are found to precipitate partially on the substrate [19]. The precipitated oligomers form a polypyrrole layer either directly on the epoxy resin or on the pyrrole (droplets).

The Fe$^{3+}$ in the polymerisation solution can react with the epoxy resin and form reactive groups. During the precipitation these groups can react with the pyrrole oligomers. In this way the polypyrrole formed directly on the epoxy resin can be chemically bonded to the epoxy resin. The polypyrrole layer formed on the pyrrole can not be chemically attached to the epoxy resin underneath because of the pyrrole, see figure 3.6. This difference in chemical bonding can explain the differences in adhesion.

The rate of the polymerisation reaction increases with the pyrrole concentration [23,24]. At a higher pyrrole concentration in the monomer bath more polypyrrole is formed in the same synthesis time and thus the polypyrrole layer becomes thicker, which results in a lower sheet resistance.
In the neighbourhood of pyrrole droplets on the epoxy resin the pyrrole concentration in the aqueous phase is higher, resulting in a higher polymerisation rate and more polypyrrole. The polymerisation occurs also closer to the surface and hence more polypyrrole is deposited onto the substrate, causing a thicker polypyrrole layer on the substrate and a rougher and thicker polypyrrole layer on the pyrrole droplets. This results in a lower sheet resistance of the polypyrrole layer.

3.6 Properties of the polypyrrole layer

Independent of the treatment or composition of the monomer bath used a layer of pyrrole was applied on the substrate after dipping into the monomer bath. The amount of the monomer solution adhering to the substrate was independent of the pyrrole concentration and hence the resulting amount of pyrrole on the substrate increases with the pyrrole concentration in the monomer solution.

For the untreated epoxy resin it was found that pure pyrrole spreads on the surface. After polymerisation in the oxidising solution the substrate had the black colour of polypyrrole. Because the pyrrole spreads on the surface the formed polypyrrole layer is not chemically attached to the substrate and thus most of the polypyrrole was rinsed off the substrate during rinsing with water. A grey layer with large yellow spots remained. The yellow colour is the colour of the epoxy resin and these spots were not conducting, indicating that this is the epoxy resin. The grey layer was conducting, indicating that this is polypyrrole. Because of the poor adhesion of the polypyrrole layer on the epoxy substrate, only a small amount of polypyrrole remained on the substrate, causing a higher sheet resistance, see table 3.7.

The corona and the cerium treatment of the epoxy resin had the same effect on the polypyrrole layer, see table 3.7. After both treatments pure pyrrole forms droplets on the epoxy substrate in the oxidant solution. After the polymerisation the polypyrrole on the substrate was black. During rinsing a part of the polypyrrole was rinsed off the substrate. A grey layer with black spots, see figure 3.7, remained and is schematically drawn in figure 3.8. The grey layer, see figure 3.8 B, and the spots, see figure 3.8 A, were conducting.
Table 3.7  Properties of the polypyrrole layer.

<table>
<thead>
<tr>
<th>treatment</th>
<th>sheet resistance (kΩ/□)</th>
<th>adhesion*</th>
<th>appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>no</td>
<td>2.8 (0.6)*</td>
<td>poor</td>
<td>grey with yellow spots</td>
</tr>
<tr>
<td>cerium</td>
<td>1.0 (0.1)</td>
<td>depending</td>
<td>grey with dark spots</td>
</tr>
<tr>
<td>corona</td>
<td>1.1 (0.1)</td>
<td>depending</td>
<td>grey with dark spots</td>
</tr>
</tbody>
</table>

* Visually detected. Depending: poor on spots and strong on remaining positions.

# The parenthesised values are standard deviations.

![Microscopy picture of a dark spot on a treated epoxy resin after polymerisation of pyrrole.](image)

Figure 3.7  Microscopy picture of a dark spot on a treated epoxy resin after polymerisation of pyrrole.

![Schematic representation of a polypyrrole layer deposited on a treated epoxy resin. A: a dark polypyrrole spot deposited on a droplet of pyrrole, B: a grey polypyrrole layer deposited directly on the epoxy resin, C: a dark spot of polypyrrole damaged after rinsing.](image)

Figure 3.8  Schematic representation of a polypyrrole layer deposited on a treated epoxy resin. A: a dark polypyrrole spot deposited on a droplet of pyrrole, B: a grey polypyrrole layer deposited directly on the epoxy resin, C: a dark spot of polypyrrole damaged after rinsing.

indicating that this is polypyrrole. The dark spots are caused by the polymerisation of the pyrrole droplets formed on the substrate preceding the polymerisation. The spots were thicker and rougher than the grey layer. During rinsing with water some of the dark spots were broken, see figure 3.8 C, because the polypyrrole on top of the droplets were not chemically bonded to the epoxy resin underneath. The layer underneath is yellow and not conducting, demonstrating that this is the epoxy resin.
Figure 3.9  Sheet resistance (kΩ/□) and appearance of the polypyrrole film polymerised with a monomer solution containing different volume percentage of pyrrole in 2-propanol (IPA). The polypyrrole layer is uniform grey in the grey area and grey with dark spots in the spotted area.

In all cases where pyrrole was diluted with IPA, the polypyrrole layer was black after polymerisation. After rinsing with water the appearance and the sheet resistance of the remaining layer was depending on the pyrrole concentration, see figure 3.9. At 60 vol% pyrrole in IPA and higher, the monomer solution does not dissolve in the water phase and pyrrole droplets remain on the surface. Therefore similar polypyrrole layers as found for the treated epoxy resins were found. At pyrrole concentrations of 50 vol% and lower the monomer solution dissolves in the water phase and hence smooth grey polypyrrole layers deposited on the substrate.

The sheet resistance of the polypyrrole film decreased with increasing pyrrole concentration because the polymerisation rate increases with the pyrrole concentration. Furthermore, the sheet resistance shows a sharp decrease when dark spots appear at the surface. Because of the pyrrole droplets on the surface the polymerisation occurs closer to the surface, which results in more deposition of polypyrrole on the substrate and thus a lower sheet resistance. Moreover, the dark spots are thicker, which also results in a lower sheet resistance.

3.7 Conclusions

In this chapter the influence of the surface pre-treatment and the influence of the pyrrole concentration in the monomer bath on the properties of the polypyrrole layer were presented.
Calculations and measurements showed that pure pyrrole spreads on an untreated epoxy substrate. The polymerisation of pyrrole occurs in the water phase and the polypyrrole partially deposits on the substrate. Because of the pyrrole layer on the substrate it is difficult to get chemical bonding between the deposited polypyrrole and the epoxy substrate, which results in a poor adhesion of the polypyrrole layer. Consequently after rinsing only a small amount of polypyrrole remained anywhere no pyrrole was present on the substrate, causing a higher overall sheet resistance.

Topology measurements with a profilometer and an AFM showed that after corona treatment the epoxy substrate is roughened while cerium treatment has no such effect. Both treatments increase the surface tension of the epoxy substrate, resulting in the formation of droplets of pure pyrrole on the treated surface in the oxidant solution. These droplets are polymerised, causing the dark spots on the surface. During the polymerisation polypyrrole is deposited on the pyrrole droplets. Hence, no chemical bonding was formed between the polypyrrole and the epoxy resin underneath, explaining the poor adhesion of the dark spots.

At volume percentage of pyrrole of 60 and higher in the monomer bath, droplets of pyrrole are formed on the surface because of the poor solubility of pyrrole in water. As seen above these droplets result in a grey polypyrrole layer with dark spots. At concentrations of pyrrole in IPA of 50 vol% and lower, the monomer solution dissolves in the water phase so no droplets are formed on the surface. Consequently, a smooth grey polypyrrole layer was formed on the epoxy substrate. Due to the lower pyrrole concentration the polymerisation rate decreases, resulting in a thinner polypyrrole layer in the same polymerisation time and thus a higher sheet resistance.

Pre-treatment of the epoxy substrate improves the adhesion of the polypyrrole layer but not the appearance. The only way to get an adhering smooth polypyrrole layer on an epoxy substrate is the use of a monomer bath with a pyrrole concentration of 50 vol% or lower.

Besides a smooth polypyrrole layer a polypyrrole layer with a low sheet resistance is required for the metallization process. The optimisation of the polymerisation conditions to achieve this will be discussed in the following chapters.

References

Effect of the Processing Time and the Temperature of the Oxidant Solution on the Properties of the Polypyrrole Layer
Abstract

For an efficient metallization process the sheet resistance of the polypyrrole layer must be lowered. Values below 10 Ω/□ are needed.

The electrical properties of the layers are influenced by the time spent in the oxidant solution. Also the temperature during oxidation is a relevant production parameter because it influences the polymerisation process. Optimisation of the polymerisation process led to a 30 minutes oxidative process at 0°C.

4.1 Introduction

Besides the roughness and adhesion of the polypyrrole layer the electrical properties are also important. De Leeuw et al. [1] showed that the lateral deposition velocity increased with the inverse root of the sheet resistance. Hence, for a fast metallization process a low sheet resistance is required. Two important process parameters, which influence the sheet resistance, are the time spent in the oxidant solution and the temperature during the oxidation. In this chapter the influence of these two process parameters on the properties of the polypyrrole layer are discussed.

4.2 Experimental

Non-conducting substrates were made out of FR4-Duraver-E-prepregs 7628 (a raw material for glass fibre-reinforced epoxy resins) obtained from Isola Benelux S.A. (B). The prepregs were cured at 180°C in 2 hours and subsequently cut into pieces of 1.0 x 7.5 cm². Pyrrole monomer (Acros Organics) was distilled and stored cool and dark prior to use. Fe(ClO4)3*9H2O (Fluka Chemika), 60% HClO4 (Fluka Chemika), and 2-propanol (Merck) were all used as received.

For the synthesis of polypyrrole on the epoxy resin, the substrate (75 x 10 x 1 mm³) was first cleaned with acetone. By carefully turning, both sides of the substrate were corona treated with a solid-state Tantec Model HV 05-2 generator at about 90 W and about 25 kHz for 10 seconds. Subsequently, the substrate was dipped in a solution of pyrrole in 2-propanol (50% v/v), to apply a layer of pyrrole. Finally the substrate was immersed in an oxidant solution containing 20.65 g of Fe(ClO4)3*9H2O (0.20 M), 12.2 ml of 60% HClO4 (0.56 M) and 200 ml demiwater. The time in this solution was varied between 5 and 60 minutes, and the temperature of this solution was varied between 0°C and 30°C. After polymerisation the substrate was rinsed with demiwater and dried at room temperature.

Sheet resistances reported here are the average values obtained by four-probe resistance measurements on at least three samples at room temperature.
4.3 Influence of time

4.3.1 Introduction

For a commercial process the time to apply a conducting layer must be as short as possible. Keeping this in mind the influence of the time spent in the oxidant solution on the weight gain of the epoxy sample, the sheet resistance and the conductivity of the polypyrrole film were studied. Other research groups investigated the influence of the polymerisation time on the thickness [2,3] or mass uptake [4], the sheet resistance [2,4,5], and the conductivity [2,6] of the polypyrrole film.

4.3.2 Results and discussion

4.3.2.1 Weight gain

The weight gain of the epoxy sample, see figure 4.1, is a measure for the thickness of the polypyrrole layer, see equation 4.1. Although the weight increased with time in the oxidant solution, the rate of the weight gain declined. This is due to the decrease in availability of the monomer pyrrole. After about 30 minutes the weight did not increase significantly. Others [2,4,7] found a similar trend in film thickness or mass uptake.

Figure 4.1 Influence of time in the oxidant solution on the sheet resistance (●) and the weight gain (■) of the polypyrrole film.
The thickness \(d\) in cm of the polypyrrole layer can be calculated from the weight gain \(w\) in g of the epoxy sample

\[
d = \frac{w}{\rho_{pp} A}
\]

where \(\rho_{pp}\) is the theoretical density of polypyrrole, being 1.4 g/cm\(^3\), and \(A\) is the surface area of the epoxy substrate, which is 16.5 cm\(^2\). Wynne and Street [8] found that anhydrous polypyrrole reversibly takes up 5 mass% water. Because in our case the polypyrrole layers were synthesised in an aqueous solution, it is assumed that these layers are saturated with water. AFM measurements of individual samples showed that the actual thickness of the polypyrrole layer is (about a factor 5) smaller than the thickness after correction for the water uptake. Therefore, the calculated thickness only gives the trend in the thickness. After 60 minutes polymerisation the thickness after correcting for the water uptake is 0.41 \(\mu\)m and this is comparable with values found by Ayad [7] and Uribe et al. [9], but thinner than those found by Yoshikawa et al. [2].

For a commercial application the optimal polymerisation time with respect to the weight of the polypyrrole layer is about 30 minutes, because at a longer polymerisation time the weight did not increase significantly.

### 4.3.2.2 Sheet resistance

Figure 4.1 shows that the sheet resistance decreased with increasing polymerisation time and levels off after about 30 minutes. Others [2,4,5] found the same trend, only the time after which the sheet resistance levels off differ. These times are 5 minutes [2], 20 minutes [4] and 45 minutes [5]. This difference was probably due to differences in synthesis of the polypyrrole layer, for instance the way pyrrole is added to the oxidant solution. Our sheet resistances are lower than those found by Saurin et al. [4], but higher than those found by Uribe et al. [5] and Yoshikawa et al. [2].

For an efficient process the optimal polymerisation time with respect to the sheet resistance is about 30 minutes, because at a longer polymerisation time the sheet resistance did not decrease significantly.

### 4.3.2.3 Conductivity

The conductivity \(\sigma\) in S/cm can be calculated from the thickness \(d\) and the sheet resistance \(R_\square\) in \(\Omega/\square\).
\[ \sigma = \frac{1}{R_{\text{ct}} d} \]  

(4.2)

Because of the water uptake, the calculated conductivity only gives the trend in the conductivity, see figure 4.2. The actual conductivity will be higher.

At short polymerisation times the error of the calculated conductivity is high because of the relative large error in the measured weight of the deposited polypyrrole layer. The conductivity decreased slowly with polymerisation time and became constant after about 30 minutes. Yoshikawa et al. [2] found comparable values and a comparable trend in the conductivity, only the decline in the conductivity is steeper. Rueda et al. [6] found conductivities, which were lower and decreased with increasing polymerisation time.

The decrease in conductivity can be explained by the acid, which is produced during the polymerisation

\[ n \text{Py} + (2n-2) \text{Fe}^{3+} \rightarrow (\text{Py})_n + (2n-2) \text{Fe}^{2+} + (2n-2) \text{H}^+ \]  

(4.3)

So the acid concentration, especially close to the surface of the substrate where the polymerisation reaction occurs, increases. At high acid concentrations the proton-catalysed polymerisation becomes significant and leads to non-conductive oligomers and polymers [10]. These non-conducting parts are incorporated in the polypyrrole layer, causing a decrease in the conductivity.

The optimal polymerisation time with respect to the conductivity is 10 minutes, because at a longer polymerisation time the conductivity decreased.

![Figure 4.2 Influence of time in the oxidant solution on the calculated conductivity of the polypyrrole film.](image-url)
4.3.3 Conclusion

The conductivity of the deposited polypyrrole layer decreased in time, while the polypyrrole layer became thicker. This led to a decline in the sheet resistance at the beginning of the polymerisation time. After a polymerisation time of 30 minutes the polypyrrole layer only grew slowly with a constant conductivity therefore the sheet resistance decreased only slightly. One of the most important factors for a fast metallization process is the sheet resistance. Therefore, the optimal polymerisation time is about 30 minutes.

4.4 Influence of polymerisation temperature

4.4.1 Introduction

A higher conductivity of polypyrrole was found at lower synthesis temperature in aqueous solutions [2,11] and organic solvents [12,13]. In aqueous solutions the maximum conductivity was obtained when the polypyrrole was synthesised at 0°C and the conductivity sharply decreased with increasing synthesis temperature [2]. Liang et al. [11] investigated the relation between the structure and the conductivity of polypyrrole synthesised at different temperatures. They also used an excess of oxidant, the ratio of Fe(III):pyrrole is 5:1. The polypyrrole synthesised at lower temperature exhibits higher conductivity, higher doping levels, higher charge carrier hopping frequency, longer conjugation length and fewer chemical defects, like carbonyls, hydroxyls, and deprotonated nitrogen. They concluded that at lower temperature the rates of the unwanted reactions become much slower relative to the rate of the desired reaction, the α-α coupling of monomer units. We studied the influence of the polymerisation temperature on the sheet resistance, weight gain, and conductivity.

4.4.2 Results and discussion

The thickness of the polypyrrole film increased with increasing synthesis temperature, as can be seen in table 4.1. The rate of the Fe(III)-catalyst reaction was lower at lower temperatures, which could also be seen in a slower colour change of the solution. Hence, the deposited polypyrrole layer was thinner. Although, the reaction rate increased with the polymerisation temperature, the sheet resistance slightly increased. Therefore we must conclude that the conductivity of the polypyrrole film has decreased with increasing synthesis temperature.

Salmon et al. [10] found that at high acid concentrations the proton-catalysed polymerisation leads to non-conducting oligomers and polymers. Therefore the proton-catalyst polymerisation was investigated at different temperatures. The same route as for the normal
Table 4.1  Influence of the temperature of the oxidant solution on the sheet resistance of the polypyrrole film and the weight gain of the substrate at a HClO₄ and Fe(III) concentration of 1.0 M and 0.20 M, respectively.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sheet resistance (kΩ/□)</th>
<th>Weight gain (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°C</td>
<td>0.47 (0.02)</td>
<td>1.1 (0.2)</td>
</tr>
<tr>
<td>20°C</td>
<td>0.51 (0.05)</td>
<td>3.6 (0.1)</td>
</tr>
<tr>
<td>30°C</td>
<td>0.68 (0.05)</td>
<td>4.3 (0.6)</td>
</tr>
</tbody>
</table>

*The parenthesised values are standard deviations.

synthesis was used, only 1.0 M HClO₄ was added to the oxidising solution. After 105 minutes the acid solution at 0°C was still colourless, the solution at 20°C was slightly yellow and the solution at 30°C was opaque yellow, while the reference solutions, which contain no Fe(III) and no HClO₄, were colourless. This suggests that the rate of the proton-catalysed polymerisation at 1.0 M HClO₄ is almost zero at 0°C and increases rapidly between 20°C and 30°C. This increase of the proton-catalyst polymerisation caused the decrease of the conductivity of the polypyrrole film at high temperatures.

This temperature dependence of the proton-catalyst polymerisation can also explain the fewer defects and longer conjugation length at lower temperatures found by Liang et al. [11] suggesting that the proton-catalysed polymerisation is the dominant unwanted reaction during the polymerisation at room temperature.

4.4.3 Conclusions

The decrease of the conductivity of the polypyrrole film with synthesis temperature was caused by the increased rate of the proton-catalyst polymerisation. Although the thickness of the polypyrrole film increased with the synthesis temperature, the sheet resistance increased. Because of the lower sheet resistance and higher conductivity the polymerisation reaction was carried out on ice in all our subsequent experiments unless it is stated differently.

The temperature dependence of the proton-catalysed polymerisation can also explain the fewer defects and longer conjugation length at lower temperatures found by Liang et al. [11] suggesting that the proton-catalyst polymerisation is the dominant unwanted reaction during the polymerisation at room temperature.

4.5 Conclusions

To decrease the sheet resistance of the polypyrrole layers the influence of the time spent in the oxidant solution and temperature during oxidation was investigated.

The polypyrrole layer became thicker with increasing time in the oxidant solution, while the conductivity decreased. This resulted in a decreasing sheet resistance of the
polypyrrole film with polymerisation time. The optimal polymerisation time is about 30 minutes.

Although the thickness of the polypyrrole film increased with the temperature of the oxidant solution, the sheet resistance also increased. This decrease of the conductivity of the polypyrrole film with synthesis temperature is caused by the increased rate of the proton-catalyst polymerisation. Hence, the optimal polymerisation temperature is 0°C.

References

Chapter 5

Influence of the Fe(ClO$_4$)$_3$ and HClO$_4$ Concentrations in the Oxidant Solution on the Properties of the Polypyrrole Layer

Abstract

For a fast metallization process the sheet resistance of the conducting layer must be as low as possible. Hence, the influence of the HClO$_4$ and the Fe(ClO$_4$)$_3$ concentration on the sheet resistance of the polypyrrole layer and on the polymerisation reaction were investigated. Furthermore, the polypyrrole layer was characterised by cyclic voltammetry.

The rate of the polymerisation reaction increases with increasing Fe(ClO$_4$)$_3$ concentration and therefore the polypyrrole layer becomes thicker and the sheet resistance decreases.

The sheet resistance depends on the HClO$_4$ concentration for Fe(ClO$_4$)$_3$ concentrations of 0.30 M and lower. Calculations of the influence of the acid concentration on the Fe$^{3+}$ hydrolysis equilibria are in good agreement with UV/VIS and pH measurements. These calculations and experiments in which HClO$_4$ was replaced by LiClO$_4$, showed that the polymerisation rate of pyrrole is determined by the perchlorate concentration and not by the acid concentration. The perchlorate ions promote the dimerisation of the radical cations by reducing the electrical repulsion between the radical cations; therefore the dimerisation of the pyrrole radical cations is the rate-determining step.

The optimisation of the diverse process steps described in the chapters 3, 4, and 5 leads to the following process. The substrate was first cleaned with acetone. By carefully turning, both sides of the substrate were corona treated with a solid-state Tantec Model HV 05-2 generator at about 90 W and about 25 kHz for 10 seconds. Subsequently, the substrate was dipped in a solution of pyrrole in 2-propanol (50% v/v). Finally the substrate was immersed in an oxidant solution containing 30.98 g of Fe(ClO$_4$)$_3$·9H$_2$O (0.30 M), 21.7 ml of 60% HClO$_4$ (1.0 M) and 200 ml demiwater at 0°C for 30 minutes. After polymerisation the substrate was rinsed with demiwater and dried at room temperature. This process is successfully used for the polymerisation of pyrrole on other plastics.

The cyclic voltammogram of polypyrrole showed that polypyrrole is in the reduced non-conducting form at potentials of -0.5 V and lower and in the oxidised conducting form at potentials of -0.2 V and higher.

5.1 Introduction

The metallization process becomes faster at decreasing sheet resistance of the conducting layer [1]. Besides the time in and temperature of the oxidant solution the sheet resistance of the polypyrrole layer also depends on the Fe(ClO$_4$)$_3$ concentration and the HClO$_4$ concentration in the oxidant solution. In this chapter the influence of both concentrations on the sheet resistance of the polypyrrole film and on the rate of the polymerisation reaction are discussed. Furthermore, the polypyrrole layer was electrochemically characterised with cyclic voltammetry.
5.2 Experimental

Non-conducting substrates were made out of FR4-Duraver-E-prepregs 7628 (a raw material for glass fibre-reinforced epoxy resins) obtained from Isola Benelux S.A. (B). The prepregs were cured at 180°C in 2 hours and subsequently cut into pieces of 1.0 x 7.5 cm². The pyrrole monomer (Acros Organics) was distilled and stored cool and dark prior to use. Fe(CIO₄)₃*9H₂O (Fluka Chemika), 60% HClO₄ (Fluka Chemika), 2-propanol (Merck), LiClO₄ (Janssen Chimica), picric acid (Fluka Chemika), m-cresol purple (Fluka Chemika), and quinaldine (Fluka Chemika) were all used as received.

For the polymerisation of pyrrole on the epoxy resin, the substrate was first cleaned with acetone. By carefully turning, both sides of the substrate were corona treated with a solid-state Tantec Model HV 05-2 generator at about 90 W and about 25 kHz for 10 seconds. Subsequently, the substrate was dipped in a solution of pyrrole in 2-propanol (50% v/v), to apply a layer of pyrrole. Finally the substrate was immersed in an oxidant solution containing 20.65 g of Fe(CIO₄)₃*9H₂O (0.20 M), 12.2 ml of 60% HClO₄ (0.56 M) and 200 ml demiwater at 0°C for 25 minutes. The Fe(CIO₄)₃ concentration was varied between 0.10 and 0.60 M and the HClO₄ concentration was varied between 0 and 2.5 M. After polymerisation the substrate was rinsed with demiwater and dried at room temperature.

For studying the influence of the perchlorate ion on the polymerisation reaction, the same process as above was used. Only the HClO₄ in the oxidant bath was replaced by LiClO₄. The Fe(CIO₄)₃ concentration was 0.20 M and the LiClO₄ concentration was varied between 0 and 2.5 M.

For the electrochemical characterisation of polypyrrole, a layer of gold with a resistance of a few ohms was vapour deposited on an epoxy substrate to assure a good ohmic contact. Subsequently, pyrrole was polymerised on the substrate according to the above method with Fe(CIO₄)₃ and HClO₄ concentrations of 0.20 and 1.0 M, respectively. The polypyrrole on the gold side was electrically disconnected from the borders with a knife to ensure a good ohmic contact between the gold and the studied polypyrrole layer. The cyclic voltammetry was conducted with an EG&G PAR 273 potentiostat in a 0.1 M LiClO₄ solution with a saturated calomel electrode (SCE) as the reference electrode and a platinum foil as the counter electrode. The cyclic voltamogram was conducted between 0.5 and −1.0 V vs. SCE and was started in the cathodic direction from the open current potential (ocp).

Sheet resistances reported here are the average values obtained by four-probe resistance measurements on at least three samples at room temperature.

UV/VIS measurements of the Fe(CIO₄)₃, HClO₄ solutions were performed on a Perkin Elmer Lambda 3B UV/VIS spectrophotometer.

The pHs of these solutions were estimated with pH indicators, because a pH measurement apparatus cannot be used in Fe³⁺ solutions.

X-ray photoelectron spectroscopy (XPS) measurements were performed by a VG 220i Imaging XPS instrument equipped with a dual anode (MgKα/AI Kα) source.
5.3 Influence of Fe(ClO$_4$)$_3$ concentration

5.3.1 Introduction

The influence of the Fe$^{3+}$ concentration on the intrinsic resistivity of polypyrrole was investigated intensively [2-6]. The intrinsic resistivity decreases with increasing FeCl$_3$ concentrations [2,3,5,6] and has the lowest intrinsic resistivity at a FeCl$_3$ concentration of 2.5 M [4]. The polymerisation rate of pyrrole is determined by the concentrations of pyrrole and Fe$^{3+}$ [3]. At high FeCl$_3$ concentrations Planche et al. [3] found that the polymerisation is second order with respect to the FeCl$_3$ concentration and explained this by the formation of a FeCl$_3$-pyrrole complex before the oxidation of pyrrole by a second FeCl$_3$.

Yoshikawa et al. [7] investigated the intrinsic resistivity of a polypyrrole layer on a non-conducting substrate. They found an increase in the intrinsic resistivity of the polypyrrole layers when the FeCl$_3$ concentration was changed from 1 M to 3 M.

Uribe et al. [8] and Chen et al. [9] investigated the influence of the oxidant concentration on the sheet resistance of a polypyrrole layer. They found a decrease in the sheet resistance with increasing oxidant concentration. We studied the influence of the Fe(ClO$_4$)$_3$ concentration on the sheet resistance of the polypyrrole film at different HClO$_4$ concentrations.

5.3.2 Results

The sheet resistance of the polypyrrole films, which were polymerised at various Fe(ClO$_4$)$_3$ and HClO$_4$ concentrations, are listed in table 5.1. The sheet resistance of the polypyrrole film decreases with increasing oxidant concentration. At higher Fe$^{3+}$ concentrations the polymerisation rate is higher [3], which is seen in a faster colour change of the solution. Therefore the polypyrrole layer is thicker and the sheet resistance lower. From an economical point of view the optimal oxidant solution with respect to the sheet resistance is a solution containing 0.30 M Fe(ClO$_4$)$_3$ and 1.0 M HClO$_4$, because at higher Fe(ClO$_4$)$_3$ concentrations the sheet resistance does not decrease significantly.

<table>
<thead>
<tr>
<th>HClO$_4$ (mol/l)</th>
<th>0.10</th>
<th>0.20</th>
<th>0.30</th>
<th>0.40</th>
<th>0.60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(ClO$_4$)$_3$ (mol/l)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.7 (0.5)*</td>
<td>0.40 (0.04)</td>
<td>0.20 (0.01)</td>
<td>0.15 (0.02)</td>
<td>0.12 (0.01)</td>
</tr>
<tr>
<td>0.00001</td>
<td>1.3 (0.2)</td>
<td>0.41 (0.02)</td>
<td>0.19 (0.02)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>1.5 (0.2)</td>
<td>0.48 (0.07)</td>
<td>0.19 (0.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>1.2 (0.3)</td>
<td>0.34 (0.02)</td>
<td>0.18 (0.02)</td>
<td>0.16 (0.01)</td>
<td>0.11 (0.01)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.38 (0.03)</td>
<td>0.18 (0.02)</td>
<td>0.13 (0.01)</td>
<td>0.14 (0.01)</td>
<td>0.12 (0.01)</td>
</tr>
</tbody>
</table>

*The parenthesised values are standard deviations.
For Fe(ClO$_4$)$_3$ concentrations of 0.40 M and higher the sheet resistance is independent of the HClO$_4$ concentration, whereas at lower Fe(ClO$_4$)$_3$ concentrations the sheet resistance of the polypyrrole film decreases with increasing HClO$_4$ concentration, see table 5.1. This dependence on the HClO$_4$ concentration was further investigated, see the next paragraph.

5.4 Influence of HClO$_4$

5.4.1 Introduction

The effect of the electrolyte concentration on the electropolymersisation of pyrrole has been studied intensively [10]. From these studies it can be concluded that metal oxide formation on the electrode, polymer oxidation, discharge of the polymer, and stabilisation of the monomer radical cations are the most important processes. The effect of the electrolyte concentration on the chemical polymerisation of pyrrole has been investigated less intensively. An increase in polymerisation rate was found with increasing anion concentration [11] or acid concentration [12,13]. The acid influences the Fe$^{3+}$ hydrolysis equilibria in such a way that the electron-transfer from pyrrole to Fe$^{3+}$ becomes easier [13]. The influence of the anion concentration is explained by temporary formation of insoluble products, which initiate the polymerisation reaction [11]. We studied in particular the influence of the HClO$_4$ concentration on the polymerisation reaction.

5.4.2 Influence of the HClO$_4$ concentration

Figure 5.1 shows that the sheet resistance of the polypyrrole films as a function of the acid concentration has a minimum at 1.5 M HClO$_4$. The increase in the sheet resistance of the polypyrrole film at high HClO$_4$ concentrations can be explained by the proton-catalysed polymerisation of pyrrole as a competing reaction to the oxidation. The proton-catalysed polymerisation occurring at high acid concentrations leads to non-conductive oligomers and polymers [14]. Furthermore the reaction rate increases with the HClO$_4$ concentration, which was seen in a faster colour change of the solution and a larger weight gain of the substrate in the same synthesis time.
Figure 5.1  Sheet resistance of the polypyrrole film at 0.20 M Fe(ClO$_4$)$_3$ as a function of the HClO$_4$ concentration.

5.4.3 Influence of the H$^+$ concentration

5.4.3.1 Calculations of the Fe$^{3+}$ hydrolysis equilibria

Bjorklund [13] observed a first order dependence of the reaction rate on Fe$^{3+}$ and pyrrole concentrations and hence concluded that the electron-transfer from pyrrole to Fe$^{3+}$ is the rate-determining step for the polymerisation. Furthermore, they assumed that the electron-transfer proceeds through an outer-sphere, activated-complex mechanism [13]. In that case the reaction rate will depend on how effectively pyrrole and the solvated Fe$^{3+}$ can approach each other. Since pyrrole is a weak base, the approach is easier for Fe$^{3+}$ ions that are solvated by water than those that have one or two hydroxide ions in the solvation sphere. Thus the polymerisation rate should increase with H$^+$ concentration as the hydrolysis equilibria are shifted to the Fe$^{3+}$ ions that are solvated by water. To discuss this influence of the H$^+$ concentration the following Fe$^{3+}$ equilibria have to be considered

$$\text{Fe(ClO}_4)_3 \rightleftharpoons \text{Fe}^{3+} + 3 \text{ClO}_4^- \quad (5.1)$$
$$\text{Fe}^{3+} + 6 \text{H}_2\text{O} \rightleftharpoons \text{Fe(H}_2\text{O)}_6^{3+} \quad (5.2)$$
$$2 \text{Fe(H}_2\text{O)}_6^{3+} \rightleftharpoons \text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+} + 2 \text{H}^+ + 2 \text{H}_2\text{O} \quad \log K_3 = -2.91 \quad (5.3)$$
$$\text{Fe(H}_2\text{O)}_6^{3+} \rightleftharpoons \text{Fe(H}_2\text{O})_5(\text{OH})^{2+} + \text{H}^+ \quad \log K_4 = -3.05 \quad (5.4)$$
$$\text{Fe(H}_2\text{O})_5(\text{OH})^{2+} \rightleftharpoons \text{Fe(H}_2\text{O})_4(\text{OH})^{2+} + \text{H}^+ \quad \log K_5 = -3.26 \quad (5.5)$$

Because of the low co-ordinating tendency of the perchlorate ion only the last three equations are important [15]. For these equilibria the following expressions for the equilibrium constants can be derived
\[ K_3 = \frac{\left[ \text{Fe}_2(H_2O)_8(OH)_{2+} \right]^2 \left[ H^+ \right]^2}{\left[ \text{Fe}(H_2O)_6^{3+} \right]^2} = \frac{x(\beta + 2x + y + 2z)^2}{(\alpha - 2x - y - z)^2} \quad (5.6) \]

\[ K_4 = \frac{\left[ \text{Fe}(H_2O)_3(OH)^{2+} \right][H^+]}{\left[ \text{Fe}(H_2O)_6^{3+} \right]} = \frac{y(\beta + 2x + y + 2z)}{(\alpha - 2x - y - z)} \quad (5.7) \]

\[ K_5 = \frac{\left[ \text{Fe}(H_2O)_3(OH)_{2+} \right][H^+]}{\left[ \text{Fe}(H_2O)_6^{3+} \right]} = z(\beta + 2x + y + 2z) \quad (5.8) \]

where \( x = [\text{Fe}_2(H_2O)_8(OH)_{2+}] \), \( y = [\text{Fe}(H_2O)_3(OH)^{2+}] \), \( z = [\text{Fe}(H_2O)_3(OH)_{2+}] \), \( \alpha \) is the added concentration \( \text{Fe(ClO}_4)_3 \), \( \beta \) is the added concentration \( \text{HClO}_4 \), \( \beta + 2x + y + 2z = [H^+] \), and \( \alpha - 2x - y - z = [\text{Fe}(H_2O)_6^{3+}] \).

Because the added concentration \( \text{Fe(ClO}_4)_3 \) (\( \alpha \)) and the added concentration \( \text{HClO}_4 \) (\( \beta \)) are known, these equations can be solved. Equation 5.8 can be written as

\[ x = \frac{1}{2} \left( \frac{K_5y}{z} - y - 2z - \beta \right) \quad (5.9) \]

After substitution in equation 5.7 we find

\[ 0 = y^2 + K_4y - \frac{zK_4}{K_5}(\alpha + \beta + z) \quad (5.10) \]

Because the \( \text{Fe}(H_2O)_3(OH)^{2+} \) concentration is positive we find for \( y \)

\[ y = -\frac{1}{2} K_4 + \left( \frac{1}{2} \left( K_4^2 + \frac{4zK_4}{K_5}(\alpha + \beta + z) \right) \right)^{1/2} \quad (5.11) \]

Combining equation 5.6 and 5.7 gives an expression for \( x \)

\[ x = \frac{K_3}{K_4} y^2 = \frac{K_3}{K_4} \left( -\frac{1}{2} K_4 + \left( \frac{1}{2} \left( K_4^2 + \frac{4zK_4}{K_5}(\alpha + \beta + z) \right) \right)^{1/2} \right)^2 \quad (5.12) \]

After using the expressions for \( x \) and \( y \) in equation 5.8 we find
\[
0 = \frac{2K_3}{K_4} \left( -\frac{1}{2} K_4 + \frac{1}{2} \left( K_4^2 + \frac{4zK_4}{K_5} (\alpha + \beta + z) \right)^{1/2} \right) + \\
\left( 1 - \frac{K_5}{z} \right) \left( -\frac{1}{2} K_4 + \frac{1}{2} \left( K_4^2 + \frac{4zK_4}{K_5} (\alpha + \beta + z) \right)^{1/2} \right) + 2z + \beta
\]  

(5.13)

This equation can be solved iteratively, so for any given concentration of added Fe(ClO₄)₃ (\(\alpha\)) and HClO₄ (\(\beta\)) the acid, Fe(H₂O)₆^{3+}, Fe(H₂O)₅(OH)²⁺, Fe(H₂O)₄(OH)₂⁺, and Fe₂(H₂O)₈(OH)₂⁺ concentrations can be calculated. A few examples are listed in Table 5.2.

The Fe(H₂O)₄(OH)₂⁺ concentration is very low in these examples and has a very small contribution to the changes in the calculated acid concentration and Fe(H₂O)₆^{3+} concentration. At least for the chosen Fe(ClO₄)₃ concentration equilibrium 5.5 can be neglected. So the question arises at which Fe(ClO₄)₃ concentration equilibrium 5.5 can be ignored.

<table>
<thead>
<tr>
<th>Added concentration (mol/l)</th>
<th>Calculated concentration (mol/l)</th>
<th>Fe₂(H₂O)₈(OH)₂⁺⁺⁺</th>
<th>Fe₂(H₂O)₇(OH)²⁺⁺⁺</th>
<th>Fe₂(H₂O)₆(OH)²⁺⁺⁺</th>
<th>H⁺⁺⁺</th>
<th>Fe(H₂O)₆³⁺⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(ClO₄)₃</td>
<td>HClO₄</td>
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<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>0.1</td>
<td>-</td>
<td>1.1E-02</td>
<td>2.68E-03</td>
<td>5.89E-05</td>
<td>2.50E-02</td>
<td>7.51E-02</td>
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<td>1.03E-01</td>
<td>9.70E-02</td>
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<td>1.00E+00</td>
<td>9.99E-02</td>
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<td>1.0</td>
<td>4.90E-05</td>
<td>1.78E-04</td>
<td>9.78E-08</td>
<td>1.00E+00</td>
<td>2.00E-01</td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
<td>2.51E-02</td>
<td>4.03E-03</td>
<td>4.07E-05</td>
<td>5.44E-02</td>
<td>2.46E-01</td>
</tr>
<tr>
<td>0.4</td>
<td>-</td>
<td>3.10E-02</td>
<td>4.47E-03</td>
<td>3.70E-05</td>
<td>6.65E-02</td>
<td>3.34E-01</td>
</tr>
<tr>
<td>0.6</td>
<td>-</td>
<td>4.15E-02</td>
<td>5.17E-03</td>
<td>3.23E-05</td>
<td>8.82E-02</td>
<td>5.12E-01</td>
</tr>
</tbody>
</table>

5.4.3.2 Ignoring equilibrium 5.5

Equilibrium 5.5 can be ignored when the contribution of this equilibrium to the acid concentration can be neglected. Therefore we have to find an expression for \(\alpha\) in terms of \([H^+]\) and \(\beta\). Equations 5.6, 5.7, and 5.8 can be written as
\[ K_3 = \frac{x[H^+]^2}{(\alpha - 2x - y - z)^2} \]  
\[ K_4 = \frac{y[H^+]}{(\alpha - 2x - y - z)} \]  
\[ K_5 = \frac{z[H^+]}{y} \]  

where

\[ [H^+] = \beta + 2x + y + 2z \]  

Using equations 5.15 and 5.17 in equation 5.16 gives an expression for \( z \)

\[ z = \frac{K_4 K_5 (\alpha + \beta - [H^+])}{([H^+]^2 - K_4 K_5)} \]  

Using this equation in equation 5.16 gives an expression for \( y \)

\[ y = \frac{[H^+]}{K_5} z = \frac{[H^+] K_4 (\alpha + \beta - [H^+])}{([H^+]^2 - K_4 K_5)} \]

Combining equation 5.14, 5.15 and 5.18 gives an expression for \( x \)

\[ x = \frac{K_3 \cdot y \cdot z}{K_4^2} \]  
\[ x = \frac{K_3 [H^+]^2}{K_4^2 K_5^2} z = \frac{K_3 [H^+]^2 (\alpha + \beta - [H^+])^2}{([H^+]^2 - K_4 K_5)^2} \]  

After using the expressions for \( x, y, \) and \( z \) in equation 5.17 we find

\[ 0 = \frac{2K_3 [H^+] (\alpha + \beta - [H^+])^2}{([H^+]^2 - K_4 K_5)^2} + \frac{K_4 [H^+] (\alpha + \beta - [H^+])}{([H^+]^2 - K_4 K_5)} + \frac{2K_4 K_5 (\alpha + \beta - [H^+])}{([H^+]^2 - K_4 K_5)} + \beta - [H^+] \]

Because the Fe(ClO\textsubscript{4})\textsubscript{3} concentration (\( \alpha \)) is positive we find
\[ \alpha = [H^+] - \beta + \left( \frac{[H^+]^2 - K_a K_5}{4K_s[H^+]^2} \right) \left( - (K_a[H^+] + 2K_4 K_5) + \left(K_5[H^+] + 2K_4 K_5 \right)^2 + 8K_4[H^+] \left[ (H^+) - \beta \right] \right)^{1/2} \]

Equilibrium 5.5 can not only be ignored if it almost does not contribute to the acid concentration, but also if the Fe(H_2O)_5(OH)^2+ concentration (y) is a factor (f) larger than \( \alpha \), the concentration Fe(H_2O)_4(OH)_2^+. \[ y = f\alpha \] Combining this equation with equation 5.16 gives an expression for [H^+]

\[ [H^+] = fK_5 \] After substitution in expression 5.22 we find for \( \alpha \)

\[ \alpha = fK_5 - \beta + \frac{f^2 K_5}{4 f^2 K_3} \left( - K_4(f + 2) + (K_5^2(f + 2)^2 + 8 f^2 K_3(f K_5 - \beta) \right)^{1/2} \]

For a certain factor (f) and any added HClO_4 concentration (\( \beta \)) the minimal added Fe(ClO_4)_3 concentration (\( \alpha \)) needed can be calculated with this equation. Furthermore the contribution (p) of equilibrium 5.5 to the acid concentration can be calculated

\[ p = \frac{\alpha}{[H^+]} = \frac{K_4 K_5 (\alpha + \beta - [H^+])}{\left[ H^+ \left( [H^+] - K_a K_5 \right) \right]} = \frac{K_4 (\alpha + \beta - fK_5)}{fK_5 (f^2 K_3 - K_4)} = \frac{K_4}{4 f^3 K_4 K_5} \left( - K_4(f + 2) + (K_5^2(f + 2)^2 + 8 f^2 K_3(f K_5 - \beta) \right)^{1/2} \]

This equation shows that the contribution of equilibrium 5.5 to the acid concentration decreases when the HClO_4 concentration (\( \beta \)) increases. Therefore equilibrium 5.5 can be neglected at lower Fe(ClO_4)_3 concentrations when HClO_4 is added, as also can be seen in table 5.3.

Furthermore table 5.3 shows that when more Fe(ClO_4)_3 is added to the polymerisation solution the contribution of equilibrium 5.5 to the acid concentration (p) decreases. If we assume that equilibrium 5.5 is negligible at a p lower than 1% we have to add more than 0.026 M Fe(ClO_4)_3. So, in our case equilibrium 5.5 can be ignored.
Table 5.3 Contribution (p) of equation 5.5 to the acid concentration and the corresponding Fe(ℓClO₄)₃ concentration calculated for several factors f and HClO₄ concentrations.

<table>
<thead>
<tr>
<th>f</th>
<th>HClO₄ (mol/l)</th>
<th>Fe(ℓClO₄)₃ (mol/l)</th>
<th>p (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-</td>
<td>0.305</td>
<td>0.07</td>
</tr>
<tr>
<td>75</td>
<td>-</td>
<td>0.202</td>
<td>0.11</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>0.114</td>
<td>0.20</td>
</tr>
<tr>
<td>50</td>
<td>0.01</td>
<td>0.086</td>
<td>0.16</td>
</tr>
<tr>
<td>25</td>
<td>-</td>
<td>0.044</td>
<td>0.56</td>
</tr>
<tr>
<td>17</td>
<td>-</td>
<td>0.026</td>
<td>0.99</td>
</tr>
<tr>
<td>16</td>
<td>-</td>
<td>0.024</td>
<td>1.08</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>0.022</td>
<td>1.18</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>0.012</td>
<td>2.10</td>
</tr>
</tbody>
</table>

5.4.3.3 The simplified model

If equilibrium 5.5 is ignored one can rewrite equation 5.6 and 5.7 to

\[
K_3 = \left[ Fe_2(H_2O)_6(OH)^{4+} \right] \left[ H^+ \right]^2 = \frac{x(\beta + 2x + y)^2}{(\alpha - 2x - y)^2} \quad (5.27)
\]

\[
K_4 = \left[ Fe(H_2O)_5(OH)^{2+} \right] \left[ H^+ \right] = \frac{y(\beta + 2x + y)}{(\alpha - 2x - y)} \quad (5.28)
\]

where \(x = [Fe_2(H_2O)_6(OH)^{4+}], y = [Fe(H_2O)_5(OH)^{2+}], \alpha\) is the added concentration Fe(ℓClO₄)₃, \(\beta\) is the added concentration HClO₄, \(\beta + 2x + y = [H^+]\), and \(\alpha - 2x - y = [Fe(H_2O)_6^{3+}]\).

Because the added Fe(ℓClO₄)₃ concentration, \(\alpha\), and the added HClO₄ concentration, \(\beta\), are known, these equations can be solved. Combining equation 5.27 and 5.28 gives

\[
x = \frac{K_3}{K_4} y^2 \quad (5.29)
\]

Substitution of this expression for \(x\) in equation 5.28 gives

\[
0 = \frac{2K_3}{K_4} y^3 + \left( 1 + \frac{2K_3}{K_4} \right) y^2 + (K_4 + \beta) y - K_4 \alpha \quad (5.30)
\]
Table 5.4 Calculated acid, Fe(H$_2$O)$_6^{3+}$, Fe(H$_2$O)$_5$(OH)$^{2+}$, and Fe$_2$(H$_2$O)$_8$(OH)$_2^{4+}$ concentrations at diverse added concentrations of Fe(ClO$_4$)$_3$ and HClO$_4$.

<table>
<thead>
<tr>
<th>Added concentration (mol/l)</th>
<th>Fe(ClO$_4$)$_3$</th>
<th>HClO$_4$</th>
<th>Fe$_2$(H$_2$O)$_8$ (OH)$_2^{4+}$</th>
<th>Fe(H$_2$O)$_5$(OH)$^{2+}$</th>
<th>H$^+$</th>
<th>Fe(H$_2$O)$_6^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-</td>
<td>1.11E-02</td>
<td>2.68E-03</td>
<td>2.49E-02</td>
<td>7.51E-02</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>1.09E-03</td>
<td>8.39E-04</td>
<td>1.03E-01</td>
<td>9.70E-02</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>1.23E-05</td>
<td>8.90E-05</td>
<td>1.00E+00</td>
<td>9.99E-02</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>-</td>
<td>1.87E-02</td>
<td>3.47E-03</td>
<td>4.08E-02</td>
<td>1.59E-01</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.1</td>
<td>3.77E-03</td>
<td>1.56E-03</td>
<td>1.09E-01</td>
<td>1.91E-01</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>1.0</td>
<td>4.90E-05</td>
<td>1.78E-04</td>
<td>1.00E+00</td>
<td>2.00E-01</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
<td>2.52E-02</td>
<td>4.03E-03</td>
<td>5.43E-02</td>
<td>2.46E-01</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>-</td>
<td>3.10E-02</td>
<td>4.47E-03</td>
<td>6.65E-02</td>
<td>3.34E-01</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>-</td>
<td>4.15E-02</td>
<td>5.18E-03</td>
<td>8.81E-02</td>
<td>5.12E-01</td>
<td></td>
</tr>
</tbody>
</table>

With this equation the acid, Fe(H$_2$O)$_6^{3+}$, Fe(H$_2$O)$_5$(OH)$^{2+}$, and Fe$_2$(H$_2$O)$_8$(OH)$_2^{4+}$ concentrations can be calculated for any given Fe(ClO$_4$)$_3$ and HClO$_4$ concentration. A few examples are listed in table 5.4.

If we compare this table with table 5.2 we see no significant difference in the calculated acid and Fe(H$_2$O)$_6^{3+}$ concentration. These numeric results confirm that the simplification of the model is allowed at the Fe(ClO$_4$)$_3$ concentrations we used.

5.4.3.4 Validation of the model

The Fe$_2$(H$_2$O)$_8$(OH)$_2^{4+}$ complex is causing the yellow colour of the iron solution [15]. In the UV/VIS spectrum this is seen as a broad shoulder at 435 nm, see figure 5.2. The absorption at 435 nm was measured for different HClO$_4$ and Fe(ClO$_4$)$_3$ concentrations and the Fe$_2$(H$_2$O)$_8$(OH)$_2^{4+}$ concentration, $x$, at these concentrations was calculated. The Lambert-Beer law gives the relation between the absorption and the concentration

$$A = \varepsilon [x] l \quad \text{(5.31)}$$

or

$$\log A = \log [x] + \log \varepsilon l \quad \text{(5.32)}$$

where $[x]$ is the concentration of $x$, $A$ is the absorption at $[x]$, $\varepsilon$ is the extinction coefficient, and $l$ is the traverse distance in the absorbing medium, i.e. 10 mm.

In order to validate the model as describes before, the measured absorption was plotted against the calculated Fe$_2$(H$_2$O)$_8$(OH)$_2^{4+}$ concentration, see figure 5.3. This figure
Figure 5.2 Visible transmission spectrum of iron solutions; 0.20 M Fe(ClO$_4$)$_3$ (—) and 0.20 M Fe(ClO$_4$)$_2$ with 1.0 M HClO$_4$ (---).

Figure 5.3 The logarithm of the measured absorption at 435.0 nm vs. the logarithm of the calculated Fe$_2$(H$_2$O)$_8$(OH)$_2$$^{4+}$ concentration (x) for different HClO$_4$ and Fe(ClO$_4$)$_3$ concentrations, and the best fit (—).

shows that the measured absorption of the oxidising solution at 435.0 nm is in agreement with the calculated Fe$_2$(H$_2$O)$_8$(OH)$_2$$^{4+}$ concentration for solutions with Fe(ClO$_4$)$_3$ concentrations of 0.20 M and 0.40 M and several HClO$_4$ concentrations. Figure 5.3 also shows the best fit obtained with equation 5.32, log A = log [x] + 1.935 with a correlation coefficient of 0.9916. The extinction coefficient calculated from this line is 86 l mol$^{-1}$ cm$^{-1}$. 
Figure 5.4 *Calculated* $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ *concentration at a* $\text{Fe(ClO}_4)_3$ *concentration of 0.20 M and increasing HClO}_4 *concentrations.*

Furthermore, the measured pHs fit the calculated pHs within the measuring accuracy. This confirms the validity of the above model and also that the used simplification of the model is allowed in our case.

If this model is used to calculate the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ concentration at different HClO$_4$ concentrations and a $\text{Fe(ClO}_4)_3$ concentration of 0.20 M, figure 5.4 is obtained. This figure shows that the maximal $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ concentration of 0.20 M is almost reached for HClO$_4$ concentrations higher than 0.5 M. Therefore the $\text{H}^+$ concentration can not explain the increase in the polymerisation rate and the decrease in the sheet resistance at HClO$_4$ concentrations higher than 0.5 M. The addition of HClO$_4$ not only increases the $\text{H}^+$ concentration but also the perchlorate concentration. The effect of the perchlorate concentration on the polymerisation reaction was further investigated, see the next paragraph.

5.4.4 Influence of the perchlorate concentration

To study the influence of the perchlorate concentration, HClO$_4$ was replaced by LiClO$_4$. An increase in the amount of LiClO$_4$ resulted in a faster colour change of the solution and a larger weight gain of the substrate in the same synthesis time, suggesting an increasing reaction rate. These effects were also observed in the case where HClO$_4$ was used, see paragraph 5.4.2.

Figure 5.5 shows that the influence of the total perchlorate concentration on the sheet resistance of the polypyrrole film is equal for HClO$_4$ and LiClO$_4$ up to a perchlorate concentration of 2.0 M. At higher concentrations the sheet resistance of the polypyrrole film, using HClO$_4$, increases because of the proton-catalysed polymerisation of pyrrole at these
Figure 5.5 Influence of the total perchlorate concentration on the sheet resistance at 0.20 M Fe(ClO$_4$)$_3$ and different concentrations of HClO$_4$ (■) and LiClO$_4$ (♦).

high acid concentrations [14]. This indicates that the reaction rate is determined by the perchlorate concentration and not by the acid concentration as suggested by others [13]. Therefore the electron-transfer from pyrrole to Fe$^{3+}$ is not the rate-determining step for the polymerisation. Furthermore figure 5.5 shows that there is almost no influence of the perchlorate concentration on the sheet resistance for perchlorate concentrations of about 1.5 M and higher. Because this perchlorate concentration corresponds to a Fe(ClO$_4$)$_3$ concentration of 0.5 M, it can be concluded that the sheet resistance becomes independent of the perchlorate concentration for Fe(ClO$_4$)$_3$ concentrations of about 0.5 M and higher. This agrees with the Fe(ClO$_4$)$_3$ concentration of 0.4 M found in table 5.1, see paragraph 5.3.2.

If we want to know how the perchlorate ions influence the polymerisation reaction of pyrrole, we first have to consider the polymerisation reactions in some detail. Polymerisation in solution can proceed by oxidation of pyrrole (Py) by Fe$^{3+}$ to form radical cations (Py$^{++}$). These radical cations can dimerise with the expulsion of H$^+$ in the manner proposed for electrochemical synthesis [16]

\[
\begin{align*}
\text{Py} + \text{Fe}^{3+} & \rightarrow \text{Py}^{++} + \text{Fe}^{2+} \quad (5.33) \\
2\text{Py}^{++} & \rightarrow \text{Py-Py} + 2\text{H}^+ \quad (5.34) \\
(\text{Py})_n\text{-Py} + \text{Fe}^{3+} & \rightarrow (\text{Py})_n\text{-Py}^{++} + \text{Fe}^{2+} \quad (5.35) \\
(\text{Py})_n\text{-Py}^{++} + \text{Py}^{++} & \rightarrow (\text{Py})_{n-1}\text{Py-Py} + 2\text{H}^+ \quad (5.36) \\
(\text{Py})_n\text{-Py}^{++} + (\text{Py})_m\text{-Py}^{++} & \rightarrow (\text{Py})_{n-1}\text{Py-Py-(Py)}_m + 2\text{H}^+ \quad (5.37)
\end{align*}
\]

Besides these polymerisation reactions, also an anion complexation reaction has to be considered
\[(\text{Py})_n \cdot \text{Py}^{++} + \text{ClO}_4^- \rightarrow (\text{Py})_n \cdot \text{Py}^{++} \cdot \text{ClO}_4^- \]  \hspace{1cm} (5.38)

The influence of the perchlorate concentration in the oxidant solution on the composition of the synthesized polypyrrole film was investigated with XPS, see table 5.5. This table shows that the ratio for carbon to nitrogen is higher than the expected four. This is in agreement with what is found by others [17].

There is found an excess of oxygen when the oxygen contents is corrected for the amount of oxygen bonded to the chlorine of the perchlorate. This indicates that some surface oxidation of the film has occurred. This is supported by evidence for oxygenated functionality in the high resolution carbon spectra. The high resolution carbon spectra show that these oxygen species are bonded to carbon in the form of carbonyls and hydroxyls.

Iron was also found in the XPS spectra. The iron was included in the polymer during polymerisation and probably in the Fe$^{2+}$ state. This is not visible in the XPS spectra due to overlapping signals but still probable. Because of electroneutrality every iron binds two anions and therefore the doping level has to be corrected for the iron concentration. The doping level of the polypyrrole layer was determined by subtracting twice the iron concentration from the sum of the perchlorate and the chloride concentration. There is no significant change in the doping level of the polymer (surface) when the perchlorate concentration in the solution is increased, see table 5.5. The observation that the

<table>
<thead>
<tr>
<th>Table 5.5</th>
<th>Atomic ratios of polypyrrole layers polymerised at 0.20 M Fe(ClO$_4$)$_3$ and different LiClO$_4$ concentrations determined with XPS.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M</strong></td>
<td>C/N</td>
</tr>
<tr>
<td>0.10 M</td>
<td>5.29</td>
</tr>
<tr>
<td></td>
<td>(0.28)$^c$</td>
</tr>
<tr>
<td>0.25 M</td>
<td>5.54</td>
</tr>
<tr>
<td></td>
<td>(0.29)</td>
</tr>
<tr>
<td>0.50 M</td>
<td>6.66</td>
</tr>
<tr>
<td></td>
<td>(0.30)</td>
</tr>
<tr>
<td>0.75 M</td>
<td>5.86</td>
</tr>
<tr>
<td></td>
<td>(0.31)</td>
</tr>
<tr>
<td>1.00 M</td>
<td>5.91</td>
</tr>
<tr>
<td></td>
<td>(0.26)</td>
</tr>
<tr>
<td>1.25 M</td>
<td>6.10</td>
</tr>
<tr>
<td></td>
<td>(0.27)</td>
</tr>
<tr>
<td>1.50 M</td>
<td>5.29</td>
</tr>
<tr>
<td></td>
<td>(0.26)</td>
</tr>
</tbody>
</table>

$^a$ The excess oxygen is calculated by subtracting the oxygen associated with the perchlorate ion from the total.

$^b$ The doping level is calculated by subtracting the anions bonded to the iron from the sum of perchlorate and chloride.

$^c$ The parenthesised values are error values representing 95% confidence limits.
polymerisation rate increases with the perchlorate concentration indicates that besides the anion complexation reaction other reactions are influenced by the presence of perchlorate ions.

On the basis of the previous results we conclude that the perchlorate ions influence the dimerisation of the radical cations, reactions 5.34, 5.36, and 5.37. The presence of perchlorate ions reduces the influence sphere of the positive charge and therefore the electrical repulsion at the pyrrole radical cations decreases. Consequently the polymerisation reaction will be easier. Wei et al. [18] showed that the formation of the bipyrrrole, reactions 5.33 and 5.34, is the slowest step in the polymerisation of pyrrole. Therefore we concluded from these results that the dimerisation of the radical cations, reaction 5.34, is probably the rate-determining step for the polymerisation.

5.4.5 Conclusions

Calculations, based on hydrolysis equilibria, show that there is no influence of the HClO₄ concentration on the Fe³⁺ equilibria for acid concentrations of 0.5 M and higher. These calculations are in agreement with UV/VIS and pH measurements.

At acid concentrations of 2.0 M and higher the sheet resistance of the polypyrrole film increases because of the acid-catalysed polymerisation of pyrrole.

If an excess of oxidant is used the polymerisation rate is determined by the perchlorate concentration and not by the acid concentration as suggested by others [13]. We conclude that the perchlorate ions promote the dimerisation of the radical cations by reducing the electrical repulsion between the radical cations. This indicates that the dimerisation of the pyrrole radical cations is the rate-determining step and not the electron-transfer from pyrrole to the Fe³⁺ as suggested by others [13].

5.5 In summary

In the chapters 3, 4, and 5 the diverse process steps used for the in-situ polymerisation of pyrrole on an epoxy substrate are investigated and optimised. The results lead to the following optimal process. The substrate was first cleaned with acetone. By carefully turning, both sides of the substrate were corona treated with a solid-state Tantec Model HV 05-2 generator at about 90 W and about 25 kHz for 10 seconds. Subsequently, the substrate was dipped in a solution of pyrrole in 2-propanol (50% v/v). Finally the substrate was immersed in an oxidant solution containing 30.98 g of Fe(ClO₄)₃*9H₂O (0.30 M), 21.7 ml of 60% HClO₄ (1.0 M) and 200 ml demiwater at 0°C for 30 minutes. After polymerisation the substrate was rinsed with demiwater and dried at room temperature.

In the following chapters, however, a slightly different process was used. All process steps were the same except the polymerisation was done in an aqueous solution containing 0.20 M Fe(ClO₄)₃*9H₂O and 1.0 M HClO₄ at 0°C for 25 minutes.
This modified process was also used for the polymerisation of pyrrole on diverse plastics, polypropene, PP Stamylan (DSM), poly(acrylonitrile-butadiene-styrene), ABS Cycolan G151 (GE Plastics), and poly-ether-imide, PEI Ultem 1000 (GE Plastics). Because of the low density of PP, PP floated on the oxidant solution. Nevertheless, the sheet resistance of the polypyrrole polymerised on PP was comparable to those polymerised on the epoxy resin. ABS was observed to be not chemically resistant against pyrrole. This resulted in the deposition of a thicker and rougher polyppyrrrole layer with a lower sheet resistance on the ABS. The polyppyrrrole layers polymerised on PEI were smooth and the sheet resistance was also comparable to those polymerised on the epoxy resin. These examples show that this process can also be used for the polymerisation of pyrrole on other polymer substrates.

5.6 Electrochemical characterisation of polyppyrrrole

5.6.1 Introduction

Because these polyppyrrrole layers were used for the electrodeposition of copper the polyppyrrrole layers were electrochemically characterised with cyclic voltammetry, especially the first cycle was studied. The electrodeposition of copper was studied between 0.0 and −0.8 V vs. SCE therefore the cyclic voltammogram was started in the cathodic direction from the open current potential (ocp) and scanned between 0.5 and −1.0 V vs. SCE.

To our knowledge the electrochemical characterisation of chemically synthesised polyppyrrrole is not reported earlier. Electrochemically synthesised polyppyrrrole has been investigated intensively with cyclic voltammetry [23-28]. The cyclic voltammogram is depending on the dopant (D) in the polymer [23], the anion (A) in the electrolyte [23,25,26], and the cation (M+) in the electrolyte [26], see equations 5.39, 5.40, and 5.41. The transport of different dopants, anions, and cations through the polyppyrrrole increase with decreasing size [26,27] hence the oxidation and reduction potentials are depending on the electrolyte and dopant used. Because in our case the dopant and the anion in the electrolyte are both perchlorate equation 5.40 can be disregarded.

\[
Pp{Py}^{+} / D^{-} \rightarrow Pp{Py}^{red} + D^{ox}^{-} \quad (5.39)
\]

\[
Pp{Py}^{+} / D^{-} \rightarrow Pp{Py}^{red} / D^{ox}^{+} + A^{-} \quad (5.40)
\]

\[
Pp{Py}^{+} / D^{-} + M^{+} \rightarrow Pp{Py}^{red} / D^{ox}^{-} / M^{+} \quad (5.41)
\]
5.6.2 Results and discussion

Depending on the potential polypyrrole can be found in the reduced, non-conducting form or in the oxidised, conducting form. The first cycle of the cyclic voltammogram of polypyrrole, see figure 5.6, is similar to the following cycles and the voltammograms reported by others [23,24]. The first reduction peak at $-0.5 \text{ V}$ can be attributed to the reduction of polypyrrole to the non-conducting state. During the reduction the electroneutrality of the polypyrrole layer is restored by either expulsion of an anion or inclusion of a cation [26]. The second reduction peak at $-0.9 \text{ V}$ is irreversible and probably caused by the degradation of the polymer. After accepting an electron the polypyrrole will react with a proton to form a partially hydrogenated pyrrole unit, which explains the observed irreversibility.

There is an oxidation peak at $-0.1 \text{ V}$, which has a shoulder at $-0.3 \text{ V}$. During the oxidation of polypyrrole to the conducting form either a cation is expelled or an anion is included. The shoulder in the oxidation peak can be attributed to the expulsion of the cation, which is faster than the inclusion of an anion [26,27].

During the synthesis small amounts of iron were incorporated in the polypyrrole layer, as was shown with XPS, see table 5.5. The two redox couples of iron, $\text{Fe}^{2+}/\text{Fe}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$, have an equilibrium potential at $-0.68 \text{ V}$ and $0.53 \text{ V}$ vs. SCE, respectively. It can decide that the iron is most probably in the $\text{Fe}^{2+}$ state, when considering the equilibrium potentials of the iron couples and the ocp ($0.325 \text{ V}$ vs. SCE). The $\text{Fe}^{2+}/\text{Fe}$ reduction peak is not found because the iron concentration was probably too low with respect to the reduction of polypyrrole. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ oxidation peak is expected at higher voltages than the voltages used in this cyclic voltammogram.

The oxidation and reduction peaks are broad. This is caused by the two different oxidation and reduction mechanisms, equations 5.39 and 5.41, and because polypyrrole is not

![Cyclic voltammogram for polypyrrole in a 0.1 M LiClO₄ solution at a scan rate of 25mV/s.](image-url)

**Figure 5.6** Cyclic voltammogram for polypyrrole in a 0.1 M LiClO₄ solution at a scan rate of 25mV/s.
a homogeneous polymer. Polypyrrole contains structural defects, like carbonyls and hydroxyls, and polymer chains of different length, which cause a slight change in the oxidation and reduction potential and thus broad peaks.

5.6.3 Conclusions

The cyclic voltammogram of polypyrrole shows that polypyrrole is in the reduced non-conducting form at potentials of \(-0.5\) V and lower and in the oxidised conducting form at potentials of \(-0.2\) V and higher.

5.7 Conclusions

The rate of the polymerisation reaction increases with increasing Fe(ClO₄)₃ concentration and therefore the polypyrrole layer becomes thicker and the sheet resistance decreases.

The sheet resistance depends on the HClO₄ concentration for Fe(ClO₄)₃ concentrations of 0.30 M and lower. Calculations of the influence of the acid concentration on the Fe³⁺ hydrolysis equilibria are in good agreement with UV/VIS and pH measurements. These calculations and experiments in which HClO₄ was replaced by LiClO₄, show that the polymerisation rate of pyrrole is determined by the perchlorate concentration and not by the acid concentration. The perchlorate ions promote the dimerisation of the radical cations by reducing the electrical repulsion between the radical cations. This indicates that the dimerisation of the pyrrole radical cations is the rate-determining step.

The optimisation of the diverse process steps described in the chapters 3, 4, and 5 leads to the following process. The substrate was first cleaned with acetone. By carefully turning, both sides of the substrate were corona treated with a solid-state Tantec Model HV 05-2 generator at about 90 W and about 25 kHz for 10 seconds. Subsequently, the substrate was dipped in a solution of pyrrole in 2-propanol (50% v/v). Finally the substrate was immersed in an oxidant solution containing 30.98 g of Fe(ClO₄)₃·9H₂O (0.30 M), 21.7 ml of 60% HClO₄ (1.0 M) and 200 ml demiwatuer at 0°C for 30 minutes. After polymerisation the substrate was rinsed with demiwatuer and dried at room temperature. This process is successfully used for the polymerisation of pyrrole on other plastics.

The cyclic voltammogram of polypyrrole shows that polypyrrole is reduced into the non-conducting form at potentials of \(-0.5\) V and lower and oxidised into the conducting form at potentials of \(-0.2\) V and higher.

References


The Electrochemical Deposition of Copper on a Polypyrrole Layer
Chapter 6

Introduction
6.1 Electrochemical deposition of metals on intrinsically conductive polymers

Intrinsically conductive polymers (ICP’s) have been electrochemically synthesised on conducting substrates to study the electrochemical deposition of metals like copper, nickel, and lead on these ICP’s [1-3]. Some investigations have focussed on the insertion of metals, like palladium and platinum, as catalysts into these ICP’s [4,5]. For some noble metals, silver and palladium, spontaneous deposition on polyaniline was reported [6].

The electrochemical deposition of copper on the ICP’s polydiethylene, polyaniline, and poly(3,4-ethylenedioxythiophene) applied on non-conducting substrates has been investigated intensively [6-11]. The sheet resistances of the polymeric films were about 0.2 – 1.0 kΩ/□. These studies have shown that the copper nuclei are formed within a short distance from the contact and have a dendritic growth. With further growth, these dendrites bridge together to form a continuous copper layer. In front of this continuous layer again a zone with nuclei is formed. The growth process is repeated and the zone with copper nuclei propagates laterally during growth, see figure 6.1. The lateral propagation velocity is henceforth called front velocity (\(v_{\text{front}}\)).

For an efficient metallization process this front velocity must be as fast as possible. The front velocity increases at more negative deposition potentials [10,11]. The use of different commercial copper baths, which contain diverse organic molecules, also influences the front velocity [11].

Besides a fast metallization process the uniformity of the electrodeposited copper layer is also important for a commercial application. During the growth in the lateral direction the copper layer also grows with a certain velocity in the vertical direction, henceforth called thickening velocity (\(v_{\text{Cu-Cu}}\)). The front velocity and the thickening velocity cause a non-uniform growth of the copper layer during deposition. De Leeuw et al. [11] demonstrated that non-uniformity of the deposited copper layers is equal to the ratio between the thickening velocity and the front velocity (\(v_{\text{Cu-Cu}}/v_{\text{front}}\)). Therefore the deposition potential and the used (commercial) copper bath influence also non-uniformity [11].

Figure 6.1  Schematic representation of the electrodeposition of copper on polypyrrole.
6.2 Choice of substrate

The electrochemical deposition of metals normally occurs at structural defects. To avoid the influence of the surface of the substrate on the electrochemical deposition of copper as much as possible a smoother substrate than the epoxy resin used in the previous chapters is needed. Because of the smoother surface and the ease of synthesis, the polypyrrole layers were applied on poly-ether-imide (PEI) for the investigation of the electrochemical deposition of copper on polypyrrole layers.

Initial experiments showed that the front velocity is depending on the width of the substrate. Hence, it was decided to use a substrate with a standard width of 1 cm.

References

Chapter 7

Increasing the Front Velocity

This chapter is a modified version of: R.C.G.M. van den Schoor, R.H.M. van de Leur, and J.H.W. de Wit, "Electrochemical deposition of copper on polypyrrole: Increasing the lateral growth velocity", to be submitted.
Abstract

A high lateral growth velocity (front velocity) of copper on a polypyrrole layer is of significant commercial interest. This chapter concerns some aspects of the copper growth process on a polypyrrole layer. First, three methods to determine the front velocity are presented. Secondly, the influence on the front velocity of the potential and the addition of the organic molecules crystal violet, benzotriazole, and thiourea to the electrolyte are discussed.

Cyclic voltammetry and resistance measurements show that not only Cu$^{2+}$ but also the polypyrrole layer is reduced during the copper deposition. However, the reduction of polypyrrole does not stop the lateral copper growth.

At more negative deposition potentials the front velocity increases and the zone where copper nucleation takes place is shorter. The shorter nucleation zone is not caused by a sharper potential decay in the polypyrrole electrode but by the promotion of the nucleation of copper at more negative potentials.

Thiourea, in contrast to crystal violet and benzotriazole, increases the front velocity at more negative potentials.

7.1 Introduction

The deposition of copper on the conducting polymers polypyrrole, polyaniline and poly(3,4-ethylenedioxythiophene) has been reported [1-4]. The copper nuclei start to grow close to the contact and show a dendritic growth [2,5]. During the deposition these dendrites bridge together to form a continuous copper layer. In front of this continuous layer a new nucleation zone is formed. The growth process is repeated and, hence, the copper front propagates laterally during growth. The lateral propagation velocity is henceforth called front velocity. Front velocities of about 1 cm/min have been reported [4,5]. The front velocity can be increased by using a more negative deposition potential [4,6] or by using different commercial copper baths, where different organic molecules which level and brighten the deposited copper layer are added to [4]. In this chapter the determination of the front velocity is discussed before the influence of the deposition potential and different additives on the front velocity is presented.

7.2 Experimental

Poly-ether-imide substrate, PEI Ultem 1000 (GE Plastics) was cut into pieces of 1.0 x 7.5 cm$^2$. CuSO$_4 \cdot 5$H$_2$O (Fluka Chemika), H$_2$SO$_4$ (Fluka Chemika), crystal violet (Fluka Chemika), thiourea (Fluka Chemika), 1H-benzotriazole (Fluka Chemika), and silver paint (Heraeus) were used as received.

A thin film of polypyrrole was synthesised on a poly-ether-imide (PEI) substrate with the method described in chapter 5. After drying, one side of the polypyrrole coated PEI
substrate was electrically disconnected from the sides by scratching the polypyrrole from the edges with a knife. Subsequently, a T-electrode was applied on the top of the polypyrrole film with silver paint to ensure good electrical contact, see figure 7.1.

All galvanic experiments were made potentiostatically in a simple one-component cell of 40 ml containing a copper foil of about 15 cm$^2$ as the counter electrode, a polypyrrole coated substrate at a distance of about 2 cm as the work electrode, and a saturated calomel reference electrode. An electrolyte containing 58.9 g CuSO$_4$ (0.94 M) and 8.2 ml H$_2$SO$_4$ (0.60 M) in 250 ml demiwater was used. The organic molecules crystal violet, benzotriazole, and thiourea, were added to the galvanic cell in a concentration of about 0.1 mM, being 1.6 mg, 0.5 mg, and 0.3 mg respectively. The potential during the deposition was controlled by an EG&G PAR 273 potentiostat/galvanostat, with EG&G PAR model 270 electrochemical analysis software 3.00.

Sheet resistances were measured by applying two parallel electrodes of silver paint with a distance of 1 cm. These electrodes have a negligible contact resistance and the sheet resistances are comparable with those measured with a standard four-probe resistance measurement.

The fraction of surface covered with copper was determined by using dark field microscopy. Because the substrate is flat the dendritical copper crystals can easily be seen with dark field microscopy. After digital storage on a computer the ratio between the dark and light areas, which is taken as the ratio between the polypyrrole and copper layer, can be determined along the surface.

### 7.3 Determination of the front velocity

There are three methods to determine the front velocity. The first two methods are based on measuring the time-dependent current. In the third method the length of the copper layer is measured.

#### 7.3.1 Method 1

For the first method we assume that after the deposition of a thin copper layer a stationary state is formed. The rate of change of the copper ion concentration in the diffusion
layer between the deposited copper and the electrolyte as a function of the distance to the substrate is given by Fick’s second law of diffusion

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial y^2}
\] (7.1)

where \( c \) is the copper ion concentration (mol/l), \( D \) is the diffusion coefficient (m\(^2\)/s) and \( y \) is the distance to the substrate (m). The boundary conditions are

\[
y = 0, \ c = 0 \quad \text{and} \quad y = \delta, \ c = c_b
\]

where \( \delta \) is the thickness of the diffusion layer (m) and \( c_b \) is the concentration of the copper ions in the bulk of the solution (mol/m\(^3\)).

In the stationary state \( \partial c/\partial t = 0 \), thus

\[
\frac{\partial^2 c}{\partial y^2} = 0
\] (7.2)

Integration and substitution of the boundary conditions gives the ion concentration

\[
c = \frac{c_b}{\delta} \ y
\] (7.3)

Fick’s first law of diffusion describes the flux, the moles copper deposited per second per unit area

\[
\Phi_a = -D \frac{\partial c}{\partial y}
\] (7.4)

After substitution of equation 7.3 in this equation we obtain

\[
\Phi_a = -D \frac{c_b}{\delta}
\] (7.5)

This equation shows that the flux per unit area is constant.

For the total flux we can write

\[
\Phi(t) = \Phi_a A(t)
\] (7.6)
where $A$ is the area covered with copper (m$^2$).

The relation between the flux and the electrolysis current ($I$) is given by

$$ I = -nF\Phi $$  \hspace{1cm} (7.7)

where $n$ is the number of electrons needed for the electrolysis reaction ($= 2$), $F$ is the constant of Faraday ($9.65 \times 10^4$ C/mol).

After substitution of equation 7.6 we obtain

$$ I(t) = 2F\Phi_0 A(t) $$  \hspace{1cm} (7.8)

and the derivative of this equation is

$$ \frac{\partial I(t)}{\partial t} = 2F\Phi_0 \frac{\partial A(t)}{\partial t} $$  \hspace{1cm} (7.9)

In the case the total surface is covered with copper the current is given by

$$ I_{\text{max}} = 2F\Phi_0 A = 2F\Phi_0 bl_{\text{Cu}} $$  \hspace{1cm} (7.10)

where $I_{\text{max}}$ is the current when the total surface is covered with copper, $b$ is the width of the area covered with copper (m), and $l_{\text{Cu}}$ is the length of the area covered with copper (m).

The area of the copper layer increases until the total surface is covered with copper. For the increasing area covered with copper we can write

$$ A(t) = bl_{\text{Cu}}(t) $$  \hspace{1cm} (7.11)

and the derivative of this equation is

$$ \frac{\partial A(t)}{\partial t} = b \frac{\partial l_{\text{Cu}}(t)}{\partial t} = bv_{\text{front}}(t) $$  \hspace{1cm} (7.12)

where $v_{\text{front}}(t)$ is the front velocity at time $t$ (m/s).

After substitution of equations 7.10 and 7.12 in equation 7.9 we obtain

$$ \frac{\partial I(t)}{\partial t} = \frac{I_{\text{max}}}{l_{\text{Cu}}} v_{\text{front}}(t) $$  \hspace{1cm} (7.13)

or
\[ v_{\text{front}}(t) = \frac{I_{\text{Cu}}}{I_{\text{max}}} \frac{\partial I(t)}{\partial t} \]  

(7.14)

With this equation the front velocity of the copper deposition can be determined at any moment during the electrolysis from the derivative of the current-time curve.

### 7.3.2 Method 2

For the second method we use the same assumptions as for the first method, but additionally we assume that the front velocity is constant from \( t = 0 \), then

\[ \frac{\partial I}{\partial t} = \frac{\Delta I}{\Delta t} = \frac{I_{\text{max}}}{t_{\text{max}}} \]  

(7.15)

where \( t_{\text{max}} \) is the time needed to get the maximal current \( (I_{\text{max}}) \) (s). Furthermore, the length of the area covered with copper \( (l_{\text{Cu}}) \) is almost as large as the length of the polypyrrole layer, which has to be deposited with copper \( (l_{\text{PPy}}) \), when the total area is covered with copper. After substitution in equation 7.14 the front velocity becomes

\[ v_{\text{front}} = \frac{l_{\text{PPy}}}{t_{\text{max}}} \]  

(7.16)

With this equation the front velocity can also be determined from the current-time curve.

### 7.3.3 Method 3

With the last method we do not have to wait till the total substrate is covered with copper to determine the front velocity. Then we can write for equation 7.16

\[ v_{\text{front}} = \frac{I_{\text{Cu}}}{t_{\text{dep}}} \]  

(7.17)

where \( t_{\text{dep}} \) is the total deposition time (s). With this equation the front velocity is determined from the length of the area covered with copper.

### 7.3.4 Comparison and conclusions

The current-time curve, see figure 7.2, shows a jump in the current at the beginning of the copper deposition. Subsequently the current increases constantly until the copper front
reaches the end of the substrate, where the current levels off and becomes constant. The jump in the current at the beginning of the copper deposition is due to the immediate deposition of copper on the ohmic contact. The constant increase of the current indicates that the front velocity is constant over almost the total length of the substrate, see equation 7.14, assuming that the deposition velocity in the vertical direction is constant over the total surface covered with copper. At the moment the current levels off the end of the substrate is reached and therefore the 3D copper growth at the crystals changes in a 2D growth when a well-connected polycrystalline copper film is formed.

With equation 7.14 the front velocity can be determined for the interval where the current increases constantly. The error in the front velocity determined with this method is estimated at 5%.

The front velocity is easier to determine with equation 7.16. However, this method includes the two deviations in the current-time curve, where the increase of the current is not constant. These two deviations have the opposite effect, so the total deviation from the actual front velocity will be small. Because the estimation of $t_{\text{max}}$ is not always apparent, see figure 7.2, the error in the front velocity is estimated at 15%.

For the determination of the front velocity with equation 7.17 the length of the area deposited with copper has to be measured. However, the front of the copper layer is very difficult to determine because of the formation of the copper nuclei in front of the well-connected polycrystalline copper film. Furthermore, this method does not correct for the irregularity at the beginning of the copper deposition. In practice we always covered the total area with copper, and therefore this method could not be used for the determination of the front velocity.

![Current Time Curve](image)

**Figure 7.2** Current time curve of the electrodeposition of copper on polypyrrole in a solution containing 0.94 M CuSO$_4$, and 0.6 M H$_2$SO$_4$ in water at -0.4 V vs. SCE.
Summarising, the front velocity can not be determined from the length of the deposited copper and the deposition time, method 3, because the total length is always covered with copper. Method 2 includes the periods where the front velocity is not constant and furthermore the determination of the time needed to reach the maximal current is not always apparent. Therefore the most suited method to determine the front velocity is from the slope and the maximal current from the current time curve, equation 7.14.

7.4 Influence of the potential

7.4.1 Cyclic voltammogram and potential

For a faster metallization process the front velocity must be increased. This can among other things be established by a more negative deposition potential [4,6]. Before discussing the influence of the deposition potential the cyclic voltammograms of polypyrrole and copper are compared, see figure 7.3.

Figure 7.3 shows the cyclic voltammogram of polypyrrole and the cyclic voltammogram of copper. The cyclic voltammogram of polypyrrole was already discussed in chapter 5. The reduction peak at $-0.5 \text{ V}$ can be attributed to the reduction of polypyrrole into the non-conducting form. The reduction peak at $-0.9 \text{ V}$ is caused by the degradation of the polymer. During the oxidation of polypyrrole either an anion is included or a cation is expelled, which respectively results in an oxidation peak at $-0.1 \text{ V}$ and a shoulder at $-0.3 \text{ V}$. From the voltammogram of copper it can be deduced that above $0.05 \text{ V}$ copper dissolves and at more negative values copper deposits. During the electrochemical deposition of copper a

![Cyclic voltammograms for polypyrrole in a 0.1 M LiClO₄ solution (--) and for copper in a 0.94 M CuSO₄ / 0.60 M H₂SO₄ solution (--) at a scan rate of 25mV/s.](image)

Figure 7.3  Cyclic voltammograms for polypyrrole in a 0.1 M LiClO₄ solution (--) and for copper in a 0.94 M CuSO₄ / 0.60 M H₂SO₄ solution (--) at a scan rate of 25mV/s.
potential is applied to the contact. Figure 7.3 shows that during the deposition two processes occur. First the copper is formed

\[ \text{Cu}^{2+} + 2e_{\text{ox}}^{\text{red}} \leftrightarrow \text{Cu} \quad (7.18) \]

and secondly as shown in chapter 5 the polypyrrole layer will become non-conducting by either expelling an anion or including of a cation, equation 5.39 and 5.41 respectively,

\[ \text{PPY}^{+} / D^- + e_{\text{ox}}^{\text{red}} \leftrightarrow \text{PPY} + D^- \quad (7.19) \]

\[ \text{PPY}^{+} / D^- + M^+ + e_{\text{ox}}^{\text{red}} \leftrightarrow \text{PPY} / D^- / M^+ \quad (7.20) \]

It was found that at all applied potentials, viz. between $-1.0$ V and $0.0$ V vs. SCE, copper is formed on the polypyrrole electrode, indicating that the copper deposition always occurred during the electrodeposition. The reduction of polypyrrole also occurred because the sheet resistance of the polypyrrole layer is higher after peeling off the copper. Furthermore, as soon as copper is deposited the current will flow through the copper because of the high conductivity of copper. Thus, before the polypyrrole layer becomes non-conductive, enough copper is deposited to conduct the current.

Figure 7.4 shows the influence of the deposition potential on the front velocity. The front velocity increases at more negative deposition potentials. The difference in the front velocity can possibly be understood by investigating the distribution of the copper nuclei in the copper nucleation zone.

![Figure 7.4](image)

**Figure 7.4** Influence of the deposition potential on the front velocity ($v_{\text{front}}$) during the deposition of copper on a polypyrrole layer.
7.4.2 The copper nucleation zone

The difference in the applied potential has an effect on the front velocity and it is probable that this is due to a different mechanism of the initial stages of the copper deposition and thus must be seen in the zone after the copper front where the copper nucleation takes place, see figure 7.5. Because of the different potential the width of the copper nucleation zone can differ [4].

The width of the copper nucleation zone and the density of the copper nuclei in the copper nucleation zone were investigated by determining the fraction of surface covered with copper ($f_{rCu}$) in the copper nucleation zone, see figure 7.6. At longer distance than 0.25 cm from the copper front some individual copper crystals were found on the polypyrrole layer.

![Diagram](image)

**Figure 7.5** Schematic representation of the electrodeposition of copper on polypyrrole.

![Graph](image)

**Figure 7.6** Fraction of the surface covered with copper ($f_{rCu}$) as function of the distance from the beginning of the copper nucleation zone at different deposition potentials, -0.20 V (●), -0.40 V (■), and -0.60 V (▲).
However, these crystals do not significantly contribute to the fraction of surface covered with copper. Figure 7.6 shows that the width of the copper nucleation zone increases at more positive deposition potentials. The different curves can be explained either by the decay in the potential in the work electrode or by a difference in the copper nucleation. The influence of the decay in the potential in the work electrode will be discussed in the next section.

7.4.3 The calculations of the decay of the potential in the work electrode

All experiments were conducted potentiostatically. For the determination of the decay in the deposition potential we consider the following system, see also figure 7.7. The counter electrode and the work electrode are at a fixed distance of each other, i.e. 2 cm. Furthermore the following assumptions are made: (I) The resistance of the counter electrode is negligible. (II) The resistance between the work electrode and the counter electrode is determined by the solution situated between these electrodes. (III) The potential drop over already plated polymer can be disregarded. (IV) The potential drop between the reference electrode and work electrode is negligible.

For the resistance in the solution at a distance \( u \) from the front we can write

\[
\partial \left( \frac{1}{R(u)} \right) = \sigma, \partial u
\]  
(7.21)

where \( \sigma \) is the conductivity of the solution per unit electrode length. For the current through the solution at position \( u \) we can write

\[
\partial I(u) = - \frac{\partial I}{\partial u} \partial u
\]  
(7.22)

![Diagram](image)

**Figure 7.7** Configuration used for the calculation of the potential decay in the electrode.
Combining these equations gives an expression for the potential drop in the solution at position \( u \)

\[
\Delta V(u) = -\frac{1}{\sigma_s} \frac{\partial I}{\partial u}
\]  
(7.23)

For the resistance in the work electrode at position \( u \) we can write

\[
R(u) = \rho_e \partial u
\]  
(7.24)

where \( \rho_e \) is the resistance of the work electrode per unit length.

For small \( \partial u \) the current through the solution at position \( u \) can be neglected, then the current at position \( u \) in the work electrode becomes

\[
I(u) = I(u + \partial u)
\]  
(7.25)

We can now write for the potential drop in the work electrode

\[
\partial V(u) = -I(u)\rho_e \partial u
\]  
(7.26)

or

\[
I(u) = \frac{1}{\rho_e} \frac{\partial V}{\partial u}
\]  
(7.27)

For the potential in the work electrode we can also write

\[
V(u) = \Delta V(u = 0) - \Delta V(u)
\]  
(7.28)

After combining this equation with equation 7.23 and 7.27 we find

\[
\Delta V = -\frac{1}{\rho_e \sigma_s} \frac{\partial^2 \Delta V}{\partial u^2}
\]  
(7.29)

For the first boundary condition the potential in the electrode must be defined. If we assume that the potential drop of the solution between the reference electrode and the work electrode is negligible, the potential in the electrode can be replaced by the overpotential, \( \eta \). Because the voltage drop over already electroplated polymer can be disregarded, the overpotential at the front is equal to the overpotential at the contact, \( \eta_0 \). The second boundary condition is that no current is flowing through the insulated end of the strip. Thus, the boundary conditions are
\[ \Delta V(\mu = 0) = \eta_0, \quad \text{and} \]
\[ I(x = L) = 0 \]

By taking the boundary conditions the potential decay in the work electrode can be solved as a function of the distance

\[
\eta(u) = \eta_0 \left( \exp \left[ -u(\rho_e \sigma_s)^{1/2} \right] + \frac{\exp \left[ u(\rho_e \sigma_s)^{1/2} \right]}{1 + \exp \left[ 2L(\rho_e \sigma_s)^{1/2} \right]} \right) \tag{7.30}
\]

Because the length of the electrode, \( L \), is much larger than the distance in which the nucleation occurs, the potential can be approximated by

\[
\eta(u) = \eta_0 \exp \left[ -u(\rho_e \sigma_s)^{1/2} \right] \tag{7.31}
\]

De Leeuw et al. [4] found a similar expression for the decay in the overpotential using the same assumptions and looking to the drop in the current due to the deposition of copper on the conducting polymer

\[
\eta(u) = \eta_0 \exp \left[ -u(R_\square c_{Cu-pol})^{1/2} \right] \tag{7.32}
\]

where \( u \) is the distance to the front (cm), \( R_\square \) is the sheet resistance of the polymer, \( c_{Cu-pol} \) is the current density for electroplating the conducting polymer at unit voltage overpotential (S/cm\(^2\)), and \( \eta_0 \) is the overpotential at the contact (V). To determine the current density, \( c_{Cu-pol} \), they assume a percolation threshold of 20\% and estimate the thickness of the copper crystals, which is difficult for dendrites. A percolation threshold of 20\% is disputable because the nuclei are not formed totally randomly on the surface, but depend on the position of the already formed crystals. Therefore it is better to use our method because the determination of the conductivity of the solution per unit length is more accurate.

To calculate the potential decay with equation 7.31 the resistance in the work electrode, \( \rho_e \), and the conductivity of the electrolyte, \( \sigma_s \), have to be determined. Because the width of the used electrode is 1 cm the resistance in the work electrode per unit length, \( \rho_e \), is equal to the sheet resistance, which is about 550 \( \Omega \). The distance between the counter electrode and the work electrode is 2 cm and the conductivity of the electrolyte is 0.17 S/cm. So, the conductivity of the solution per unit electrode length, \( \sigma_s \), is 0.085 S/cm. Because the equilibrium potential of the copper deposition is about 0.05 V vs. SCE and the applied potentials are -0.2, -0.4, and -0.6 V the overpotentials are -0.25, -0.45, and -0.65, respectively.

Figure 7.8 shows the overpotential as function of the distance to the front calculated with equation 7.31. This figure shows that the overpotential is negligible after a distance of about 0.5 cm from the front for all potentials. Nuclei are deposited over a distance to the
Figure 7.8 Overpotential as function of the distance to the front, \( u \), calculated with equation 7.31 for diverse overpotentials, -0.65 V, -0.45 V, and -0.25 V.

front where the overpotential still is significant. Therefore, almost no copper nuclei are expected at a distance of more than 0.5 cm from the front.

Because the factor, \( (\rho_0 \sigma)^{0.5} \), in equation 7.31 is the same for every overpotential at the contact, \( \eta_0 \), all the functions at any potential can be converted into each other, there is only a shift in the \( u \)-direction. Therefore it is expected that from the percolation point the copper nucleation zone is longer and the surface area percentage of copper decreases more gradually at more negative potentials. However, the opposite is found in figure 7.6 and therefore the potential decay can not explain the difference in length of the copper nucleation zone. The influence of the potential on the copper nucleation will be discussed in the next paragraph.

7.5 Influence of additives on the copper deposition

7.5.1 Introduction

The results of De Leeuw et al. [4] show that the front velocity depends on the type of (commercial) bath used. The additives used in these baths can possibly increase the front velocity by suppressing the vertical growth and/or promoting the lateral growth of the copper crystals [7].

Nichols et al. [8,9] already investigated the influence of a benzothiazole derivative on the initial stages of copper electrodeposition on electrochemical synthesised polypyrrole. However, they found no influence of this additive and therefore we chose other additives, viz. crystal violet, benzotriazole, and thiourea. The influence of these organic molecules on the deposition of copper on other materials than polypyrrole was already investigated.
Nichols et al. [10,11] investigated the influence of crystal violet on the electrochemical deposition of copper on gold and found that crystal violet suppresses the vertical growth of copper.

Benzotriazole diminishes the copper crystal growth and the copper crystals become flatter [7]. The former is caused by the formation of a Cu(I)BTA complex [12,13]. The latter is due to the diminishing of the surface diffusion of copper ions [14]. Furthermore, benzotriazole co-ordinates to the copper surface with two triazole nitrogen's [13,15,16]. After adding benzotriazole the deposition potential of copper shifts to more negative potentials [15].

Although thiourea causes a continuous development of fresh small nuclei on the surface [14,17], thiourea is not incorporated during the copper deposition [18]. These copper nuclei exhibit an inhibition growth limited in the vertical and diffusion limited growth in the lateral direction by thiourea [7]. Furthermore, thiourea co-ordinates with its sulphur to the copper surface [18,19]. At thiourea concentrations of 0.07 mM the deposition potential of copper onto a glassy carbon electrode is already shifted to more negative potentials [17]. On the other hand, at 0.1 mM thiourea had only little effect on the electrochemical behaviour of the copper electrode [18]. In this paragraph the influence of these additives, viz. crystal violet, benzotriazole, and thiourea, on the front velocity is discussed.

**7.5.2 Additives**

The dependence of the front velocity on the different additives at several deposition potentials is given in figure 7.9. This figure shows that the front velocity increases at more negative deposition potentials. The addition of crystal violet and benzotriazole does not
improve the front velocity. However, if thiourea is used there is an increase in the front velocity at more negative potentials. This influence of thiourea is studied by investigating the copper nucleation zone.

### 7.5.3 Copper nucleation zone

Because the front velocity increases after addition of thiourea this must also be noticed at the copper nucleation zone. Therefore the copper nucleation zones deposited at diverse potentials and with and without thiourea are investigated. First the width of the copper nucleation zone is investigated. The width of the copper nucleation zone deposited with thiourea increases with increasing deposition potential as was also found in the case where no additives were used, see paragraph 7.4. However, the crystal structure changes when thiourea is added, see figure 7.10 and 7.11. At −0.2 V the copper dendrites with thiourea are slightly larger than without thiourea, see figure 7.10. However, at −0.6 V there are more and smaller dendrites when thiourea is used, indicating that thiourea promotes the nucleation of copper crystals. Because the deposits are smaller and thinner, less copper is needed to cover an equal area. Therefore the front velocity is faster when thiourea is used.

![Figure 7.10](image1.png) **Figure 7.10** Dark field microscopy picture of copper deposited on polypyrrole at −0.2 V without (left) and with (right) thiourea.

![Figure 7.11](image2.png) **Figure 7.11** Dark field microscopy picture of copper deposited on polypyrrole at −0.6 V without (left) and with (right) thiourea.
Furthermore, figure 7.11 with thiourea shows clearly two types of copper crystals; large crystals and small ones in between. For copper nucleation zones at other potentials and without additives more or less the same results were found. In general there are individual copper nuclei formed far from the front. Closer to the front these nuclei become larger and some new nuclei are formed in between. Even if the copper crystals cover almost the entire surface we still see some larger crystals with smaller crystals in between. However, the number of small crystals decreases at more positive deposition potentials, especially when thiourea was added only a few small crystals were found between the larger crystals at −0.2 V. This indicates that the copper is deposited depending on the potential. At −0.2 V the copper deposits in one phase on the substrate. However, at −0.4 V and lower the copper deposits in two phases. First there is the formation of the initial nuclei in front of the continuous copper layer. Secondly, there is the formation of the nuclei between the initial nuclei.

If we assume that this second phase starts at a potential between −0.2 V and −0.4 V the width of the copper nucleation zone can be explained. At −0.2 V the width of the copper nucleation zone is longer because the deposition of the nuclei between the initial nuclei is not promoted at this potential. However, at −0.4 V and lower the deposition between the initial nuclei becomes easier and therefore the spaces between the initial copper nuclei will be filled faster, resulting in a smaller copper nucleation zone, as already seen in figure 7.6.

If furthermore, is assumed that thiourea promotes the nucleation in the second phase and not the initial nucleation the influence of thiourea can also be explained. The front velocity at −0.2 V does not increase after addition of thiourea because the second phase does not occur at this potential. At more negative deposition potentials, however, the second phase becomes more important and therefore the effect of thiourea becomes larger with decreasing deposition potential, resulting in an increase in the front velocity, as already seen in figure 7.9.

7.6 Conclusions

For a faster metallization process the front velocity must be increased. The most suited method to determine the front velocity is from the slope and the maximal current from the current time curve, equation 7.14.

Cyclic voltammetry and sheet resistance measurements showed that beside the reduction of Cu²⁺ the polypyrrole layer is also reduced during the copper deposition. However, this does not stop the copper growth.

The front velocity can be increased by lowering the deposition potential down to −0.6 V. At more negative deposition potentials, the deposition of copper nuclei between the initial nuclei is promoted, resulting in a smaller copper nucleation zone.

The additives benzotriazole and crystal violet do not influence the front velocity. On the other hand, thiourea increases the front velocity at more negative deposition potentials. Thiourea additionally promotes the nucleation of copper crystals between the initial nuclei, which occurs at more negative deposition potentials. Because the deposits are smaller and thinner, less copper is needed to cover an equal area and therefore the front velocity is faster.
References

Influence of Thiourea on the Growth of Copper Crystals: an Electrochemical Atomic Force Microscopy Study
Abstract

Electrochemical atomic force microscopy (EC-AFM) was used to study the effect of thiourea on the growth and the form of the copper crystals. The AFM data show that without thiourea the copper crystals are smooth and the form is determined by the morphology of surface. Thiourea inhibits the growth velocity of the copper crystals in the vertical and lateral direction, causing the layered structure of the copper crystals.

8.1 Introduction

Thiourea increases the front velocity by promoting the nucleation of the copper crystals between the initial crystals as shown in the previous chapter. In this chapter the influence of thiourea on the growth of the copper crystals is discussed.

With Electrochemical Atomic Force Microscopy (EC-AFM) it is possible to follow the topographic changes of a surface in-situ while conducting a controlled electrochemical experiment. Nichols et al. [1,2] investigated the influence of the additive benzothiazole on the initial stages of copper electrodeposition on polypyrrole with in-situ EC-AFM. They polymerised pyrrole electrochemically on gold and therefore the deposition of copper on the polypyrrole layer occurred on the total surface. The copper concentration, however, decreases significantly during deposition because of the low volume of the electrochemical cell. This is not representative for the copper growth as discussed in chapter 7. In section 8.2 an improved measurement set-up is introduced.

The effect of additives on the growth of copper on various conducting substrates has been investigated with Scanning Probe Microscopy (SPM) [3-7]. Schmidt et al. [3] found that thiourea inhibited the surface diffusion of copper ions on gold. On Highly Ordered Pyrolytic Graphite (HOPG) thiourea exhibits an inhibition growth limited in the vertical and diffusion limited growth in the lateral direction [7]. In this chapter the in-situ EC-AFM measurements and the effect of thiourea on the growth of the copper crystals are discussed.

8.2 Electrochemical Atomic Force Microscopy

8.2.1 Experimental set-up

Poly-ether-imide substrate, PEI Ultem 1000 (GE Plastics) was cut into pieces of 1.0 x 7.5 cm². CuSO₄·5H₂O (Fluka Chemika), H₂SO₄ (Fluka Chemika), thiourea (Fluka Chemika), and silver paint (Heraeus) were used as received.

In-situ EC-AFM measurements were conducted with a Nanoscope III scanning force microscope in the electrochemical AFM mode using standard Si₃N₄ tips at room temperature.

Before describing the experimental set-up of the EC-AFM, the principals of the AFM are discussed. An AFM can operate in different modes. Because the EC-AFM operates in the
contact mode only this mode is discussed. In this mode the AFM tip makes a soft contact with the sample. The tip has a low spring constant and hence during scanning the contact force causes the tip to bend to accommodate changes in topography.

The position of the tip is monitored with a laser. The laser is pointed to the top of the tip and the reflection is collected in a quadruple photodiode as depicted in figure 8.1. Because of the relative large distance between the tip and photodiode with respect to the bending of the tip, a small bending of the tip will cause a reasonable shift of the position of the laser on the photodiode and thus a change in the signal of the photodiode.

In the constant force mode a feed back loop is used to keep this signal, and thus the total force applied to the sample, constant, i.e., the signal is kept (nearly) constant by adjusting the vertical position of the sample with the piezo tube. In this way the vertical position of the piezo tube gives information on the topography of the sample during scanning.

For the EC-AFM measurements a glassy fluid cell made for these measurements, see figure 8.2, was placed on the sample. An O-ring separated the cell and the sample. The inner diameter of the O-ring was about 6.4 mm. The cantilever with AFM tip must be placed in the notch on the fluid cell. Furthermore, there is an inlet and an outlet for adding a liquid to the cell. The inlet is also connected to a tube where the reference electrode can be placed. The counter electrode can be put through a hole in the fluid cell, see figure 8.2. This hole was

![Figure 8.1 Schematic representation of an atomic force microscope (AFM).](image-url)
sealed with Teflon tape after the counter electrode was placed in it. The top of the piezo tube is linked as working electrode. However, the copper must be deposited on our sample. Therefore the sample (1.0 x 1.0 cm²) was attached onto a metal plate and the top of the sample was electrically connected to the metal plate with silver paint. The metal plate can be placed on the magnetic top of the piezo tube.

To compare the results in this chapter with the results in chapter 7 the experimental set-up as described in chapter 7 was maintained as much as possible. However, in the fluid cell a saturated calomel electrode (SCE) could not be used as reference electrode, instead a copper reference electrode was used, which had a potential of about 80 mV vs. SCE in the used copper solution. For practical reasons the counter electrode is very small in this electrochemical set-up and consequently a copper electrode will be dissolved fast, causing the reaction to stop. Therefore platinum was used as counter electrode.

A similar copper solution as in chapter 7 containing 0.94 M CuSO₄ and 0.60 M H₂SO₄ was used. When thiourea was used it had a concentration of about 0.1 mM in the copper solution.

The polypyrrole layer was applied on the PEI substrate with the same method as described in chapter 5. The sheet resistance of the polypyrrole layer was about 850 Ω/□.

To follow the copper growth an adequate area must be scanned continuously and as fast as possible. Therefore a scan size of 15 µm with a scan rate of 20 Hz was chosen.

### 8.2.2 Copper deposition

Because platinum was used as counter electrode two problems occurred. First, the copper concentration in the solution decreased slowly. The volume of the cell was about
28.65 mm³. For the experiments in chapter 7 the copper concentration decreased with maximal 1 % during growth. In the present experiment such a decrease corresponds to a coverage of 6.5 % assuming an average thickness of the copper crystals of 1.5 μm. Therefore, before the measurement was completed the copper concentration was reduced significantly and thus the copper growth was affected.

Secondly, the following anodic reaction is taking place on the platinum counter electrode

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\overline{\text{e}} \] (8.1)

The O₂ gas, which was formed, could not escape and at a certain moment this gas bubble was so large it interfered with the laser of the AFM. At that moment the surface topography could not be followed and the measurement was stopped. Moreover, the acid concentration increases, which has also an effect on the copper deposition [8].

To avoid the above problems the experimental set-up was changed. The copper solution was pumped through the cell with a Cole-Parmer Instrument Company Masterflex Microprocessor Pump Drive with a speed of 0.16 ml/min, so the solution was refreshed about every 10 seconds.

For the investigation of the copper deposition, in first instance, similar potentials as used in chapter 7 were applied. However, at these potentials the growth of the copper nuclei is so fast it can not be followed with the AFM. Therefore we chose a less negative deposition potential. At these potentials it was possible to follow the copper growth without and with thiourea as additive, see figure 8.3 and 8.4, respectively.

Due to the fact that the potential decay in the polypyrrole layer and the position of the measured area with respect to the copper front are not known, the potentials at the measured areas are not known exactly and thus should be compared with reserve. However, the differences between the used potentials are small, hence the potential at the crystals will not significantly differ.

The settings of the AFM are depending on the substrate and can not be changed during the measurements. Because in our case copper is growing on the polypyrrole surface the used settings were not always optimal for the copper and hence sometimes the tip did not follow the surface. An example is found in figure 8.4 b,c,d. Comparing figure 8.4 b and 8.4 c the copper crystal looks to be grown to the left parallel in the scanning direction. However this is disappeared in figure 8.4 d, indicating that the AFM settings are not optimal.

Occasionally the formed copper crystals disappeared. In figure 8.4 i,j, for instance, the formed copper crystal in the right corner of the scanned area was suddenly gone. This disappearing of the copper crystals is probably caused by the contact between the tip and the surface, suggesting that the AFM measurements influence the copper deposition.

Thiourea influences the copper deposition by adsorption on the copper surface through the sulphur [9,10]. The contact between the tip and the surface will affect this adsorption and therefore can affect the copper growth. However, the contact was not so dominant that thiourea did not influence the copper growth, as will be shown below.

93
Figure 8.3  Sequence of in-situ EC-AFM images during copper electrodeposition on a polypyrrole layer. The electrolyte was 0.60 M H₂SO₄ + 0.94 M CuSO₄ and the applied electrode potential was -35 mV vs. Cu/Cu²⁺.
Figure 8.4  Sequence of in-situ EC-AFM images during copper electrodeposition on a polypyrrole layer. The electrolyte was 0.60 M H₂SO₄ + 0.94 M CuSO₄ + 0.1 mM thiourea and the applied electrode potential was −70 mV vs. Cu/Cu²⁺.
8.3 Copper crystals

8.3.1 Growth velocity

The increase in the width (in the AFM scan direction) and the height of the copper crystals in time are a measure for the rate of the copper growth in the lateral and vertical direction, respectively. The width in the perpendicular direction to the scan direction can not be used because this width is elongated significantly during scanning. Hence, the width in the scan direction is used. For the copper solutions with and without thiourea the height and the width at the top of the copper crystals and the time interval between measuring the top were determined, see figure 8.5. This figure shows that the increase of the width and height of the copper crystals slowly decreased in time.

Although the increase in the width and height of the copper crystal for the bath with or without thiourea do not differ a lot the increase without thiourea is in general faster than with thiourea. This indicates that thiourea affects both the lateral and vertical growth of the copper crystals.

At the used potentials the copper crystals have a pyramidal-like structure, see figure 8.3 and 8.4. From the width ($w$) and the height ($h$) the volume ($vol$) of a pyramidal shape can be calculated

$$vol = \frac{1}{3} w^2 h$$

(8.2)

![Graph](Image)

**Figure 8.5** Width and height of the copper crystals in time during electrodeposition of copper on polypyrrrole without (--) and with (---) thiourea. Width without (•) and with thiourea (■), and height without (○) and with thiourea (▲).
Figure 8.6 Volume of the copper crystals in time during electrodeposition of copper on polypyrrole without (●) and with (■) thiourea.

From the width and the height of figure 8.5 the volume of the crystals in time were determined, see figure 8.6. Without thiourea the first two points, which are the volumes of the surface humps, were not used for calculating the best fit. With thiourea beside these points from the surface humps also the first two points of the copper crystal were not included for calculating the fit because the copper growth showed in this case a slower starting period. Both fits have a correlation coefficient of 0.99. These fits show that the volume of the copper crystals increased linearly in time.

The increase of the volume in time is a measure for the current at the crystal and hence the current at the crystal was constant and the current with thiourea was lower than without. If it is assumed that the potentials at the crystal with and without thiourea are equal, thiourea increases the resistance for the copper deposition and inhibits the growth of the copper crystals.

8.3.2 Form

When no thiourea was added to the copper bath, the nucleation started at surface defects as is generally found during electrochemical deposition of metals. In figure 8.3 the nucleation starts on the top of a hump on the surface. However, this was not necessarily the highest hump on the surface, cf. figure 8.3 a. These defects are normally found on the surface after the polymerisation of pyrrole and are not present on the bare PEI surface which is smoother, see figure 8.7.

Without thiourea the form of the copper crystal depends on the form of the surface defect where the copper deposition starts, as can be seen in figure 8.8. This figure shows that
there is a resemblance between the form of the hump, where the nucleation starts and the form of the copper crystal. This form remains visible during further growth of the crystal. Furthermore, figure 8.8 shows that the borders of the copper crystal follow the small morphology changes of the surface. The influence of large surface defects can be seen in figure 8.3. Figure 8.3 d shows the copper crystal with a surface defect below it. During the growth of the copper crystal there was formed a strip of copper between the crystal and the surface defect, figure 8.3 d-h. This strip remained during further growth, figure 8.3 h-j. These examples show that in a copper bath without thiourea the form of the crystals is determined by the surface morphology.

The sides of the crystals formed without thiourea were smooth. In the scan direction the sides of the copper crystals are straight from the bottom to the top and level off at the top of the crystal.
For the solution with thiourea the copper crystal also started at a hump on the surface, see figure 8.9. Because this surface hump is small, the form could not be compared with the form of the copper crystal.

Similar to the bath without thiourea it can be deduced from the zoomed images that the borders of the copper crystal follow the small morphology changes of the surface. On the other hand the large surface defects have not such a large effect on the form of the crystals, as is the case in the bath without thiourea.

With thiourea the crystal does not have the same smooth surface as the crystal formed without thiourea. The sides of the copper crystals do not grow to the top of the crystal, see e.g. figure 8.4 j. The growth along the side was inhibited, causing the layered structure of the copper crystal. On a side of the crystal different planes can arise which are not parallel to each other, see e.g. the front of the crystal in figure 8.4 j.

Copper crystals have a face centred cubic lattice. The most relevant angles between the different planes are listed in table 8.1. Because the AFM images show a growing crystal the angles between the planes that lie in the scanning direction can only be determined properly. To determine this angle a line parallel to the planes that lie in the scanning direction was chosen. Because the crystals level off at the top the angle between the lower straight parts of the copper planes was determined. These measured angles between the planes are always (a few degrees) smaller or equal to the theoretical ones.

Without thiourea the angle between the planes of the crystal is always larger than 125.3° and the angle is comparable with the angle of the initial surface defect, see table 8.1. Furthermore, the form of the crystals was determined by the surface morphology. Hence, the crystal formed in the copper bath without thiourea is not a mono crystal.
Table 8.1  Calculated angles between different crystal planes in a copper crystal and the measured angles between the planes of the crystal.

<table>
<thead>
<tr>
<th>calculated plane I</th>
<th>calculated plane II</th>
<th>angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>-111</td>
<td>109.5</td>
</tr>
<tr>
<td>111</td>
<td>-111</td>
<td>70.5</td>
</tr>
<tr>
<td>111</td>
<td>001</td>
<td>125.3</td>
</tr>
<tr>
<td>010</td>
<td>001</td>
<td>90</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>measured no additives</th>
<th>measured thiourea</th>
<th>angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface defect</td>
<td>surface defect</td>
<td>127.7 (0.2)*</td>
</tr>
<tr>
<td>crystal</td>
<td>crystal</td>
<td>127.3 (0.4)</td>
</tr>
</tbody>
</table>

* The parenthesised values are the standard deviations of the angles measured on the defect or the growing crystal of at least three different AFM images.

With thiourea the angle of the planes of the crystal is always larger than 109.5° and is comparable with the angle of the initial surface defect, see table 8.1. Furthermore, on one side of the crystal different planes arise which are not parallel to each other. Therefore, this crystal is also not a mono crystal.

8.4 Conclusions

With EC-AFM it is possible to follow the copper growth. Without thiourea the form of the copper crystals was mainly determined by the surface defects. With thiourea the growth of the copper crystals was inhibited in the lateral and vertical direction. The latter also caused the layered planes of the copper crystal. Hence, the front velocity was not increased by influencing the growth of the copper crystals.

References

The Non-Uniformity and Other Properties of the Copper Layer
Abstract

For commercial applications the electrodeposited copper layer must have a flat surface, be ductile, and be uniform in thickness. The effect of the deposition potential, thiourea, and additional deposition time on the non-uniformity of the copper layer were studied. Also the effect of the deposition time, and organic molecules, viz. crystal violet, benzotriazole, and thiourea, on the structure, toughness, and appearance of the copper layer were investigated.

Because of the electrical resistance of the polypyrrole layer a non-uniform copper layer is formed. This non-uniformity is independent of the deposition potential, is improved by thiourea, and decreases with additional deposition time.

The addition of the organic molecules to the copper solution results in a ductile copper layer at deposition potentials of −0.6 V and lower. Thiourea and benzotriazole improve also the roughness and the appearance of the copper layer at these low deposition potentials.

9.1 Introduction

For commercial applications a uniform thickness of the copper layer is required. The copper growth on conducting polymers starts at the ohmic contact and propagates laterally during deposition. The non-uniformity of the final deposit is determined by the difference in lateral propagation velocity, henceforth called front velocity, and ongoing thickening velocity of already metallized parts. De Leeuw et al. [1] found that without additive the non-uniformity of the copper layer did not change with deposition potential. In a commercial bath which contains additives the non-uniformity varied between 0.03 and 0.67 μm/mm depending on the commercial bath used and the applied potential. Generally non-uniformity is introduced by a concentration of lines of electric field and by geometric concentration-field effects [2].

For commercial applications besides a uniform thickness the deposited layer must also be ductile and have a flat upper surface. Normally this is achieved by adding organic molecules to the electrolyte, which act as brightening and levelling agents. For crystal violet, benzotriazole, and thiourea it was already found that these molecules inhibit the perpendicular growth of copper [3-6]

In this chapter the influence of the deposition potential, thiourea, and additional deposition time on the non-uniformity of the copper layer were investigated. Also the effect of the deposition time, and organic molecules, viz. crystal violet, benzotriazole, and thiourea, on the structure, toughness, and appearance of the copper layer were studied.

9.2 Experimental

Poly-ether-imide substrate, PEI Ultem 1000 (GE Plastics) was cut in pieces of 1.0 x 7.5 cm². CuSO₄·5H₂O (Fluka Chemika), H₂SO₄ (Fluka Chemika), crystal violet (Fluka
Chemika), thiourea (Fluka Chemika), 1H-benzotriazole (Fluka Chemika), and silver paint (Heraeus) were all used as received.

A thin film of polypyrrole was synthesised on a poly-ether-imide (PEI) substrate with the method described in chapter 5. Subsequently a T-electrode was applied as described in chapter 7.

Sheet resistances were measured by applying two parallel electrodes of silver paint with a distance of 1 cm. These electrodes have a negligible contact resistance and the sheet resistances are comparable with those measured with a standard four-probe resistance measurement.

All galvanic experiments were made potentiostatically in a simple one-component cell of 40 ml containing a copper foil of about 15 cm² as the counter electrode, a polypyrrole coated substrate at a distance of about 2 cm as the work electrode, and a saturated calomel reference electrode at room temperature. An electrolyte containing 58.9 g CuSO₄ (0.94 M) and 8.2 ml H₂SO₄ (0.60 M) in 250 ml demiwater was used. The organic molecules crystal violet, benzotriazole, and thiourea, were added to the galvanic cell in a concentration of about 0.1 mM, being 1.6 mg, 0.5 mg, and 0.3 mg respectively. The potential during the deposition was controlled by an EG&G PAR 273 potentiostat/galvanostat, with EG&G PAR model 270 electrochemical analysis software 3.00.

For the determination of the thickness of the copper layer two lines of polypyrrole, which have a distance of 0.5 cm from each other, were removed with a knife to electrically disconnect the polypyrrole layer on the outside, see figure 9.1. In this way copper can only be deposited on the middle of the polypyrrole layer. After deposition of copper the thickness of the copper layer was determined every 2.5 mm from the ohmic contact with an UBM microfocus profilometer.

Roughness measurements were performed at room temperature on an UBM microfocus profilometer with a point density of 500 points/mm. The profiles (10 mm) were analysed using a cut off of 2 mm and further according DIN 4768.

SEM micrographs were made with a JEOL JXA-8900R WD/ED combined microanalyser.

**Figure 9.1** T-electrode applied on the top of the polypyrrole film with silver paint.
9.3 Non-uniformity

9.3.1 Determination of the non-uniformity

The nucleation of the copper starts at the ohmic silver contact and then propagates parallel towards the end of the substrate. Because the copper layer also grows in the vertical direction the layer becomes non-uniform in thickness.

This non-uniformity of the copper layer can be determined by simply measuring the thickness of the deposit as function of the distance along the electrode. However, it is also possible to derive a theoretical non-uniformity from process parameters.

The non-uniformity of the copper layer depends on the front velocity \( v_{\text{front}} \) and thickening velocity \( v_{\text{Cu-Cu}} \), see figure 9.2. If not the total area is deposited with copper we can write for the thickness \( d(x,t) \) of the deposited copper layer as function of the distance along the substrate, \( x \), at time \( t \)

\[
d(x,t) = v_{\text{Cu-Cu}} \left( t - \frac{x}{v_{\text{front}}} \right)
\]  

(9.1)

The non-uniformity \( U \) of the deposited copper layer can be defined as the absolute value of the partial derivative of the thickness of the copper layer to the distance along the substrate

\[
U = \left| \frac{\partial d}{\partial x} \right| = \frac{v_{\text{Cu-Cu}}}{v_{\text{front}}}
\]

(9.2)

As shown in chapter 7 the front velocity of the copper deposition can be determined from the derivative of current-time curve with the following equation (equation 7.14)

![Diagram](image)

**Figure 9.2**  *Schematic representation of the electrodeposition of copper on polypyrrole.*
\[ v_{\text{front}}(t) = \frac{l_{\text{Cu}}}{I_{\text{max}}} \frac{\partial I(t)}{\partial t} \]  

(9.3)

where \( I_{\text{max}} \) is the current when the total surface is covered with copper, and \( l_{\text{Cu}} \) is the length of the area covered with copper.

The thickening velocity can be determined either from the current-time curve or by measuring the copper thickness at the electrical contact.

For the first method we assume that a diffusion layer and a stationary state are formed. For the ongoing thickening of already metallized parts, \( v_{\text{Cu-Cu}} \), we can write

\[ v_{\text{Cu-Cu}} = \frac{M_{\text{Cu}}}{\rho_{\text{Cu}}} \frac{\Phi_a}{\rho_{\text{Cu}}} \]  

(9.4)

where \( M_{\text{Cu}} \) is the atomic weight of copper (63.546 g/mol), \( \rho_{\text{Cu}} \) is the density of copper (8.92 g/cm\(^3\)), and \( \Phi_a \) is the flux, the moles copper deposited per second per unit area. According to this equation the thickening velocity is constant.

In the case the total surface is covered with copper the current is given by

\[ I_{\text{max}} = 2F \Phi_a A = 2F \Phi_a b l_{\text{Cu}} \]  

(9.5)

where \( F \) is the constant of Faraday (9.65*10\(^4\) C/mol), and \( b \) is the width of the area covered with copper.

If the total area is covered with copper, equations 9.4 and 9.5 can be combined

\[ v_{\text{Cu-Cu}} = \frac{M_{\text{Cu}}}{2F \rho_{\text{Cu}}} \frac{I_{\text{max}}}{b l_{\text{Cu}}} \]  

(9.6)

With this equation the average thickening velocity can be determined from the current-time curve when the total area is covered with copper.

For the second method the thickening velocity can be determined by measuring the copper thickness at the electrical contact, \( d(x = 0) \), divided by the total deposition time (s), \( t_{\text{dep}} \).

\[ v_{\text{Cu-Cu}} = \frac{d(x = 0)}{t_{\text{dep}}} \]  

(9.7)

9.3.2 Evaluation of the thickening velocity

Before discussing the influence of the potential on the non-uniformity, the determination of the thickening velocity is evaluated, see table 9.1. For the determination of
Table 9.1  Thickening velocity, \( v_{\text{Cu-Ce}} \), determined from the current-time curve and determined at the contact. Surface roughness, \( R_s \), of the copper layer deposited on a polypyrrole layer at diverse deposition potentials, with and without thiourea.

<table>
<thead>
<tr>
<th>E (V vs. SCE)</th>
<th>( v_{\text{Cu-Ce}}^{a} ) ((\mu\text{m/min}))</th>
<th>( v_{\text{Cu-Ce}}^{b} ) ((\mu\text{m/min}))</th>
<th>( R_s ) ((\mu\text{m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>no additive</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.2</td>
<td>1.2</td>
<td>1.1</td>
<td>0.74</td>
</tr>
<tr>
<td>-0.4</td>
<td>2.5</td>
<td>2.3</td>
<td>0.92</td>
</tr>
<tr>
<td>-0.6</td>
<td>2.6</td>
<td>3.9</td>
<td>1.38</td>
</tr>
<tr>
<td>thiourea</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.2</td>
<td>0.8</td>
<td>0.5</td>
<td>0.50</td>
</tr>
<tr>
<td>-0.6</td>
<td>2.8</td>
<td>2.3</td>
<td>0.65</td>
</tr>
</tbody>
</table>

\( a \) Thickening velocity determined from the current-time curve.

\( b \) Thickening velocity determined at the contact.

The thickening velocity from the current-time curve it is assumed that all electrons are used for the deposition of copper and no side reactions occur and that the density of the deposited copper layer is equal to the density of crystalline copper.

The sheet resistance of the polypyrrole layer decreases during the deposition of copper, indicating that some electrons are used to reduce the polypyrrole layer. However, at the diverse deposition potentials it was found that the total weight of deposited copper is comparable with the weight calculated from the current-time curve, indicating that almost all electrons are used for the deposition of copper.

The thickening velocity determined at the contact is not very accurate because of the surface roughness of the deposited copper layer, see table 9.1. The thickening velocity determined at the contact and determined from the current-time curve are same within the experimental accuracy, except at \(-0.6\) V without thiourea. This agreement indicating that the density of the copper layer is equal to the density of crystalline copper. Except at \(-0.6\) V without additive where the copper layer is less dense. Because this difference in density the thickening velocity can better be determined by measuring the thickness of the copper layer at the electrical contact, equation 9.7. The thickening velocity determined with this equation increases with decreasing deposition potential. Furthermore, thiourea inhibits the thickening velocity.

9.3.3 Influence of the potential and thiourea

The uncertainty in the non-uniformity determined from the front and thickening velocity is large because of the large uncertainty in the thickening velocity. Therefore, these calculated non-uniformity's are the same within the experimental accuracy with the measured ones and is the calculated non-uniformity a good estimation for the non-uniformity, see table 9.2.

108
Table 9.2  Measured non-uniformity, $U$, and calculated non-uniformity, $v_{Cu-Cd}/v_{front}$, of the copper layer deposited on a polypyrrrole layer at several deposition potentials, with and without thiourea.

<table>
<thead>
<tr>
<th>E (V vs. SCE)</th>
<th>$U^a$ (μm/mm)</th>
<th>$v_{Cu-Cd}/v_{front}^b$ (μm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>no additive</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.2</td>
<td>0.36</td>
<td>0.45</td>
</tr>
<tr>
<td>-0.4</td>
<td>0.38</td>
<td>0.47</td>
</tr>
<tr>
<td>-0.6</td>
<td>0.37</td>
<td>0.49</td>
</tr>
<tr>
<td><strong>thiourea</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.2</td>
<td>0.18</td>
<td>0.14</td>
</tr>
<tr>
<td>-0.6</td>
<td>0.17</td>
<td>0.19</td>
</tr>
</tbody>
</table>

$^a$ Measured non-uniformity
$^b$ Thickening velocity determined at the contact.

Without additive the non-uniformity of the copper layer does not change with the potential although the copper layer became less dense at a potential of $-0.6$ V. Thiourea improves the non-uniformity of the deposited copper layer with a factor two and the non-uniformity does also not change with the potential. On the contrary, De Leeuw et al. [1] found that the non-uniformity varied with the potential when a commercial bath (a copper bath with diverse additives) was used.

9.3.4 Effect of the deposition time

In our experimental set-up the counter electrode is broader and longer than the work electrode and the top of the work electrode lies just under the level of liquid. Because of this geometry the non-uniformity caused by a concentration of electric field lines and by geometric concentration-field effects [2] can especially arise at the end of the work electrode. Whether or not this non-uniformity occurs in our experiments was investigated by measuring the non-uniformity after the total surface was covered with copper and after every additional 5 minutes of copper deposition on this layer, see table 9.3.

This table shows that for deposition with and without thiourea at different potentials the non-uniformity decreased in time and hence this non-uniformity occurs in our experimental set-up. The effect is larger at more negative deposition potentials and at a potential of $-0.6$ V the non-uniformity even reversed after 5 minutes of additional copper deposition.
Table 9.3  Influence of additional deposition time on the measured non-uniformity of the copper layer deposited at diverse potentials, with and without thiourea.

<table>
<thead>
<tr>
<th>Potential (V vs. SCE)</th>
<th>without additive</th>
<th>0</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.2</td>
<td>-0.36*</td>
<td>-0.23</td>
<td>-0.12</td>
<td></td>
</tr>
<tr>
<td>-0.4</td>
<td>-0.38</td>
<td>-0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.6</td>
<td>-0.37</td>
<td>0.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thiourea</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.2</td>
<td>-0.18</td>
<td>-0.06</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>-0.6</td>
<td>-0.17</td>
<td>0.37</td>
<td>1.02</td>
<td></td>
</tr>
</tbody>
</table>

* A negative value indicates that the copper layer is thicker at the contact and a positive value indicates that the copper layer is thinner at the contact.

9.4 Properties of the copper layer

9.4.1 Influence of the potential

The influence of the potential on the appearance, structure, and toughness of the copper layer was investigated. At more negative potentials the copper surface became rougher, see table 9.4, and the copper structure changed from a more crystal like structure into a cauliflower-like structure, see figure 9.3. Chen et al. [7] also found this change in structure. Due to this change the colour of the copper layer changed from pink into dark red and the copper layer became less dense. Because of the less dense structure the copper layer became brittle, resulting in the release of parts of the copper layer at -0.8 V.

Figure 9.3  SEM picture of a copper layer deposited on a polypyrrole layer at -0.2 V (left) and -0.6 V (right).
Table 9.4  Surface roughness, $R_s$ (µm), toughness, and colour of the copper layer deposited without and with several additives at diverse potentials.

<table>
<thead>
<tr>
<th>additive</th>
<th>potential (V vs. SCE)</th>
<th>$R_s$ (µm)</th>
<th>toughness</th>
<th>colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-0.2</td>
<td>0.7</td>
<td>ductile</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td>-0.4</td>
<td>0.9</td>
<td>ductile</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td>-0.6</td>
<td>1.4</td>
<td>brittle</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td>-0.8</td>
<td>3.5</td>
<td>brittle</td>
<td>dark red</td>
</tr>
<tr>
<td>crystal violet</td>
<td>-0.2</td>
<td>1.0</td>
<td>ductile</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td>-0.4</td>
<td>2.0</td>
<td>ductile</td>
<td>dark red</td>
</tr>
<tr>
<td></td>
<td>-0.6</td>
<td>1.7</td>
<td>ductile</td>
<td>dark red</td>
</tr>
<tr>
<td>benzotriazole</td>
<td>-0.2</td>
<td>1.2</td>
<td>ductile</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td>-0.4</td>
<td>1.2</td>
<td>ductile</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td>-0.6</td>
<td>1.2</td>
<td>ductile</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td>-0.8</td>
<td>0.9</td>
<td>ductile</td>
<td>pink</td>
</tr>
<tr>
<td>thiourea</td>
<td>-0.2</td>
<td>0.5</td>
<td>ductile</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td>-0.4</td>
<td>0.7</td>
<td>ductile</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td>-0.6</td>
<td>0.7</td>
<td>ductile</td>
<td>pink</td>
</tr>
<tr>
<td></td>
<td>-0.8</td>
<td>0.6</td>
<td>ductile</td>
<td>dark red</td>
</tr>
</tbody>
</table>

9.4.2 Influence of the additives

The influence of the additives, crystal violet, benzotriazole, and thiourea, on the appearance, structure, and adhesion of the copper layer was also investigated.

With crystal violet as additive the copper layer became rougher than without additive, see table 9.4. At a microscopic scale the copper layer became also rougher, see figure 9.4. These two effects let to a dark red copper layer.

Figure 9.4  Microscopy picture of a copper layer deposited on a polypyrrole layer at −0.4 V without additive (left) and with crystal violet (right).
When benzotriazole was added the copper layer became also rougher. The surface roughness was, however, independent of the deposition potential. At deposition potentials of $-0.2$ V and $-0.4$ V this resulted in a slight darker copper layer than without additive and at a potential of $-0.8$ V a lighter copper layer than without additive was found.

With thiourea the surface became smoother and the surface roughness was independent of the deposition potential. This resulted in brighter copper layers. For both benzotriazole and thiourea it is possible to deposit ductile adhering copper layers at deposition potentials of $-0.6$ V and lower.

9.5 Conclusions

Because the density of the copper layer is not always equal to the density of crystalline copper the thickening velocity was determined from the thickness of the copper layer at the electrical contact and not from the current-time curve. The thickening velocity increases with decreasing deposition potential and is inhibited by thiourea. The non-uniformity can also be determined from the thickening and front velocity.

Although the copper layer becomes less dense at more negative deposition potentials the non-uniformity remains at 0.37 $\mu$m/mm. When thiourea was added to the copper solution the non-uniformity decreased with a factor two. The non-uniformity decreases with additional deposition time and even inverses at a deposition potential of $-0.6$ V due to the geometry of our experimental set-up.

At deposition potentials of $-0.6$ V and lower the copper layer became rougher, less dense, and brittle. The addition of an organic molecule, viz. crystal violet, benzotriazole, and thiourea, resulted in a ductile copper layer with the density of crystalline copper at these more negative deposition potentials. Crystal violet roughened the copper layer, resulting in a dark red copper layer. After adding benzotriazole the roughness of the copper layer was not depending on the deposition potential. At a deposition potential of $-0.2$ V and $-0.4$ V the copper layer was rougher and darker than without additive. After addition of thiourea the copper layer became smoother and the roughness was also independent on the deposition potential.

References


Summary and Conclusions

Metals are applied on plastics because of their (shining) appearance and their good thermal and electrical conductivity. There are several methods to apply a metal on a plastic substrate. The method used is depending on the substrate. The application of patterned metal layers, e.g. in printed circuit boards, is nowadays realised by etching previously deposited smooth layers.

A relative new method is based on the use of intrinsically conducting polymers (ICP’s). A conductive layer containing an ICP is applied on a substrate and subsequently a metallic layer is electrochemically deposited on this layer. An advantage of this method is that it is less substrate depending than other methods. Moreover, when a high electrically conducting layer can be applied this method can also be used for patterned deposition. In that case this method can also be used for printed circuit boards because the ICP layer can be made non-conducting.

For a fast metallization process and a uniform metal layer the sheet resistance of the conductive layer should be as low as possible. Furthermore, a smooth well-adhering polypyrrole layer is required. For patterned deposition the sheet resistance of the ICP layer has to be lower than 10 $\Omega / \square$.

This thesis is divided into two parts. In part A the influence of the diverse process steps on the application of polypyrrole on an epoxy substrate is investigated and the diverse process steps are optimised. In part B the electrochemical deposition of copper on these polypyrrole layers is discussed.

In part A, the following method for the polymerisation of pyrrole on the epoxy substrate was chosen for further optimisation. First, the substrate (75 x 10 x 1 mm$^3$) was cleaned with acetone and after drying, it was pre-treated by immersion in a solution containing 10 g of Ce(SO$_4$)$_2$*4H$_2$O (0.12 M), 2.7 ml of H$_2$SO$_4$ (0.25 M) and 200 ml demiwater for 5 minutes. Subsequently, to apply a layer of pyrrole, the substrate was dipped in a monomer bath containing a solution of pyrrole in 2-propanol (20 % v/v). Finally the substrate was immersed in an oxidant solution containing 20.65 g of Fe(ClO$_4$)$_3$*9H$_2$O (0.20 M), 12.2 ml of 60% HClO$_4$ (0.56 M) and 200 ml demiwater at 0°C for 5 minutes. After polymerisation the substrate was rinsed with demiwater and dried at room temperature.

In chapter 3, the influence of the pre-treatments of the epoxy substrate, the cerium and the corona treatment respectively, and the influence of the pyrrole concentration in the monomer bath on the properties of the polypyrrole layer are described. Measurements with a profilometer and an atomic force microscope (AFM) demonstrate that the epoxy substrates are roughened by the corona treatment, while the cerium treatment did not demonstrate this effect. Contact angle measurements show that in an aqueous solution pyrrole spreads on the untreated epoxy substrate, but forms droplets on the treated epoxy substrates. At pyrrole concentrations of 50 vol% and lower in the monomer bath, the monomer solution dissolves in water and hence no droplets are formed on the epoxy substrate.
The polymerisation of pyrrole occurs in the water phase, resulting in polypyrrole deposition on the epoxy substrate. Due to the pyrrole layer formed on the untreated epoxy substrate, no chemical bonding is formed between the polypyrrole and the substrate, resulting in a poor adhesion and a high overall sheet resistance. On the treated epoxy substrate the pyrrole droplets polymerise, causing the black spots on the surface. No chemical bonding is formed between the polypyrrole deposited on the pyrrole droplet and the epoxy substrate underneath, explaining the poor adhesion of the black spots. At decreasing pyrrole concentrations in the monomer bath the polymerisation rate decreases and less polypyrrole is formed and deposited on the substrate in the same synthesis time, resulting in a higher sheet resistance of the polypyrrole layer. At pyrrole concentrations of 50 vol.% and lower in the monomer bath no droplets of the monomer solution are formed on the epoxy substrate and hence a smooth adhering polypyrrole layer is formed on the epoxy substrate.

In chapter 4 the dependence of the electrical properties of the polypyrrole layer on the time spent in the oxidant solution and the temperature during oxidation are studied. Optimisation of the polymerisation process led to a 30 minutes oxidative process at 0°C.

The influence of the HClO₄ and the Fe(ClO₄)₃ concentrations in the oxidant solution on the sheet resistance of the polypyrrole layer and on the polymerisation reaction are discussed in chapter 5. The rate of the polymerisation reaction increases with increasing Fe(ClO₄)₃ concentrations and therefore the polypyrrole layer becomes thicker in the same synthesis time and the sheet resistance decreases.

For Fe(ClO₄)₃ concentrations of 0.30 M and lower the sheet resistance depends on the HClO₄ concentration. Calculations of the influence of the acid concentration on the Fe³⁺ hydrolysis equilibria are in agreement with UV/VIS and pH measurements. These calculations and experiments in which HClO₄ was replaced by LiClO₄, show that the polymerisation rate of pyrrole is determined by the perchlorate concentration and not by the acid concentration. We conclude that the perchlorate ions promote the dimerisation of the radical cations by reducing the electrical repulsion between the radical cations, indicating that the dimerisation of the pyrrole radical cations is the rate-determining step.

The optimisation of the diverse process steps described in the chapters 3, 4, and 5 leads to the following process. The substrate was first cleaned with acetone. By carefully turning, both sides of the substrate were corona treated with a solid-state Tantec Model HV 05-2 generator at about 90 W and about 25 kHz for 10 seconds. Subsequently, the substrate was dipped in a solution of pyrrole in 2-propanol (50% v/v). Finally the substrate was immersed in an oxidant solution containing 30.98 g of Fe(ClO₄)₃·9H₂O (0.30 M), 21.7 ml of 60% HClO₄ (1.0 M) and 200 ml demiiwater at 0°C for 30 minutes. After polymerisation the substrate was rinsed with demiiwater and dried at room temperature. This process is successfully used for the polymerisation of pyrrole on other plastics, viz. polypropene, poly(acrylonitrile-butadiene-styrene), and poly-ether-imide. The best sheet resistance found for the applied polypyrrole layer is about 150 Ω/□. This is too high for patterned deposition, and hence these polypyrrole layers can only be used effectively for small deposition areas.
Finally, the polypyrrole layer is characterised by cyclic voltammetry. The cyclic voltammogram shows that polypyrrole is in the reduced non-conducting form at potentials of –0.5 V and lower and in the oxidised conducting form at potentials of –0.2 V and higher.

In part B, the electrochemical deposition of copper from a copper solution containing 0.94 M CuSO₄, 0.60 M H₂SO₄ and optionally 0.1 mM of an organic molecule, viz. crystal violet, benzotriazole, or thiourea, on a polypyrrole layer on poly-ether-imide at diverse potentials is discussed. The copper deposition starts within a short distance from the electrical contact and propagates laterally during deposition.

In chapter 7, the influence on the lateral growth velocity (or front velocity) of the potential and the addition of an organic molecule, viz. crystal violet, benzotriazole, or thiourea, to the electrolyte are described. At more negative deposition potentials the front velocity increases and the zone where copper nucleation takes place is shorter. The shorter nucleation zone is not caused by a sharper potential decay in the polypyrrole electrode but by the promotion of the nucleation of copper at more negative potentials.

Thiourea, in contrast to crystal violet and benzotriazole, increases the front velocity at more negative potentials by promoting the nucleation of copper.

Cyclic voltammetry and resistance measurements show that not only Cu²⁺ but also the polypyrrole layer is reduced during the copper deposition. However, the reduction of polypyrrole does not stop the lateral copper growth.

In chapter 8, the growth of the copper crystals on polypyrrole and the effect of thiourea on this growth are studied with in-situ electrochemical atomic force microscopy (EC-AFM). The AFM data show that the crystal growth starts at humps on the polypyrrole surface. Without thiourea the copper crystals are smooth and the form is determined by the morphology of polypyrrole surface. Thiourea inhibits the growth velocity of the copper crystals in the vertical and lateral direction, resulting in the layered structure of the copper crystals.

The effect of the deposition time and organic molecules, viz. crystal violet, benzotriazole, and thiourea, on the non-uniformity, structure, toughness, and appearance of the copper layer is described in chapter 9. A non-uniform copper layer is formed due to the electrical resistance of the polypyrrole layer. This non-uniformity is independent of the deposition potential, is improved by thiourea, and decreases with additional deposition time.

The addition of the organic molecules to the copper solution results in a ductile copper layer. Thiourea and benzotriazole improve also the roughness and the appearance of the copper layer at deposition potentials of –0.6 V and lower.
Samenvatting

Metalen worden aangebracht op kunststoffen vanwege hun (glanzend) uiterlijk en hun goede thermiscn en elektrisch geleidende eigenschappen. Er bestaan diverse technieken om een metaal op een kunststof aan te brengen. De meest geschikte techniek is sterk afhankelijk van de gebruikte kunststof. Het patroonmatig aanbrengen van metalen, voor bijvoorbeeld printplaten, wordt tegenwoordig gedaan door het gedeeltelijk wegetsen van eerder aangebrachte gladde lagen.

Een relatief nieuwe methode voor het aanbrengen van metalen op kunststoffen is gebaseerd op het gebruik van zogenaamde intrinsiek geleidende polymeren (IGP’s). Op een kunststof wordt eerst een geleidende laag, die zo’n IGP bevat, aangebracht. Vervolgens wordt op deze laag met behulp van galvanische technieken een metaal aangebracht. Een voordeel van deze methode is dat het op bijna iedere kunststof toegepast kan worden. Bovendien is deze techniek, indien een goed geleidende laag aangebracht kan worden, geschikt voor het patroonmatig aanbrengen van metalen. In dit geval is deze techniek ook geschikt voor het maken van printplaten, omdat de IGP-laag niet geleidend gemaakt kan worden.

Voor een snel metallisatie proces en een uniforme metaallaag is een zo laag mogelijke vierkantsweerstand van de geleidende laag nodig. Bovendien moet de IGP-laag vlak zijn en goed hechten op de kunststof. Voor het patroonmatig aanbrengen moet de vierkantsweerstand onder de 10 Ω/□ liggen.

Dit proefschrift is verdeeld in twee delen. In deel A is de invloed van de verschillende processtappen op het aanbrengen van polyprrool op het epoxysubstraat onderzocht en zijn de verschillende processtappen geoptimaliseerd. In deel B is de electrochemische depositie van koper op deze polyprrool lagen beschreven.

In deel A is de volgende procedure voor de polymerisatie van pyrrool op een epoxysubstraat geoptimaliseerd. Eerst wordt het substraat (75 x 10 x 1 mm³) schoongemaakt met aceton. Na drogen, wordt het substraat voorbehandeld door het 5 minuten onder te dompelen in een oplossing van 10 g Ce(SO₄)₂*4H₂O (0,12 M), 2,7 ml H₂SO₄ (0,25 M) en 200 ml demiwater. Vervolgens wordt een laag van het monomeer pyrool aangebracht door het substraat onder te dompelen in een monomeerbad dat een oplossing van pyrrool in 2-propanol (20% v/v) bevat. Tenslotte wordt het substraat 5 minuten bij 0°C ondergedompeld in een oxidantoplossing van 20,56 g Fe(CIO₄)₃·9H₂O (0,20 M), 12,2 ml 60% HClO₄ (0,56 M) en 200 ml demiwater. Na polymerisatie wordt het substraat gespoeld met demiwater en gedroogd bij kamertemperatuur.

In hoofdstuk 3 is de invloed van de voorbehandelingen van het epoxysubstraat, respectievelijk de cerium en de corona behandeling, beschreven. Ook de invloed van de pyrroolconcentratie in het monomeerbad op de eigenschappen van de polyprroollaaq is beschreven. De metingen met een profilometer en een atomic force microscopie (AFM) tonen aan dat het epoxysubstraat ruwer wordt door de corona behandeling, terwijl de cerium
behandeling geen effect heeft op de ruwheid. Contacthoekmetingen laten zien dat pyrrool zich in een waterige oplossing uitspreidt over een onbehandelde epoxysubstraat, en druppels vormt op de behandelde epoxysubstraten. Bij pyrroolconcentraties in het monomeerbad van 50 vol% en lager lost de monomeeroplossing op in water en worden geen druppels gevormd op het epoxysubstraat.

De polymerisatie van pyrrool vindt plaats in de waterfase, en resulteert in de neerslag van polypyrrool op het substraat. Omdat op het onbehandelde epoxysubstraat zich een pyrrooloplossing gevormd heeft, wordt geen chemische binding gevormd tussen het neerslagen polypyrrool en het epoxysubstraat. Dit resulteert in een slechte hechting en een hoge totale vierkantsweerstand van de polypyrrooloplossing. Op het behandelde epoxysubstraat veroorzaken de gepolymeriseerde pyrrooldruppels de zwarte vlekken op het oppervlak. Tussen het polypyrrool neerslagen op de pyrrooldruppels, en het eronder gelegen epoxysubstraat wordt geen chemische binding gevormd. Dit verklaart de slechte hechting van de zwarte vlekken. De polymerisatiesnelheid daalt met de pyrroolconcentratie in het monomeerbad. Daardoor wordt in dezelfde tijd minder polypyrrole gevormd en neergeslagen op het substraat, wat resulteert in een hogere vierkantsweerstand van de polypyrrooloplossing. Bij pyrroolconcentraties in het monomeerbad van 50 vol% en lager worden geen druppels van de monomeeroplossing gevormd op het epoxysubstraat. Dit resulteert in een gladde hechting van polypyrrooloplossing op het epoxysubstraat.

In hoofdstuk 4 is de invloed van de tijd doorgebracht in de oxidantoplossing en van de temperatuur gedurende de oxidatie op de elektrische eigenschappen van de polypyrrooloplossing bestudeerd. Optimalisatie van het polymerisatietransformeren leidde tot een 30 minuten durend oxidatief proces bij 0°C.

In hoofdstuk 5 is de invloed van de HClO₄- en de Fe(ClO₄)₃-concentraties in de oxidantoplossing op de vierkantsweerstand van de polypyrrooloplossing en op de polymerisatieroactie besproken. De snelheid van de polymerisatieractie neemt toe met toenemende Fe(ClO₄)₃-concentratie. Daardoor wordt de polypyrrooloplossing dikker en daalt de vierkantsweerstand gedurende dezelfde synthetetijd.

Voor Fe(ClO₄)₃-concentraties van 0,30 M en lager is de vierkantsweerstand afhankelijk van de HClO₄-concentratie. Berekeningen van de invloed van de zuurconcentratie op de Fe³⁺ hydrolyse equilibria komen overeen met UV/Vis en pH metingen. Deze berekeningen en experimenten waarbij HClO₄ is vervangen door LiClO₄, laten zien dat de polymerisatiesnelheid van pyrrool wordt bepaald door de perchloraatconcentratie en niet door de zuurconcentratie. Wij concluderen dat de perchloraat ionen de dimerisatie van de radicaal kationen bevorderen door de elektrische afstoting tussen deze radicaal kationen te verminderen. Dit wijst erop dat de dimerisatie van de pyrrool radicaal kationen de snelheidsbepalende stap is.

De optimalisatie van de verschillende processtappen beschreven in de hoofdstukken 3, 4 en 5 kan leiden tot de volgende methode. Eerst wordt het substraat schoongemaakt met aceton. Door voorzichtig te draaien worden beide zijden van het substraat corona behandeld met een solid-state Tantec Model HV 05-2 generator bij ongeveer 90 W en 25 kHz
gedurende 10 seconde. Vervolgens wordt het substraat ondergedompeld in een monomeerbad dat een oplossing van pyrool in 2-propanol (50 % v/v) bevat. Tenslotte wordt het substraat 30 minuten bij 0°C ondergedompeld in een oxidantoplossing van 30,98 g Fe(ClO₄)₃*9H₂O (0,30 M), 21,7 ml 60% HClO₄ (1.0 M) en 200 ml demiwater. Na polymerisatie wordt het substraat gespoeld met demiwater en gedroogd bij kamertemperatuur. Deze methode is succesvol gebruikt voor de polymerisatie van pyrool op andere polymeren, namelijk polypropene, poly(acrylonitril- butadieen -styreen), en poly-ether-imide. De laagst gevonden vierkantsweerstand voor de aangebrachte polypyrroollagen is ongeveer 150 Ω/□. Deze weerstand is te hoog om deze lagen toe te kunnen passen voor patroonmatige depositie van metalen. Deze lagen kunnen wel effectief gebruikt worden voor de depositie van metalen op kleine, aaneengesloten oppervlakten.

Tenslotte zijn de polypyrroollagen gekarakteriseerd met behulp van cyclische voltammetrie. Deze metingen laten zien dat polypyrrool bij potentiaal van -0,5 V en lager in de gereduceerde, niet-geleidende vorm is en bij potentiaal van -0,2 V en hoger in de geoxideerde geleidende vorm.

In deel B is de electrochemische depositie van koper uit een oplossing die 0,94 M CuSO₄, 0,60 M H₂SO₄ en optioneel 0,1 mM van een organisch molecuul, namelijk kristalviolet, benzoatriazol, of thiourea, bevat, op een polypyrroollaag op poly-ether-imide besproken. De koperdepositie start binnen een korte afstand van het elektrisch contact en zet zich tijdens verdere depositie in laterale richting voort.

In hoofdstuk 7 is de invloed van de potentiaal en het toevoegen van organisch moleculen, namelijk kristalviolet, benzoatriazol, of thiourea, aan de elektrolyt op de laterale groeisnelheid (of frontsnelheid) beschreven. Bij negatievere depositiepotentiaal neemt de frontsnelheid toe en is de zone waar de kopernucleatie plaats vindt, kleiner. De kortere nucleatiezone wordt niet veroorzaakt door een scherper potentiaalverval in de polypyrrool-elektrode maar door de promotie van de nucleatie bij negatievere potentiaal.

Thiourea vergroot, in tegenstelling tot kristalviolet en benzoatriazol, de frontsnelheid bij negatievere potentiaal door de promotie van de kopernucleatie.

Cyclische voltammetrie en weerstandmetingen laten zien dat niet alleen Cu²⁺ maar ook de polypyrroollaag wordt gereduceerd gedurende de depositie van koper. Ondanks deze reductie van polypyrrool stopt de laterale kopergroei niet.

In hoofdstuk 8 is met behulp van in-situ electrochemische atomic force microscopie (EC-AFM) de groei van koperkristallen op polypyrrool en het effect van thiourea op deze groei bestudeerd. De AFM-data laten zien dat de kristalgroei begint op hobbels op het polypyrrool-oppervlak. Zonder thiourea zijn de koperkristallen glad en wordt de vorm van de kristallen bepaald door de morfologie van het polypyrrool-oppervlak. Thiourea remt de groeisnelheid van de koperkristallen in de verticale en laterale richting. Dit resulteert in een gelaagde structuur van de koperkristallen.
Samenvatting

In hoofdstuk 9 is het effect van de depositietijd en van organische moleculen, namelijk kristalviolet, benzotriazol en thiourea, op de dikte, structuur, taaiheid en het uiterlijk van de koperlaag beschreven. Door de elektrische weerstand van de polypyrroollaag wordt een koperlaag met een niet uniforme dikte gevormd. Deze niet uniforme dikte is onafhankelijk van de depositiepotentiaal, wordt verbeterd door thiourea en neemt af indien de depositietijd wordt verlengd nadat het totale polypyrrool-opervlak bedekt is met koper.

Het toevoegen van de organische moleculen aan de koperoplossing resulteert in koperlagen die taaier zijn. Thiourea en benzotriazol verbeteren bovendien de ruwheid en het uiterlijk van de koperlagen bij potentialen van -0,6 V en lager.
Curriculum Vitae

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Roger