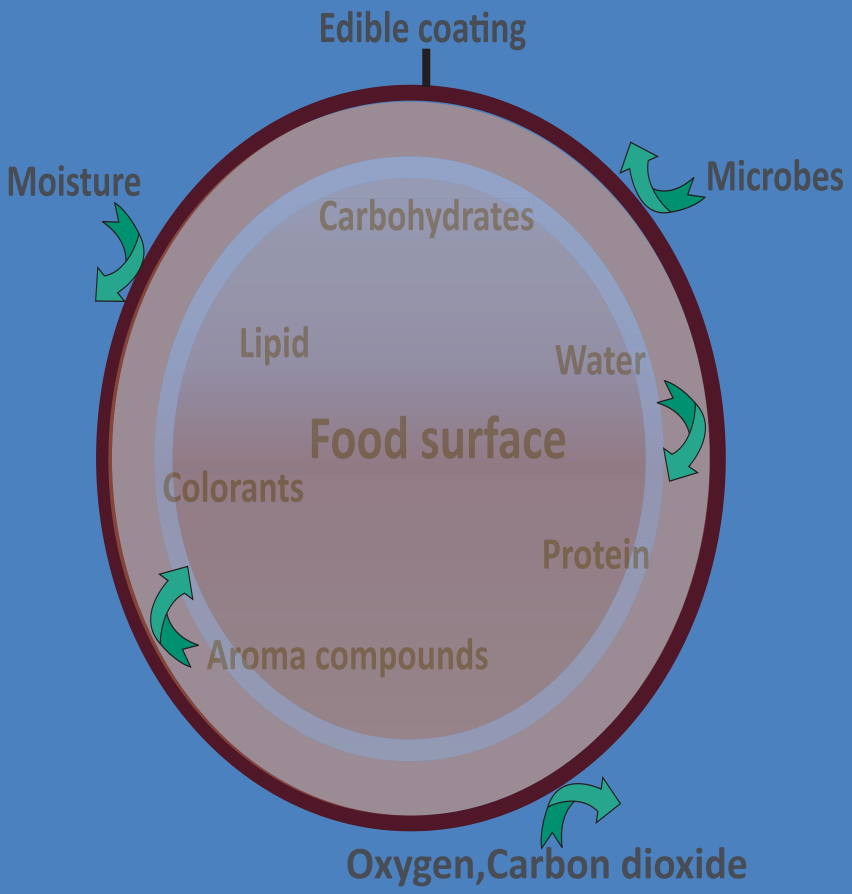
Electrospraying
for efficient coating of foods



Muhammad Kashif Iqbal Khan

Propositions

1. For even coating with electrospraying, charge leakage is more important than charge to mass ratio (this thesis).
2. Micro-scale film defects determine the macro-scale shelf life of a product (this thesis).
3. Technology has revolutionized the world at the expense of traditions.
4. The aim of young scientists should be a Nobel Prize instead of a good H-factor.
5. Open access literature leads to a better life for everyone.
6. Common sense is a sense that is not common in common people.
7. Combining Pakistani and Dutch food will lead to a new dimension in fusion cooking.
8. Completing a PhD-project is like seeing the sun after a long drive in foggy weather.

Propositions belonging to the thesis

Electrospraying for efficient coating of foods

Muhammad Kashif Iqbal Khan

Wageningen, 11th March 2013

Electrospraying

for efficient coating of foods

Muhammad Kashif Iqbal Khan

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Electrospraying

for efficient coating of foods

Muhammad Kashif Iqbal Khan

Thesis

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Dedicated to

my Family

and

beloved home land

Contents

Chapter 1

Introduction

Introduction

This chapter describes the application of edible coatings as a strategy to improve the quality and extend the shelflife of foods. Moreover, it introduces an efficient coating technique for foods, namely electrospraying, capable of preparing ultra-thin films and coatings. Finally, the principles of electrospraying are explained, followed by aims and outline of the thesis.

1.1. Edible coatings

Nature has provided barriers to foods like fruits and nuts, in the form of skin and shell. Amongst others, these regulate the moisture and gaseous exchange, and reduce the loss of flavour and aroma compounds. When processing foods, the natural barrier function of the raw material is often lost. Efforts have been and are being made to protect the foods from the influences of its environment. As early as 5000 BC, food was placed in animal skin or leaves (Miller & Krochta, 1997), while the use of edible coatings on food products started in 12th century when citrus was preserved by applying wax as a protective layer (Debeaufort et al., 1998; Hossein, 2011). Recently, edible coatings have been applied to facilitate the demand for safe, high quality, and minimally processed foods (Andrade et al., 2012; Lin & Zhao, 2007).

Nutritional, organoleptic, and microbiological properties determine the food quality, which changes by the interactions between the food product and its environment (Andrade et al., 2012; Debeaufort et al., 1998; Debeaufort & Voilley, 2009). For instance, a decrease in quality may occur either due to oxidation as a consequence of oxygen migration, or the loss of a specific constituent such as water or aroma components (Miller & Krochta, 1997). Edible barriers can be used to retard these effects. In addition to barrier properties, edible coatings can also improve the mechanical handling and the structural integrity of food products (Andrade et al., 2012). For example, edible coatings on fruits and vegetables may replace and/or reinforce the natural skin layer, reduce the loss of moisture, and control the gaseous exchange such as oxygen, carbon dioxide, and ethylene (Pavlth & Orts, 2009).

Additional ingredients may be included in the coating formulation to enhance the shelf life, or the nutritional and/or sensory attributes of foods (Khan et al., 2012b; Rojas-Grau et al., 2009). For instance, incorporation of micronutrients such as vitamins and minerals (Dhanalakshmi et al., 2011), addition of anticaking agents, and applying antimicrobial agents to improve shelf life have been reported (Ahlberg, 2001; Elayedath & Barringer, 2002; Khan et al., 2012b; Miller & Barringer, 2002). An overview of various functionalities of edible coating is given in figure 1.1.

Fats, proteins, and polysaccharides are the basic ingredients of edible coatings. The exact formulation depends on the desirable functional properties of the film. For mechanical strength and low oxygen permeability, proteins and polysaccharides are often included in the formulation, whereas fats are included for enhanced water vapour barrier functionality (Debeaufort & Voilley, 2009; Khan et al., 2012a; Khan et al., 2012c).

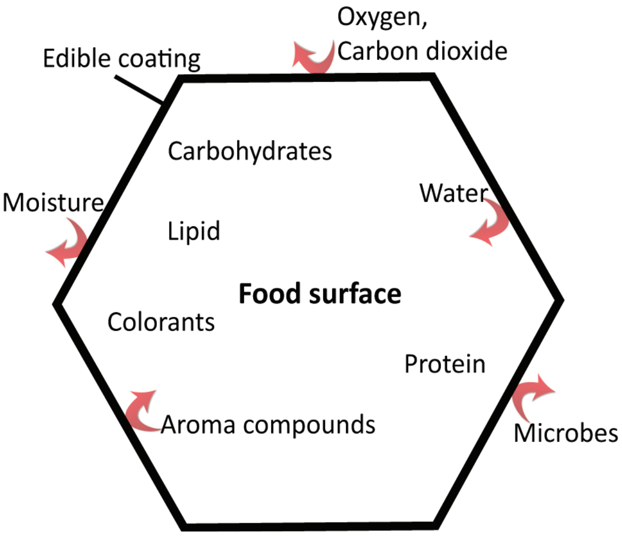

Figure 1.1. An overview of the edible coating's functionalities when applied to foods.

An edible coating that acts as a barrier should not change the sensory attributes of product to a large extent. A flexible product has to be coated with a material that provides at least the same flexibility in order to avoid breakage of the film during the handling process. Combining fats with proteins and/or polysaccharides in an emulsion may result in a film with an appropriate balance between moisture barriers properties and mechanical strength (Bourlieu et al., 2009; Khan et al., 2012a; Wu et al., 2002).

1.2. Coating techniques

One of the major challenges is to prepare the defect-free coatings. Even small defects may be detrimental to the barrier property of a film. For example, a paraffin film with a moisture permeability of $0.002{\cdot}10^{-13}$ kg/(m·s·Pa) is potentially a very good barrier. If it has a defect with a surface porosity of 0.01% which will increase the permeability about 150 times (assuming that the defect is filled with air, and using the diffusive permeability of air, and neglecting any convection).

A defect-free film can be created by applying a thick film; however this would negatively affect the sensory quality. Therefore, the challenge is to make thin and defect-free films. This requires a method that can deposit films uniformly, even on irregular surfaces. Unfortunately, many coating procedures suffer from significant coating material losses (50%) and provide a heterogeneous distribution of coating material across the target surface (Boom et al., 2011; Jaworek, 2007; SAS, 2012). Losses in material can also contribute to additional cleaning costs and safety issues (Khan et al., 2012b; Ratanatriwong, 2004). Therefore, any coating method that increases the effective targeting and even distribution of the coating material on the product is of great practical relevance.

1.2.1. Electrostatic coating

Electrostatic coating is a promising and efficient method for food coating. It originates from the paint industry and has been applied to reduce the use of solvents and waste production through its higher transfer efficiency, even and reproducible coatings on the target surfaces (Meng et al., 2009). Besides the paint industry, it is a commonly used method for coating in the pharmaceutical and automotive industry but it is less popular in the food sector until now (Khan et al., 2012b; Luo et al., 2008; Mayr & Barringer, 2006).

A comparison between electrostatic and non-electrostatic powder coating methods is presented in figure 1.2. Electrostatic coating exhibits a higher transfer efficiency of the material to the target surface, provides better and even coverage of targets, and saves coating material. Additionally, it reduces the contamination of the environment and the equipment with spilled coating material and hence reduces the cleaning cost. Moreover, electrostatic coating often results in better adhesion of the coating material (Xu & Barringer, 2008), which prevents the coating material to drop off during further processing and reduces the amount of coating material that needs to be used. Thus, electrostatic powder coating is a more efficient and cost effective coating process.

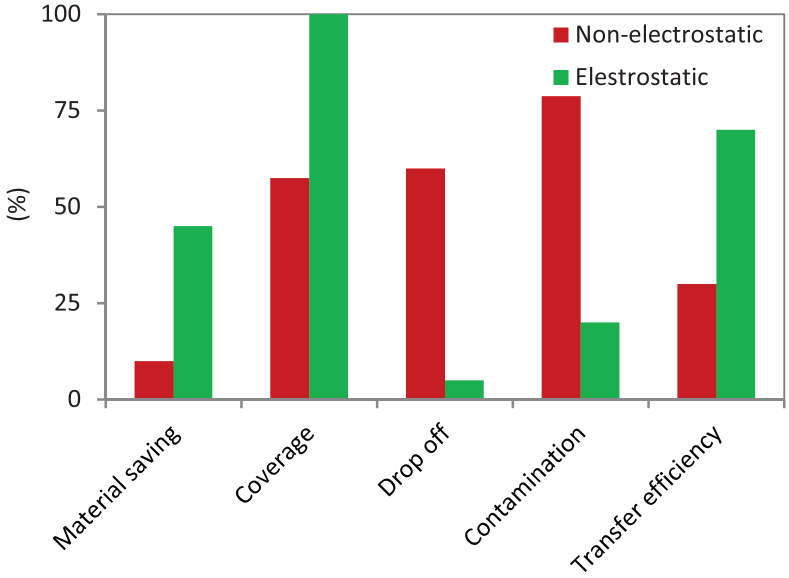

Figure 1.2. A comparison of electrostatic with non-electrostatic powder coating methods (Amefia et al., 2006; Barringer et al., 2005; SAS, 2012).

Electrostatic coating uses charged particles or droplets that are attracted by a grounded target. Because of the charge, they repel each other and uniformly spread out while airborne. Afterward, they deposit evenly on the target. In electrostatic coating, two different charging methods can be distinguished. The first method involves the dispersion of powder or liquid material in the air and subsequent charging of the material by passing it through an ion rich region, created by corona discharge. The charged particles are then attracted by the grounded target (Bailey, 1998; Khan et al., 2012b; Luo et al., 2008; SAS, 2012). In addition, powders can be charged by tribo-electrification, although, this method is not as widely applied as corona charging (Khan et al., 2012b).

1.2.2. Electrospraying

Another method, suitable for dispersing liquids is known as electrospraying or electro-hydrodynamic atomization (EHDA). In this method, an electric potential is applied on a liquid passing through a capillary, which breaks the liquid into fine charged droplets. The electrostatic forces arising from the accumulation of charge on the liquid surface, overcomes the surface tension, which results in the instability of liquid surface and the break-up into many small droplets. These small droplets are then attracted by the grounded target resulting in high deposition efficiency (80%) (Wilhelm et al., 2003). After the emergence from the nozzle, the electrostatic repulsion among the droplets causes the dispersion and prevents their coalescence in air. During electrospraying, various spraying modes can be achieved: dripping (micro, spindle, and multi-spindle) and jet (cone-jet, multi-jets, oscillating jet, and ramified jet) (Enayati et al., 2011; Jaworek, 2008). Amongst these modes, the cone-jet mode is used mostly because it is operationally the most stable and provides small droplets with a narrow size distribution (Bock et al., 2012; Jaworek, 2008; Khan et al., 2012c).

Since the process has mostly been applied for the coating of metal constructions (bridges, buildings; cars), the process of electrospraying is not yet well understood for surfaces that have low electrical conductivity. The accumulation of charge on the surface, after the deposition of sprayed material may well influence the process. Secondly, so far it is unknown how the process performs with surfaces that are very irregular or even porous, as that of many food products such as corn flakes, apple pieces, and baked products.

1.3. Aim and outline

The aim of this thesis is to increase understanding of the electrospraying process, and its interaction with the morphology and characteristics of the target surface. Based on that, we explored the possibilities of the process for surfaces that represent the characteristics of food products.

Chapter two evaluates the electrostatic powder coating technique for food applications. Since moisture and oxygen barrier properties are of great relevance for food, **chapter three** describes the investigation of thin films prepared by electrospraying of liquids. The major process parameters (i.e. flow rate, conductivity, and voltage) and target properties that influence droplet formation and deposition are studied, respectively. In **chapter four**, the mechanism of film formation on different porous target surfaces is investigated by CSLM, and water vapour permeation through the films formed is evaluated. The acquired insight is translated to prepare films on the food target surfaces (**Chapter five**). Water uptake is investigated as function of the characteristics and the amount of coating material applied. In the last experimental chapter, emulsion-based coatings are prepared by electrospraying (**Chapter six**). The influence of solvent properties (water content and dispersed phase conductivity) and water soluble components on droplet size and barrier functionality of the film are elucidated. Finally, the discussion section (**Chapter seven**) gives an overview of the entire study and presents an outlook for the application of electrospraying in food and related industries.

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Chapter 2

Electrostatic powder coating of foods

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Abstract

Edible coatings and incorporation of active ingredients can improve food quality (appearance, taste, flavours, and increased shelf life). In this chapter, specific emphasis is given to electrostatic application of powder coatings that is known for its high transfer efficiency and even coating. This technique has potential to reduce excessive use of coating material (up to 68%) and minimize dust release (up to 84%) to the environment. Different parameters are discussed that influence powder coating quality and efficiency for both non-electrostatic and electrostatic powder applications. Typical food processing systems are reviewed that can be combined with electrostatic powder coating. Finally, an overview of electrostatically coated food products and a short outlook of electrostatic powder coating are given.

2.1. Introduction

Powder coating involves the application of powder particles on a sizeable product in order to deliver new functionalities. Conventionally, powder coatings are applied to provide colour and flavour to food products. It is an effective way to improve appearance and taste of the products, which ultimately increases consumer acceptability (Dhanalakshmi et al., 2011; Mayr & Barringer, 2006; Ricks et al., 2002; Yousuf & Barringer, 2007). Other reasons to apply powder coatings are: to increase nutritional value of products (e.g. dosing of powdered micronutrients such as vitamins and minerals) (Dhanalakshmi et al., 2011), to provide anticaking properties (e.g. powdered wheat flour on cookies), or to enhance shelf-life (e.g. adding antimicrobial agents to fresh food products) (Ahlberg, 2001; Elayedath & Barringer, 2002; Miller & Barringer, 2002; Pfeffer et al., 2001). More information on the various applications can be found in table 2.1 (Page 31).

For effective powder coating, the material should be evenly distributed across the target surface, to ensure an identical appearance of all product sides (Clark, 1995; Lusas & Rooney, 2001). In regular powder coating, products need to be turned around when coated on a conveyer belt, which makes it almost impossible to coat uniformly all sides of a (thick) three-dimensional product. In a system where the product is actively mixed during the coating procedure, the distribution of coating material occurs more in a chaotic manner, which inherently leads to uneven distribution of coating material. Another aspect of powder coating is that powder particles should remain intact at the product, despite any further handling. To fixate powder particles to the product surface, sometimes fats are first sprayed on the target surface that provides a sticky layer and promote adhesion of particles.

The efficiency of powder coating, defined as the amount of material that adheres to the target compared to the applied amount, is often not very high. In a typical food factory, much coating material does not reach the product, but is spilled, e.g. on the conveyer belt (after which it still may be re-used if hygienic regulations allow), or is emitted to the surrounding air. To compensate the losses, excessive amounts of coating material are used. Apart from loss in efficiency, this leads to additional cleaning costs (Ratanatriwong, 2004), and safety issues such as reduced air quality and increased risk of dust explosions

(Clark, 1995). Although coating material is sometimes inexpensive, excessive use is always undesirable, also from a sustainability point of view. Therefore, any coating method that improves effective targeting of the coating material to the product with even distribution of powder particles could be of great relevance to food industry.

In the last two decades, paints, metal, and wood finishing industry have introduced new coating techniques (Meng et al., 2009; Shah et al., 2006a). These industries were pushed towards water-born and powder coating methods because it was recognised that the use of solvent-based coatings imposed serious risks for human health. Electrostatic powder application has become a standard in these industries for its capability to produce even coating layers with high transfer efficiency (Luo et al., 2008; Misev & Van Der Linde, 1998). After electrostatic powder coating, usually a curing step is applied at high temperatures, during which the applied material melts and fuses to provide a smooth coated surface. Although a temperature-based curing step is not applicable to every food. Electrostatic coating of powders alone could already introduce an improvement to conventional powder coating operations.

The aim is to introduce conventional (non-electrostatic) coating and to provide an outlook for electrostatic powder coating with respect to food products. The following sections discuss different factors that influence the coating efficiency during conventional and electrostatic powder coating. The quality and efficiency of coating depend upon the characteristics of the applied material (powder), and the process systems used to transport the powder to the target product (Dhanalakshmi et al., 2011). Section 2.2 shortly discusses the conventional coating systems and the influence of material properties, while section 2.3 is completely dedicated to electrostatic powder coating.

2.2. Conventional food powder coating

In food industry, powder-coating methods are mostly basic, e.g. dosing of powder from a small hopper or a vibrating gutter. In these methods, either powder is fluidized or gravity fed on substrates (Burns & Duggan, 1997; Jainia, 1994; King, 2002). One of the dispensing methods is pneumatic transport, in which an air flow drags the powder from a feed hopper into a nozzle and subsequently spreads over the target surface (Jr, 1997).

Alternatively, powder dosage may occur by vibration or stirring action i.e. using a screw feeder. By screw movement, powder moves from the hopper to the feeder outlet. Subsequently, gravitational forces carry the powder to the target surface where it coats the product (Biehl & Barringer, 2004; Hanify, 2001). As discussed previously, these methods often poorly spread the coating material across the target surface and suffer from low transfer efficiencies. The influence of the powder properties on coating quality and efficiency for conventional coating systems is described; these properties are also important for electrostatic coating and will be discussed in the respective sections as well.

2.2.1. The influence of powder properties

2.2.1.1. Particle size and shape

Small particles, which can be easily carried away by airflow, are distributed evenly on the target surface but exhibit lower transfer efficiency compared to larger particles (Biehl & Barringer, 2003; Miller & Barringer, 2002). It has also been shown that coating transfer efficiency increased with increasing particle size as large particles fall directly on the product, while small particles remain airborne for longer time and may miss the target (Ratanatriwong et al., 2003; Ricks et al., 2002). The efficiency of operation can be increased by proper design, i.e. using a specific combination of aerodynamic and gravitational forces, directing particles towards the food product and thus optimising coating evenness and transfer efficiency; however, production of high quality coatings is still a challenge (Ratanatriwong & Barringer, 2007; Yousuf & Barringer, 2007).

2.2.1.2. Flowability

Flowability describes the ease with which a powder will flow under specific conditions. It is dependent on particle size, shape, and in particular the chemical composition of a powder (Dhanalakshmi et al., 2011). Powders are categorised into three different flowability categories: free flowing, fairly free flowing, and cohesive powders. Free flowing powders exhibit greater coating efficiency than cohesive powders. As cohesiveness of powders increases, particles tend to adhere and make clumps that can choke container outlets, stop powder flow, and lead to intrinsic uneven distribution of the coating material (Amefia et al., 2006; Ratanatriwong et al., 2003). Powder flowability depends amongst others on particle size (Teunou et al., 1999); powders with small particles are more cohesive with poor flowability (Ratanatriwong & Barringer, 2007), due to their high surface to volume ratio. In powder coating, free flowing powders are preferred for uniform application. The differences in flowability determine the dispensing behaviour.

2.3. Electrostatic coating

2.3.1. General aspects

Electrostatic powder coating has been widely used in automotive painting industry for years. It produces even, uniform, and reproducible coatings with less waste compared to conventional coatings. In preparation of snacks, it is used as an alternative to conventional powder coating processes, and has reduced dust formation in production lines and increased transfer efficiency (Amefia et al., 2006; Biehl & Barringer, 2003).

The first step in electrostatic coating is charging of powders. Due to similar charge, these particles repel each other, forming an even cloud across the target surface (Amefia et al., 2006); at higher charge, the powder is more widely spread and has higher transfer efficiency (Meng et al., 2009). Powder charging can be achieved by two mechanisms: corona charging and tribo-charging. In corona charging, powder particles pass through an ion rich region, and get charged based on their permittivity. Subsequently, they are transported towards target and deposited due to the charge difference (Figure 2.1).

Another method is tribo-charging, which relies on frictional charging of powder that is transported through a pipe of a specific material, such as PTFE, metal or other powder particles (Figure 2.2) (Bailey, 1998; Luo et al., 2008; Pawar et al., 2010). Tribo-charging produces less charge on particles than corona charging (Sumonsiri & Barringer, 2010), thus the corona charging mechanism is mostly used for electrostatic powder coating (Mazumder et al., 2006). A combination of aerodynamic, gravitational, and columbic forces transport charged powders to the target surface.

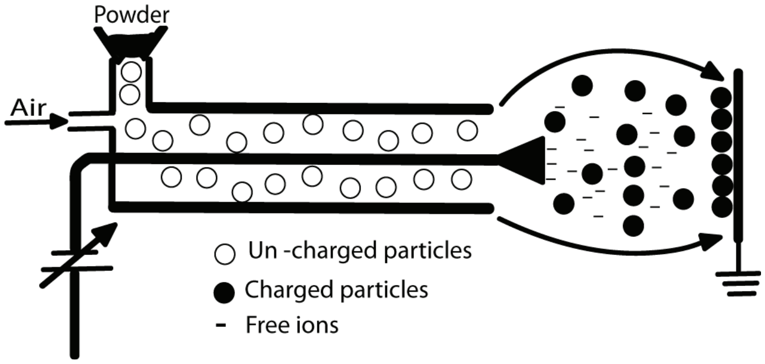

Figure 2.1. A graphical representation of corona charging; powder are fed by air flow in the ion rich region to get charged.

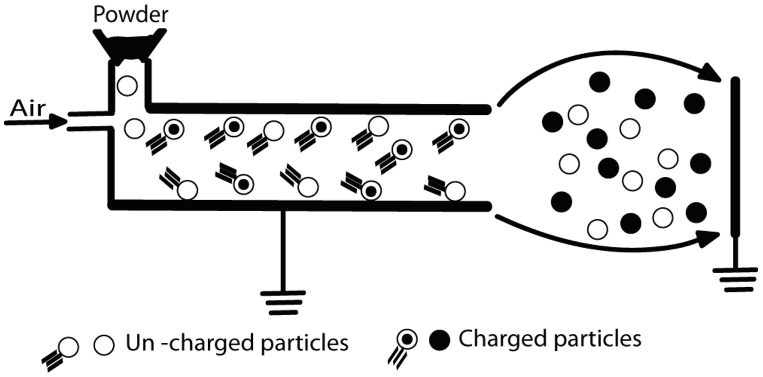

Figure 2.2. A graphical representation of Tribo-charging; friction between powder particles and metal tube produces charge on particle.

The major advantages of electrostatic coating technology (also for food stuffs like sugar or starch) are reduction in coating materials loss (68%), reduction of dust formation (values between 40 - 84% were reported for particles of different sizes), and lower operational costs compared to conventional coating techniques (Luo et al., 2008; Mayr & Barringer, 2006; Mazumder et al., 2006; Ratanatriwong, 2004; Ricks et al., 2002). Spice Application Systems, a supplier of electrostatic spray equipment, claims powder savings between 10 - 45% and lowers line contamination levels (15 - 20%) compared to conventional coating technologies (70 - 90%) (SAS, 2012). Lower line contamination helps in reducing the cleaning cost of equipment and environment. Moreover, the electrostatic coating process is not significantly influenced by the variations in environmental conditions (Xu & Barringer, 2008).

2.3.2. Powder properties

Similar to conventional coating, for electrostatic coating powder properties have influence on coating quality and transfer efficiency. For example, particle size determines the maximum charge or saturation charge on particles. The theoretical relation between particle size and saturation charge (Q_{max}) during corona charging is described by (Meng et al., 2009):

$$Q_{max} = \frac{12\pi\varepsilon_0\varepsilon_r r^2 E}{\varepsilon_r + 2}, \qquad (2.1)$$

where r is the radius of particle, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the particle, and E is the electric field strength. Under the specific applied corona charging conditions the *time* required to reach the saturation charge is defined as (Bailey, 1998):

$$\tau = \frac{4\varepsilon_0 E}{J}, \qquad (2.2)$$

where τ is the time required to reach the half saturation charge and J is the corona current density. Particle size is also related to the charging efficiency, which is described by the charge to mass ratio (Q/M) (Meng et al., 2009; Wu, 1976). The maximum charging efficiency is given by:

$$\frac{Q_{max}}{M} = \frac{9\varepsilon_0\varepsilon_r E}{(\varepsilon_r + 2) r\rho}, \qquad (2.3)$$

where ρ represents the particle density. From the latter equation, it is clear that charging efficiency is inversely related to particle size. Ultrafine powders may thus be preferred for electrostatic coatings, since their charging efficiency is higher and will mostly better adhere to surfaces (Amefia et al., 2006; Mazumder et al., 1997; Meng et al., 2009). This is contrary to conventional coating methods, where ultrafine powders exhibit low transfer efficiencies. For both conventional and electrostatic coating, the particle size distribution of the coating material will affect coating efficiency, but in a different way.

Another factor that influences the chargeability of the powders is the resistivity. The powder resistivity is related to the amount of charge a powder particle can pick up and lose when in contact with the target product. If resistivity is high, the powder charge decays at a low rate resulting in high electrostatic adhesion (Ratanatriwong, 2004; Xu & Barringer, 2008). Powders can be categorized into three different resistivity classes:

- Powders with resistivity below 10^{10} Ω·m are conductors and pick up charge easily and will lose charge again upon contact with targets. This makes them unsuitable as coating materials (Luo et al., 2008).
- For powders with resistivity between 10^{10} Ω·m and 10^{13} Ω·m, powder behaviour is hard to predict. Charge decay takes place in only a few seconds and adhesion is poor (Luo et al., 2008). However, some powders may exhibit good adhesion, which is probably due to the specific combination of powder and surface properties used (Sumonsiri & Barringer, 2010).
- Powders with resistivity more than 10^{13} Ω·m are insulators with a charge decaying time of minutes to hours, which allows sufficient time for charged particles to be processed further (Bailey, 1998). These particles will have strong attraction with the target, which will result in good adhesion (Sumonsiri & Barringer, 2010). It is worthwhile to mention that the presence of many charged particles on a non-conducting surface may negatively influence settling of new incoming powder particles; it is clear that optimisation of various effects is needed to make ‘optimal’ coatings with high transfer efficiency.

Besides particle size and chargeability, particle shape also affects coating efficiency, for example, cube crystals are more efficient than pyramid and flake shape particles of similar size (Buck & Barringer, 2007; Miller & Barringer, 2002); note that this is different for other coating methods. An additional benefit of electrostatic coating is that powder wraps around the food target and coats all sides (Bailey, 1998; Maski & Durairaj, 2010; Sumonsiri & Barringer, 2010). Some authors have claimed that particle density is a significant factor in transfer efficiency in electrostatic coating (Miller & Barringer, 2002; Ricks et al., 2002;

Yousuf & Barringer, 2007). It is however not clear why increasing density would improve transfer efficiency. Most probably, this effect is small as compared to that of particle size.

2.3.3. Target properties

In electrostatic coating, coating properties also depend upon target properties. The most important target property is target conductivity; if the target surface is conductive, new incoming charged particles, and deposited particles on the target surface will not electrostatically interact, thus increasing the transfer efficiency and coating effectiveness. On less conductive target surfaces, charges will accumulate and incoming charged powder particles may be repelled by this charge (Khan et al., 2012; Sumonsiri & Barringer, 2010). Furthermore, the charge build up can potentially result in a back corona discharge, which arises from the high electric field created within the deposited particle layer. Back corona produces gaseous ions of polarity opposite to the charged powder particles and thus neutralizes the charge of incoming particles. Back corona lowers transfer efficiency and reduces layer thickness, as the intensity of back corona discharge is highest near the product surface (McLean, 1988; Meng et al., 2009; Shah et al., 2006b).

In electrostatic coating, deposition is a competing process between air-borne charged particles and the back corona from the deposited particles (Meng et al., 2008; Xiangbo & et al., 2009). Besides these factors, mostly it is required that the powder stays dry after application, and because of this relatively dry products (such as potato chips and popcorn) can be treated efficiently by this technology since the water activity of product and powder are in close proximity. When uniform dosing is preferred (e.g. in delivering smoke flavour), the powder may dissolve, and there are no limits to the target as long as it is sufficiently conductive to release the charge timely (**Chapters 3**, **4**, and **5**).

2.4. Electrostatic powder coating in practice

Electrostatic coating, in combination with standard processing equipment, can be used to coat a number of foods as described in the next part. In addition, the hazards and safety measures related with electrostatics are discussed.

2.4.1. Applications

Conventionally, powder coating has been carried out in combination with a variety of food processing systems to overcome some of their drawbacks. For example, a conveyor belt system can be equipped with a corona charging powder applicator. Different products have been treated by this method, such as French fries with glucose powder and smoke extract, which had more uniform colour and texture compared to conventional methods (Amefia et al., 2006). These products have been coated without any pre-treatment of powders and target surface, which reduces the number of processing steps, and ultimately reduces the processing time and cost.

Other examples are grated cheese with antimycotic powder which leads to improved functionality and increased shelf life (Amefia et al., 2006), potato chips with more even coating and colouring through spices (Ratanatriwong et al., 2003). Other applications are: coating of meat with smoke extract to improve flavour uniformity (Pie-Yi Wang, 2000), delivery of bactericides, flavours on candy and chocolate (Ahlberg, 2001; Ratanatriwong, 2004), salt and other seasonings on potato chips (Ratanatriwong et al., 2003).

In addition, a tumble drum can be equipped with a corona charging powder applicator. In the drum, powder is continuously dispensed (e.g. via a vibrating hopper) and charged via corona wire discharge; for example popcorn has been successfully coated with sugar and starch at high transfer efficiency (Biehl & Barringer, 2003). Besides corona charging devices, also tribo-charging devices have been evaluated. For example, bread has been coated with cocoa powder and corn starch on conveyer belt systems (Sumonsiri & Barringer, 2010).

2.4.2. Hazards and safety measures

Dust explosions, fire, and ignition of materials are common hazards in powder industry, and they are considerably less and more manageable in electrostatic compared to regular powder coating. The main source of hazards are mechanical; yet electrostatic hazards can also occur (Ireland, 2010b; Ndama et al., 2011), mainly due to charge accumulation (Glor, 1985; Glor, 2003; Ireland, 2010a, b; Ndama et al., 2011). Prolonged charge accumulation may result in ignition of powder with lower ignition energies, which determine how flammable powder is (Beloni & Dreizin, 2009, 2011). Charge accumulation can be reduced by using low resistive powders or by using ionizing devices (Thomas III et al., 2009).

Suitable safety measures are needed that will reduce hazards, such as prevention of discharges that may ignite dust clouds or providing some form of explosion protection. Combinations of grounding all equipment and personnel, controlled charge generation, and dissipation can achieve this. In general, overall design of plant and operation should be such that it puts off charge accumulation (Gibson, 1997; Thomas III et al., 2009), and this is technically feasible.

2.5. Conclusions

In dry coating techniques, electrostatic coating emerges as a novel technique, which is quite common in non-food industry. This chapter provides information about this technique, which can be used in the food industry in combination with e.g. conveyer belt and tumble drum. In this way, coating procedures can be improved through higher transfer efficiency, better adhesion, low energy usage, less waste production, and air borne dust, which makes this method cost effective. Moreover, this technique does not require pre-treatment steps of coating material or target surface. Altogether, it can be concluded that electrostatic powder coating shows much potential for food applications yet some specific safety measures have to be taken obviously.

Table 2.1: Overview of electrostatically coated food applications.

Applications	Targets	Coating materials	References
Seasonings	Potato chips, crackers, and pretzels	Salts	(Madl, 2000; Matz, 1984)
Shelf life	Meat	Anti-microbial agents	(Ahlberg, 2001)
Flavour	Candy and chocolate	Flavours	(Clarke, 1968)
Shelf life	Cheese	Natamycin and cellulose	(Elayedath & Barringer, 2002)
Flavour	Meat	Smoke particles	(Abu-Ali & Barringer, 2008)
Colour and flavour	Potato chips	Salts and nacho cheese	(Ratanatriwong et al., 2003)
Coating adhesion	Saline cracker and bread	Cellulose, whey, sugar, and cocoa powders	(Halim & Barringer, 2007)
Shelf life	Cheese	Sodium erythorbate and smoke extracts	(Amefia et al., 2006)
Browning and shelf life	Potato chips	Glucose and smoke extracts	(Amefia et al., 2006)
*Flavour, colour, and adhesion	Popcorn	Sugar, salt, cellulose, and malto-dextrin	(Biehl & Barringer, 2003; Miller & Barringer, 2002)

*This is carried out by combination of electrostatic coating and tumble drum, while others are with conveyer belt.

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Chapter 3

Electrospraying for hydrophobic film formation

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Abstract

There is a continuous need for thinner edible coatings with excellent barrier properties which requires new application methods. Electrospraying is known to yield fine droplets of 20 µm size, giving the potential of very thin and even coatings. A single electrospraying nozzle was used to characterize droplet formation and to investigate the formation of thin films on model surfaces. The experimental droplet size was successfully described as a function of operational parameters and liquid properties using scaling relations. Thin film deposition was experimentally investigated for sunflower oil electrosprayed on a highly conductive (aluminium) and insulating target surface (parafilm). For both aluminium foil and parafilm the droplet deposition was random. For aluminium foil, this was expected because the repulsion between droplets on the surface and new droplets is low, due to charge leakage. For parafilm, droplet repellence appeared so large that droplets deposited on empty spots or even pushed away from the surface. To evaluate the film formation performance, Monte Carlo simulations were carried out, which is a useful tool to characterise droplet deposition and film formation characteristics.

3.1. Introduction

Edible coatings are important in foods. They can be barriers against migration of moisture, colorants, oxygen or other components, and thus increase the shelf life, attractiveness to the consumer, and may enable new product design. For a good barrier function, the film should be as thin as possible without defects. The application method in combination with coating formulation and target properties determine the thickness, permeability, and homogeneity of the films produced (Domnick et al., 2005).

Spray coating is amongst the most commonly used method to coat foods. Sprays can be created using various types of nozzles, e.g. hydraulic spray nozzles, gas assisted, and ultrasonic atomizers. For foods, an attractive and less well-known atomization method is electrospraying. Electrospraying has received significant attention in scientific literature due to its ability to produce small droplets, even down to submicron size (Jaworek, 2007a, 2008); however, application in food has been scarcely reported.

In electrospraying, the to-be-atomized liquid is charged by passing it through a metal capillary, where high electric potential is applied. The electrical potential acts as a shear stress on liquid drawn from nozzle and therefore produces a fine cone-jet (Jaworek, 2007a). If the electric potential exceeds the Raleigh limit, jet breaks up into a fine spray. Because of charge, droplets repel each other and do not coalesce in air which results in even distribution (Xu et al., 2006). The advantage of generating charged droplets is high transfer efficiency (80%), because they are accelerated towards grounded targets (Jung et al., 2010; Wilhelm et al., 2003), while their small size may yield better defined, thin films.

Electrospraying has been applied in painting, pharmaceuticals, and foods industry. For example, nano-capsules for controlled drug release were produced with electrospraying (Xie & Wang, 2007; Xu & Hanna, 2008). Other applications are for nano-particle production (Loscertales et al., 2002), ionization and characterization of protein and DNA in mass spectrometry, and respiratory drug delivery (Ijsebaert et al., 2001; Xu et al., 2006). In foods, electrospraying has been evaluated to apply chocolate (Gorty & Barringer, 2011), smoke flavour to meat, polishing and coating agent on sugar, confectionary and chocolate products (Abu-Ali & Barringer, 2008), flavour application on snacks, and to produce cocoa butter microcapsules (Bocanegra et al., 2005). Further, lipid is sometimes used as a sticking agent for solid ingredients (e.g. spices) that are afterwards applied to the target surface. For most of these applications, the film does not need to be completely developed; however if it can be achieved, it would result in a barrier, which can be of great added benefit in foods.

In this study, emphasis was given to film formation by electrostatic coating. The hydrophobic film forming materials are suitable to be atomized because their resistivity can be tuned between $1 \cdot 10^5$ to $1 \cdot 10^{10}$ $\Omega \cdot m$ (Hayati et al., 1987b). In this study, electrospraying of sunflower oil was used as a model hydrophobic coating material. Most commonly used hydrophobic coating materials (in order of decreasing barrier efficiency) are waxes, lacquers, fatty acids, alcohols, acetylated glycerides, and cocoa based compounds (Debeaufort & Voilley, 2009). Lipid coatings have been found the most effective in creating barriers against moisture migration. Typical applications are in coating fresh fruits and vegetables to control desiccation, ready-to-eat products (e.g. pizza) to prevent moist migration or in crispy products to prevent water and flavour loss from an aqueous filling (e.g. ice-cream cone). Although it also should be mentioned that electrostatics may affect the food which was not visually observed in this study; therefore, focus was on film formation and surface coverage.

One of the major challenges for thin film production is complete coverage of the target area. Small pinholes can dramatically affect barrier properties. Electrospraying in this respect is promising, as small droplets are more efficient to achieve homogeneous surface coverage. Therefore, a thinner film may be produced with this technique, while ideally; barrier properties are similar to conventional films, or even better if pinholes can be prevented.

We present atomization behaviour of sunflower oil as a function of liquid's properties and flow rate for electrospraying in the cone-jet mode and compared to a recently developed scaling law (Gañán-Calvo & Montanero, 2009). In addition, operating parameters such as spraying height and potential difference were investigated. Finally, the deposition patterns of droplets on two model target surfaces (moving on a conveyer belt) were studied, and the mechanism of film fabrication was evaluated using Monte Carlo simulations.

3.2. Materials and methods

A single nozzle (Terronics Development Cooperation, USA) was used to electrospray sunflower oil, as shown in figure 3.1. The nozzle consisted of a metal capillary to which a high electric potential (0-20kV) was applied through a high voltage source (Glassman High voltage Inc., USA). The oil was supplied to the nozzle by a syringe pump (Harvard 11 plus, Harvard Inc., USA), atomized by the nozzle and subsequently distributed across a moving and grounded conveyor belt of aluminium foil.

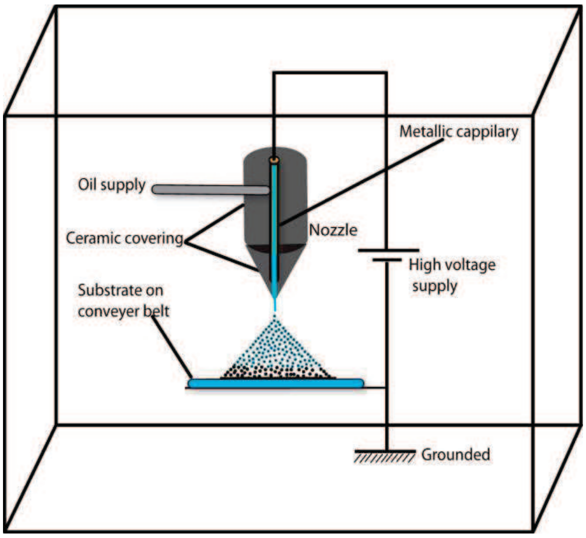

Figure 3.1. Schematic drawing of single nozzle system for electrospraying of sunflower oil.

Pieces of aluminium foil (FORA Folienfabrik GmbH, Germany) and parafilm (Pechiney Plastic Packaging, Inc., USA) were placed on the conveyor belt to investigate droplet deposition and surface coverage behaviour. The dielectric constants or relative permittivities of aluminium foil and parafilm are 10.8 and 2.2, respectively. This means that parafilm, being an insulator, polarizes and holds charge more easily. The films formed on aluminium foil and parafilm were examined with a light microscope. Pictures were taken and analysed with image processing tools (Mat lab, Math works Inc., USA) to obtain droplet shape and surface coverage data. For the average value of droplet size, the average of five pictures containing at least twenty droplets was taken.

The spreading diameters of deposited droplets depend on contact angle of droplet on target surface in air. By assuming that the droplet volume does not change during spraying and deposition, the original diameter of a free falling droplet can be calculated. In the following formula, dependency of base radius ($2a$) on falling droplet diameter ($2R_d$) and contact angle *(θ)* is described:

$$a = R_d \left(\frac{4sin^3\theta}{2-3cos\theta+cos^3\theta} \right)^{1/3}, \qquad (3.1)$$

The minimum electrostatic potential (voltage) required for stable cone jet-spray operation varied with flow rate and conductivity of coating material. The optimum electric potential was determined by visual inspection of the spray.

Alcolec-S Lecithin (American lecithin company, Oxford, CT, USA) was used as an additive to sunflower oil to vary its conductivity. The electrical conductivity (K) was measured at room temperature using a resistivity cell and calculated according to the following formula:

$$K = k.\frac{I}{V} \ , \qquad (3.2)$$

where k is the dimensionless cell constant in the order of unity, I (A) is the current produced by applied electrical potential V (V) in solution. The surface tension was analysed by a Profile Analysis Tensiometer PAT 1 (Sinterface Technologies, Germany). Contact angles were measured using a Drop Shape Analysis System G10 (Kruss, advance surface sciences, Germany). The values found for the conductivity, surface tension, and contact angle are summarized in table 3.1. Conductivity is strongly influenced by the lecithin concentration while, other parameters are mildly influenced. It is worth mentioning that the colour of oil is affected when lecithin concentration exceeded 10% w/w.

Table 3.1. Properties of sun flower oil with varying concentration of lecithin.

Concentration %w/w	Conductivity nS/m	Surface tension mN/m	Contact angle θ	
			Aluminium	Parafilm
0	0	31.0	29±4	-
1	0.35	31.5	39±1	44±1
3	0.92	31.6	35±1	48±1
5	1.3	30.5	38±3	49±0.2
10	3.1	26.1	31±5	45±1
15	3.3	26.3	25±1	49±4
20	5.9	25.4	33±4	47±1

3.3. Modelling

3.3.1. Droplet size

Several studies reported on the atomization mechanisms of electrospraying in cone jet mode (Fernandez de La Mora & Loscertales, 1994; Ganan-Calvo, 2004; Gañán-Calvo & Montanero, 2009; Hartman et al., 2000). Scaling laws were established that describe the influence of liquid's properties and operating conditions on the droplet size. The exact break-up behaviour of cone jet depends on the electric charge of liquid and gives rise to repulsive stress (electrostatic repulsion between ions) which, when large enough to overcome the surface tension.

A minimum flow rate is required to obtain a stable spray in cone-jet mode. At this flow rate, the jet breaks up due to axisymmetric or varicose instabilities and forms a conical spray. Recently, Gañán-Calvo and Montanero (2009) made a revision of the underlying physics of the cone-jet spraying. In their approach, an effective pressure drop (ΔP), caused by electric potential and resulting in electrical stresses, could be described as a function of liquid properties only. It appeared that this pressure drop was independent of operational parameters such as flow rate and applied voltage:

$$\Delta P = k_p \left(\frac{\sigma^2 K^2 \rho}{\varepsilon_0^2}\right)^{1/3}, \quad (3.3)$$

where σ is the surface tension of a liquid (N·m^{-1}), ρ is the liquid density (kg·m^{-3}), ε_o is the permittivity of vacuum, and k_p is a constant in the order of unity. Based on analysis of the stability limits of the cone-jet mode, a new scaling law for the cone-jet radius was derived, which is a good estimate of the final droplet radius:

$$R_d = \left(\frac{Q^2\rho}{2\pi^2\Delta P}\right)^{1/4} \text{if} \qquad We = \frac{\rho Q^2}{\sigma\pi^2 R_d^3} \leq 20, \qquad (3.4)$$

where Q is the flow rate and We is the dimensionless Weber number. This scaling law was compared to experimental droplet data collected in our study.

3.3.2. Droplet deposition

Trajectories of electrosprayed droplets are influenced by electrostatic, gravitational, and aerodynamic forces. Electrostatic forces may arise from interactions between charged droplets in air and deposited droplets charge. These interactions play an important role for droplet deposition on surfaces (Meng et al., 2009; Shah et al., 2006) which are not included in the modelling approach of this study. A Monte Carlo approach has been chosen in which droplets are randomly distributed across a defined surface. Additionally, an alternative deposition mechanism was simulated by assuming that incoming particles search for the spots with lowest energy levels, i.e. resulting in minimal overlap between particles.

From a thin film perspective, it is desired that droplet deposition is not completely random which means that each droplet finds a random position irrespective of previously deposited droplets. Ideally, each incoming droplet would chose a position having minimal overlap with other droplets, thus new incoming droplet would fill the empty gaps on the target surface, resulting in a closed thin film of minimal thickness.

Two theoretical extreme film formation paths are thus identified:

1. Completely random deposition: no interaction between incoming droplets and deposited droplets
2. Fully repulsive deposition (gap filling deposition): repulsion between deposited and incoming droplets preferentially fills the remaining empty gaps on the surface.

A Monte Carlo based approach was applied to simulate both types of deposition behaviour. For both situations, a finite, squared box (length x width = 1 x 1) was defined in which spherical droplets were deposited. The droplets that are positioned in box always remained spherical, and do not deform. It may be clear that this is not always true in practice; for example, when two droplets overlap some fluid will rearrange which will influence the resulting shape of two merged droplets.

The droplets were positioned randomly from the centre of box: for the gap filling deposition mechanism, initially no overlap between deposited droplets was allowed. This is of course only possible if space is still available. After a while no free space is available in the box (using 10,000 attempts) and a slight overlap is subsequently allowed between droplets. In first instance, the distance between droplets should be at least equal to the droplet diameter. This distance is reduced with 10%, allowing some overlap. Again 10,000 attempts are used to find a gap. With increasing surface coverage the allowed overlap is gradually increased following the same procedure.

The area of blobs, the entities of connected and partially overlapping droplets (Figure 3.2), is an interesting parameter to follow effective coverage behaviour of the surface. The area was calculated with an image analysis procedure during which the number of pixels of the different blobs in the image was counted. At complete surface coverage, the blob area is equal to the box area, whereas in the beginning blob area is equal to the area of a single droplet. To facilitate the comparison between model and experiment, the ratio between individual droplet area and picture area was set equal in both experiment and model. Additionally, the surface coverage was calculated (the percentage of covered area in the box). Ratio between areas of blob and single droplet is plotted against surface coverage for the effectiveness and deposition behaviour of droplet on target surfaces. To obtain statistically relevant data for blob area and surface coverage, the deposition of droplets and analysis procedures were repeated 100 times.

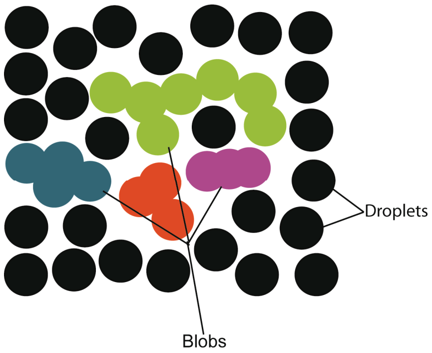

Figure 3.2. An illustration of the difference between, individual droplets and a blob which consist of overlapped and connected droplets.

3.4. Results and discussion

3.4.1. Droplet size

Sunflower oil with varying concentrations of lecithin was electrostatically sprayed and analysed to obtain the droplet size. In figure 3.3, experimental and predicted droplet sizes (base droplet radius) are shown for sunflower oil with 5%w/w lecithin and compared to equation 3.4. The droplet size increases with flow rate, which is in reasonable agreement with the theory. A slight underestimation of the droplet radius is known to occur for many applications and is related to a slightly smaller jet radius compared to the droplet radius (Gañán-Calvo & Montanero, 2009). As expected for equally charged droplets, it can be further concluded that coalescence of droplets in air is not of great influence on the results.

The obvious increase in droplet size with increasing flow rate is due to the reduced charge of the liquid at higher flow rates. Thus, a larger jet radius and different jet break-up behaviour resulted in different droplet size. If the flow rate is larger than 14 ml/h, the measured droplet size is found larger than predicted droplet size. This may be explained by a less stable cone spray, due to decreased residence time of oil in capillary which leads to wider size distributions that are not covered by the physical model.

The predicted droplet radius decreased slightly with increasing conductivity (Figure 3.4). From the experiments it appeared that only the oil with the lowest conductivity ($9.17 \cdot 10^{-10}$

S/m) produced a somewhat larger droplet size. No significant decrease of the droplet size could be further observed as function of conductivity. The combined effect of flow rate and conductivity is illustrated in figure 3.5, and it is clear that the droplet radius is most significantly affected by flow rate.

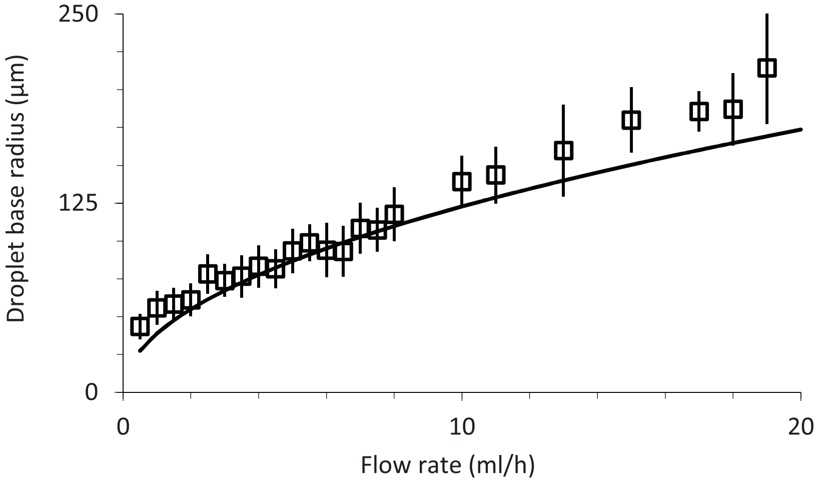

Figure 3.3. Influence of flow rate on droplet base radius of electrosprayed sunflower oil with 5% lecithin (□ measured and — predicted values).

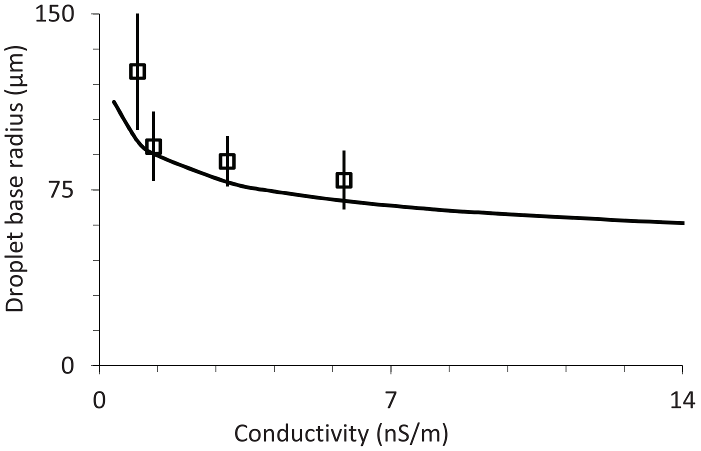

Figure 3.4. Representation of predicted (–) and experimental (□) values of droplet radius as a function of electrical conductivity at a flow rate of 5 ml/h.

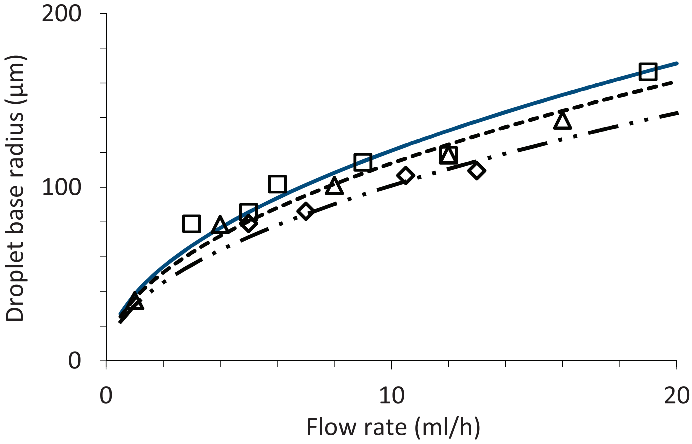

Figure 3.5. Average droplet radius as a function of flow rate and conductivity of sunflower oil (predicted values – 3.07 nS/m, - - - 4.20 nS/m, – · · – 5.87 nS/m, measured values □ 3.07 nS/m, Δ 4 4.20 nS/m, ◊ 5.87 nS/m).

For stable operation, a stable cone jet is needed, which develops above a critical electrostatic potential value (Hayati et al., 1987a; Jaworek, 2007b). It also needs a certain minimum height between nozzle and target surface. Figures 3.6a and 3.6b show the effects of these parameters. The minimum electrostatic potential value varies with flow rate and conductivity (Figure 3.6a) since sufficient charge needs to be supplied to the droplets. At very high potential differences, secondary jet formation can occur (Hayati et al., 1987a; Hayati et al., 1987b; Jaworek, 2008), leading to still smaller droplets.

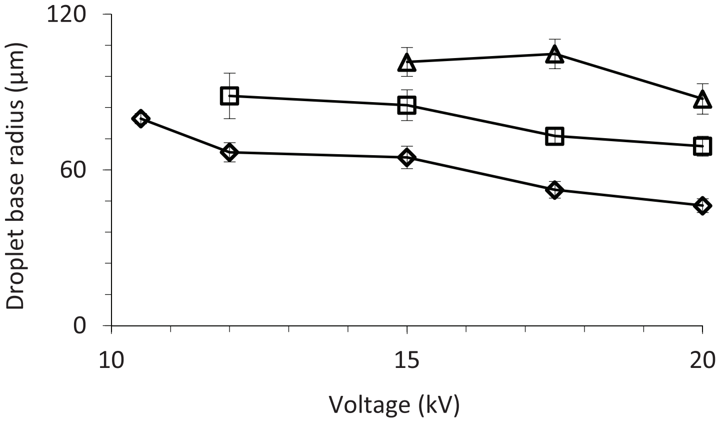

Figure 3.6a. Influence of voltage on droplet radius at Δ flow rate of 5ml/h having 1.3 nS/m conductivity, □ flow rate of 5ml/h having 5.87 nS/m conductivity, ◊ flow rate of 3 ml/h having 5.87 nS/m conductivity.

The minimum height required to allow expansion of the cone jet, is determined by both liquid properties and flow rate, and is in most cases around 12 cm (Figure 3.6b). At conductivity 9.17 nS/m and height 9.5 cm, the jet was not stable, which resulted in very large and coalesced droplets. A stable jet was achieved by increasing the liquid conductivity or increasing the height between nozzle and target surface. All experimental results presented in this paper, are obtained at stable cone jet operation (except at 9.17 nS/m and 9.5 cm).

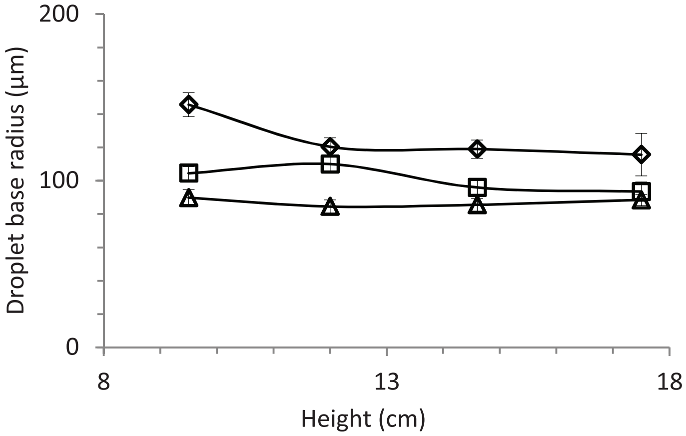

Figure 3.6b. Droplet base radius as a function of height at a flow rate of 5 ml/h with different conductivity values of ◊ 0.92 nS/m, □ 1.3 nS/m, and Δ 3.07 nS/m.

3.4.2. Droplet deposition

The deposition of droplets was investigated on aluminium foil and parafilm. The latter target surface is better capable of holding charge, as it is an insulator, whereas aluminium foil will quickly transfer charge of droplets. It is expected that this will influence deposition behaviour through charge interaction. The two surfaces are model for food surfaces that are conductive and non-conductive, e.g. due to varying water content. At low surface coverage, deposition on parafilm was relatively uniform across the spray lane width compared to aluminium foil (Figure 3.7) most probably because of charge accumulation on the parafilm surface, which affected the deposition of subsequent droplets. For aluminium foil, a higher concentration of droplets was detected in the middle of the spray lane. Droplet deposition was probably not influenced by previously deposited droplets since the deposited charge was lost. This is also in agreement with previously published results (Oh et al., 2008).

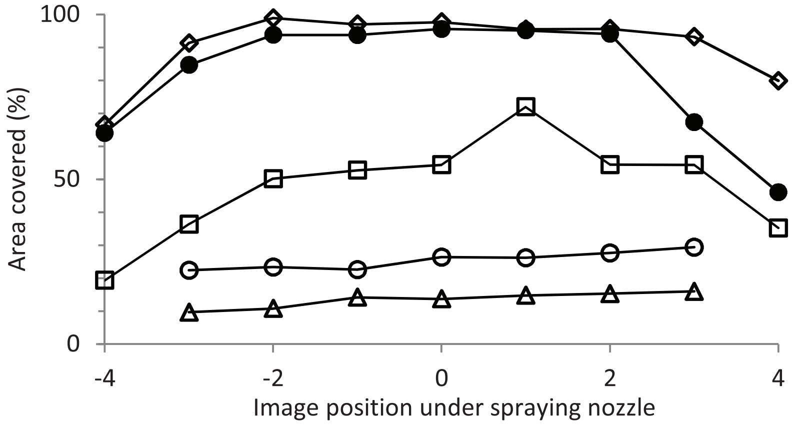

Figure 3.7. Area covered by droplets sprayed at 5 ml/h on Para-film (Δ 3rd pass and O 5th pass) and aluminium (□ 1st pass, ● 2nd pass and ◊ 3rd pass) as a function of the position below the spray nozzle (position zero).

The droplet deposition profile on aluminium foil was examined after several spray passes (Figure 3.7). During the first pass (conveyer belt speed 4.4 mm/s), the surface was covered for approximately 55% in the centre and less than 20% at the sides. Complete coverage was achieved in the centre of the foil after 2-3 passes, while the coverage at the sides moved up to 65-75%, most probably because the charge of the droplets is effectively transferred by this target surface, and incoming droplets are not affected by sessile droplets. For parafilm, complete film formation was not achieved even in five passes. This is most probably due to charge accumulation on the surface, which ultimately prevents further deposition of droplets.

It was expected that initially oil deposition on the conducting aluminium foil is more random, whereas on parafilm, incoming droplets try to find empty places due to charge interactions, until a certain surface coverage is reached, after which the accumulation of charge may prevent further coating. The two theoretical deposition mechanisms were simulated using the Monte Carlo approach and compared to experimental results. In figure 3.8, a sequence of pictures is shown that gives an idea about the simulated distribution of droplets on a surface for the two extreme deposition mechanisms.

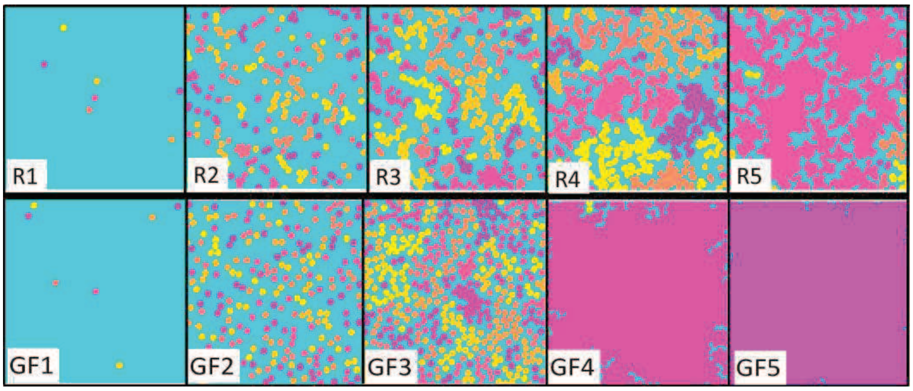

Figure 3.8. Sequences of simulated droplet depositions for the two theoretical mechanisms (R = random shown on top, GF = gap filling shown at the bottom) at equal number of droplets deposited. Individual droplets and isolated blobs have been given different colours. A completely coherent film is a big blob of one colour.

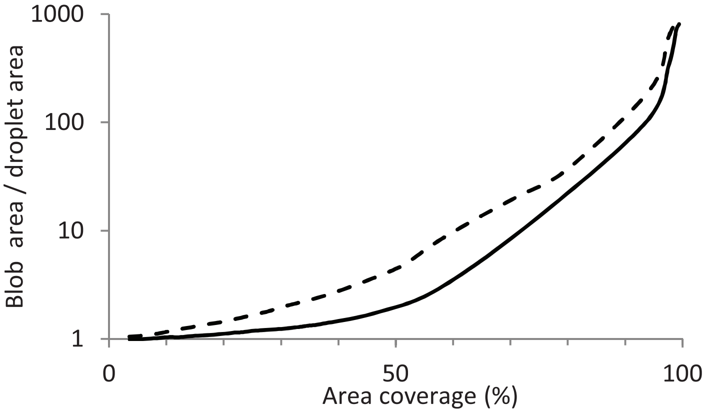

Figure 3.9. Blob area as a function of surface coverage for two theoretical deposition mechanisms (—— random and — gap filling depositions) having same blob to box ratio as experimentally observed (see figure 3.10).

The average blob area was used as a measure to describe the effective coverage. As expected, the effective surface coverage of randomly deposited droplets is much less than for gap filling deposition. In figure 3.9, the blob area (normalized by dividing it by the area of an individual droplet) is shown as a function of the percentage of the surface that is covered. For random deposition, a faster increase in blob area is found than for gap filling deposition. This is in line with the visual, experimental impression from figure 3.10. The sudden increase in blob area for the gap filling mechanism at a surface coverage of approximately 60% coincides with the moment at which no empty gaps (tightest sphere packing) are available for new incoming droplets. At this moment, new droplets start to overlap deposited droplets.

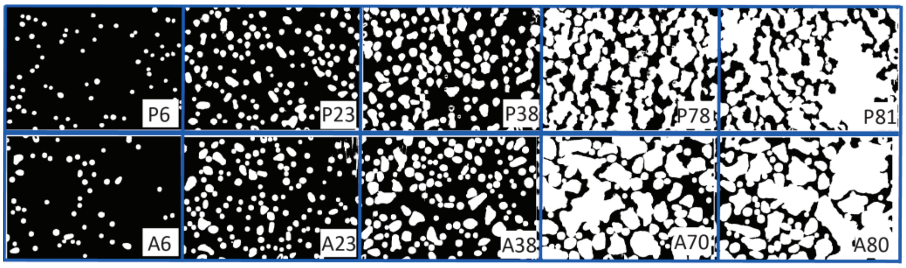

Figure 3.10. Snapshots of experimentally measured surface coverage behaviour for parafilm (upper ones) and aluminium foil (lower ones) with increasing number of droplets deposited and covered surface area (the numbers correspond to % covered area). White is oil; black is uncovered surface.

In figure 3.11, the theoretical deposition mechanisms are compared to experimental results. The experimental results are well aligned with the model predictions. The gradual increase in blob size on both surfaces is due to network formation of connected droplets (Figure 3.10). Both target surfaces follow random deposition trajectory rather than the gap filling deposition trajectory. For aluminium foil this was expected and could be explained by the leakage of charge, which causes minimal repellence between new droplets and droplets lying on the surface.

However, it was expected that the droplet deposition on parafilm would be closer to the gap filling mechanism; however, it followed random deposition. Probably the charge of all droplets act as one, relatively homogenous potential field above the surface. At distances from the surface that are larger than the typical distance between droplets on the surface, one would expect the potential field to be relatively homogeneous, and this initially yields random deposition of droplets while at a certain critical coverage it will prevent further deposition of droplets.

It is clear that the electrical characteristics of the surfaces have a strong influence on the deposition of droplets; insulating surfaces would (eventually) repel incoming droplets and are not suited for electrospraying. Model results indicated that gap filling deposition mechanism was effective (ideal), but practice shows random deposition because of early film development was obtained on aluminium. From these findings, it can be hypothesized that surfaces with intermediate conductive properties (between aluminium foil and parafilm) may lead toward effective coverage and complete film formation; because of less charge interaction than parafilm, thus may follow a deposition pattern closer to gap filling mechanism.

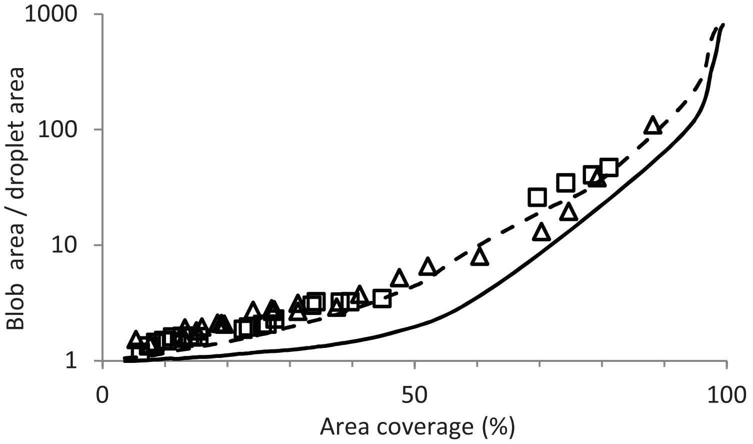

Figure 3.11. Predicted (——random and— gap filling depositions) and experimental droplet deposition patterns on Δ aluminium foil and □ parafilm. Please note that the data generated at area coverage higher than 60% is obtained by multiple passes during electrospraying.

3.5. Conclusions

Electrospraying was evaluated for the formation of homogeneous films on conductive and non-conductive surfaces. The droplet size obtained for electrospraying of sunflower oil was in agreement with the scaling law. Film formation was then investigated on two model surfaces, conductive (aluminium foil) and non-conductive (parafilm). The deposition patterns on both surfaces were analysed, using the formation of contiguous blobs as a measure for the degree of film formation on the surfaces. The experimental results could be well described by a random deposition mechanism for both aluminium foil and parafilm. For parafilm it was expected that new droplets would fill empty gaps due to droplet repellence. However, the charge build-up on the surface is probably so large that a relatively homogeneous potential field above the surface results. This gives random deposition at the beginning, and complete blockage of droplet deposition after a certain degree of coverage, which is in line with experimental observations.

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Chapter 4

Creating lipid-based coatings on model surfaces

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Abstract

Electrospraying is an efficient way to apply coatings on complex surfaces. We report on coating of porous model surfaces with a multiple nozzle electrospraying system. The model surfaces like nickel membranes with large rectangular straight-through pores (13 µm width), polyether sulfone membranes (PES) with small, interconnected pores (0.2 µm), and dense cellulose membranes were used in this study. The coating materials penetrate into the pores of PES and nickel membranes, filling them up and thereby significantly decreasing the water vapour permeation flux. Once the pores were (partially) filled, application of additional coating material caused only minor further flux reduction. For cellulose membrane, materials accumulated on the membrane surface and resulted in reduction of rate water vapour permeation which was much lower compared to other membranes. Surface coverage was simulated using a Monte Carlo approach and appeared in agreement with experimental values at lower amounts of applied coating material (<0.03 kg/m^2). After deposition of larger amounts, using repeated electrospraying, the water vapour permeation flux reduction was larger than expected because of re-melting and fusion of droplets, which indicated that repeated electrospraying of lipids, could be an attractive method to create thin coatings with excellent barrier properties for foods and pharmaceuticals that typically have such complex, porous surfaces.

4.1. Introduction

Edible films have been applied to protect foods from their environment and thus reduce spoilage and loss of quality (Sánchez-González et al., 2011). They may act as barriers to mass transfer between different compartments in a food product or between the food and its environment (Bravin et al., 2006; Fernández et al., 2007). Besides providing a barrier functionality, films can increase sensory attributes, improve mechanical strength and adhesion, enhance stability against microbes, or act as a carrier for antioxidants, flavour, colour, and nutrients (Bravin et al., 2006; Diab et al., 2001).

Edible films are mainly prepared from proteins, lipids, and polysaccharides (Sánchez-González et al., 2011). Lipids are excellent moisture barriers due to their low affinity with water (Bourlieu et al., 2009; Diab et al., 2001; Fernández et al., 2007). Most commonly used lipid coating materials (in order of decreasing barrier efficiency) are waxes, lacquers, fatty acids, alcohols, acetylated glycerides, and cocoa based compounds (Debeaufort & Voilley, 2009). The fatty acids composition and their structure influence the water barrier properties of lipids (Kokoszka et al., 2010; Scramin et al., 2011). Unfortunately, it is difficult to apply a well-defined lipid-continuous film because the resulting films have poor mechanical properties (rigid and brittle). Therefore, these films are frequently enriched with proteins and/or polysaccharides (Debeaufort & Voilley, 2009; Diab et al., 2001; Fernández et al., 2007) in order to give them sufficient flexibility and elasticity.

Barrier properties are determined by the thickness, internal structure, and film component properties (Domnick et al., 2005). Various coating techniques have been developed for thin film formation; spray coating (mechanical or ultrasonic) may be the most common method, because of low equipment cost, good control, and the availability of various spraying materials. During spraying, droplets are formed through atomization and their size co-determines the quality of the coatings (Domnick et al., 2005; Oh et al., 2008). In addition, the structure of the target surface strongly influences the barrier properties. Porous surfaces may absorb the coating material, if the surface is wetted by the coating material (if it is not wetted the coating will not adhere).

Electrostatic coating (electrospraying) is a novel and cost effective technique mainly applied in pharmaceutical and paint industries but less commonly for food products (Bose & Bogner, 2007). Applying a potential difference over a droplet causes accumulation of electric charge near the surface of the nascent droplet, which compensates the surface tension. As a result the surface becomes unstable, which then spontaneously breaks up into fine and relatively mono-disperse charged droplets (Jaworek, 2007, 2008). The charged droplets do not coalesce in the air since they all have the same charge and follow a trajectory to the nearest grounded surface, being the target object. Since charged droplets are electrostatically attracted to the grounded object, this method exhibits a higher transfer efficiency compared to spraying methods that apply uncharged droplets (Luo et al., 2012; Maski & Durairaj, 2010; Oh et al., 2008). After hitting the target surface, the droplets should be able to release their charge. If this is the case, the following droplets can impact freely. Though electrospraying may produce uniform droplets, but the performance with regard to creation of a barrier on porous products is still unknown.

The deposition behaviour during electrospraying was therefore investigated in relation to morphology of well-defined porous targets. In this study, the focus is on lipid films produced by electrospraying, using sunflower oil- and butter-based coating materials. Films were prepared on three target surfaces as models for porous food products. The permeability of the films was compared to model predications based on ideal pore filling and surface coverage. Monte Carlo simulations were used to predict the local film thickness of the coated surface area and its permeability. The modelling results were compared with experimental results on water vapour permeability and strategies for efficient electrospraying have been discussed in relation to target and process properties.

4.2. Materials and methods

4.2.1. Film preparation

A multi-nozzle electrospraying system (Terronics Development Cooperation, USA) was used to prepare films at 50±5 ^{o}C in a temperature-controlled cabinet (Figure 4.1). Coating material was supplied at the rate of 15 µl/sec via a syringe pump (Harvard 11 plus, Harvard Inc., USA). The nozzles were subjected to an electrostatic potential (20-25 kV) through a high voltage source (Heinzinger electronic GmbH). The applied flow rate and electrostatic potential were optimized such that electrospraying resulted in the cone-jet mode, which was ideal for coating purposes. Besides, the belt speed was optimized so that small amounts of coating material were supplied to the target, in order to ensure thin films.

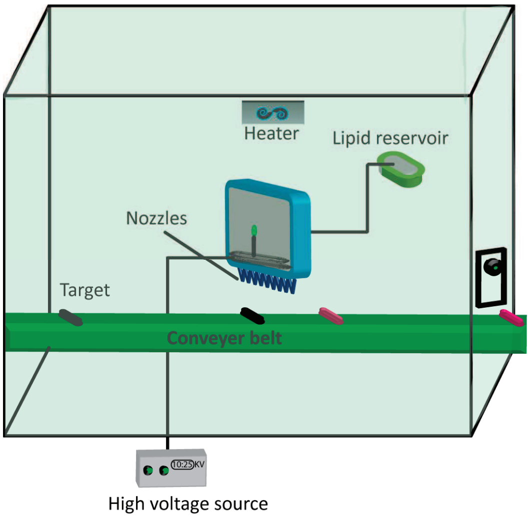

Figure 4.1. A schematic representation of multiple nozzle system for electrospraying in a closed cabinet.

Two different lipids were used, i.e. butter and sunflower oil, purchased from the local supermarket. Alcolic-S Lecithin (American lecithin company, Oxford, CT, USA) was used as an additive (20% w/w) in order to increase conductivity of the lipids, which facilitated the electrospraying. As sunflower oil is a liquid, stearic acid (10% w/w) was added to increase the average melting temperature of sunflower oil to 47 ^{o}C. The butter and sunflower oil-based coating materials were sprayed at elevated temperature (50±5 ^{o}C); subsequently the samples were cooled down to ambient temperature, which led to solidification of the coating. The solidification was also observed for butter-based coatings. Thus, this approach provided a solid film, after cooling to ambient temperature, which is known to give more mechanical stability than a liquid film.

Three different membranes: nickel (Stork Veco BV, the Netherlands), cellulose (dialysis membrane from Akzo Nobel N.V., the Netherlands) and polyether sulfone (Sartorius, Germany), were used as model targets for electrospraying (See table 4.1 for a summary of their properties). These membranes were chosen because of their well-defined morphologies (as described in the next section) which facilitated measurement of coating properties. The nickel sieves featured slit-shaped, straight-through pores, polyether sulfone membranes had smaller, interconnected pores (Figure 4.2), and the cellulose membranes were permeable to air but had no pores. The water vapour flux of all membranes was very comparable, in spite of their different pore geometry and thickness.

Table 4.1. Properties of different membranes used as model surfaces to carry films.

Membrane material	Membrane thickness µm	Water vapour flux $g/m^2.h$	Pore size µm	Surface porosity
Cellulose	8	43±8	<1 nm	0.8
Polyether sulfone	120	42±6	0.2	0.5
Nickel (smooth side)	200	34.5 ± 1.5	13x120 (W x L)	0.04
Nickel (rear side)	200	34.5 ± 1.5	150 x 330 (W x L)	0.45

The thickness, porosity and pore geometry of the membranes were determined by microscopic analysis, while water vapour fluxes were calculated using the method describing the barrier properties of the film as defined in materials and methods section.

These membranes were coated by electrospraying while moving on a conveyer belt (1-5 mm/s) and the amount of coating material applied was measured after various passes. By varying the belt speed or application of multiple passes, films of different thickness could be prepared. Alternatively, films were prepared by casting pre-heated coating material on the membranes and allowing the coating to cool down at ambient temperature.

4.2.2. Film analysis

Prepared films were analysed for their water vapour permeability, which was determined gravimetrically using a modified ASTM (1983) procedure (Bourlieu et al., 2009; Hirte et al., 2010). The coated membranes were placed on top of a permeation cell containing MilliQ water (tightly sealed; relative humidity (*RH*) inside the cell was assumed 100%), and kept in a larger chamber maintained at 20 °C and 60% RH (equilibrium in the cell was established within 2 hours after placing the membrane). Regular periodic measurements for the membrane cells were recorded.

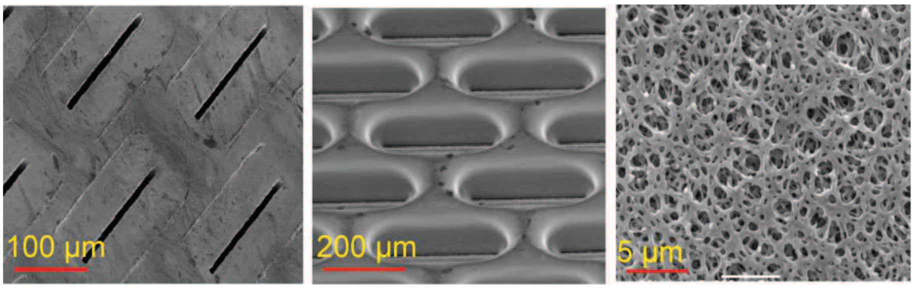

Figure 4.2. SEM analysis of membranes showing the difference in pore structure. a) front view of nickel membrane having straight pores, b) rear view of nickel membrane, and c) PES membrane with interconnected pores.

The weight loss as function of time was registered, and analysed by linear regression (which was appropriate in the investigated range of conditions). As soon as the R^2 value dropped below 0.98, the linear range of weight loss was considered over. A minimum of three replicates were measured for each film preparation. The measured water vapour permeability (*WVP*) of the film was determined as follows:

$$WVP = \frac{M.L}{A.\Delta P_v}\ , \qquad (4.1)$$

where *M* is the weight loss as function of time (g/h), *L* is the film thickness (m), *A* is the film area available for water vapour migration (m^2), and ΔP_v is the vapour pressure difference across the film (Pa); the saturated vapour pressure at 20 °C is 2.3 kPa.

The resistance against water vapour transport was observed in the membrane and the applied film and not in the air phase (i.e. the layer between the water and the membrane). This was affirmed by assessing the water vapour flux through partially coated membranes, prepared by partial casting of a thick film), as shown in figure 4.3. It was found that the uncoated surface was proportional to the water vapour flux measured.

Confocal laser scanning microscopy (CLSM) was used to investigate the morphology of the films prepared by electrospraying on the different targets. Sudan red was used to label the sun flower oil-based coating material. The confocal microscope (Carl Zeiss Axiovert 200 microscope, Zeiss, Jena, Germany) was equipped with a LSM 5 Exciter and He-Ne laser lamp operating at a wavelength of 633 nm. Analysis of CLSM images was performed with “Image J” software. The membrane and actual film thickness was measured by a micrometer (Mitutoyo Scandinavia, Sweden), taking at least three measurements at three different positions and averages values were reported along with standard deviation.

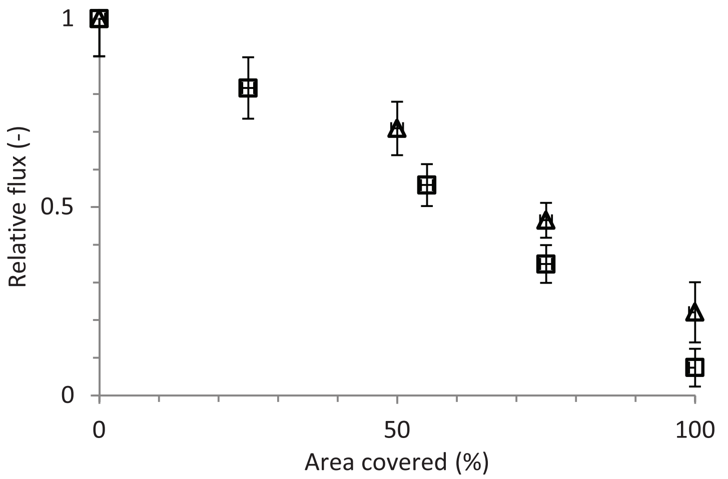

Figure 4.3. Water vapour flux as a function of partially coated membranes prepared by the casting method; nickel membrane (□) and cellulose (Δ) membrane. The flux was determined at 20 °C and 60% relative humidity.

The pore geometry of the membranes was studied by scanning electron microscopy (Jeol Jsm 6360LA, Japan). The images of PES membranes coated with Au/Pt were taken at a voltage of 20/30 and a resolution of 1280 x 960 pixels. For the nickel membrane, the images were taken without coating in a field emission scanning electron microscope (Magellan 400, FEI, Eindhoven, The Netherlands). The sieves were fixed on sample holders by carbon adhesive tabs (EMS Washington, USA) which subsequently analysed at 2 KV at room temperature and images were digitally recorded.

4.2.3. Modelling

A Monte Carlo simulation approach was chosen to evaluate droplet deposition behaviour on target surfaces; for details see **chapter 3** (Section 3.3.2). Two extreme situations were modelled:

a) Random deposition, assuming no interaction between incoming droplets and deposited droplets. This situation was expected to occur when the charge of deposited droplets leaks away quickly; hence conductive target surfaces are expected to exhibit this droplet deposition mechanism.

b) Gap filling deposition, in which empty gaps on the surface were filled preferentially, as expected to occur for electrically insulating substrates that resist leakage of the droplet charge.

In the Monte Carlo simulation, deposited droplets corresponded with disk-shaped domains, which may or may not overlap. Overlapping disks created larger contiguous areas or blobs. The effective coverage on the surface was evaluated from the number of pixels that were ‘covered’ by droplets. At complete surface coverage, the blob area was equal to the box area, whereas in the beginning, a ‘blob’ area was equal to the disk of a single droplet. The uncovered area (*A*) was calculated by subtracting the covered surface from the total surface. Moreover, information was collected on the number of droplets deposited on each pixel, which represented the local thickness of the film. Subsequently, the information was converted into permeability values of the films (as show in equation 4.2), which was assumed proportional to the amount of deposited coating material:

$$Relative\ flux\ = \frac{AP_m + CP_c}{A_{tot}P_m}, \qquad (4.2)$$

where, A, C, and A_{tot} are the uncovered, covered and total area of membrane, respectively. While, P_m and P_c are the water vapour permeation through the membrane (11.8 mg/m^2.s) and the coating material (7.5 mg/m^2.s), respectively. To obtain statistically relevant data, the Monte Carlo simulation was repeated ten times.

4.2.4. Statistical analysis

All measurements were carried out in triplicate and values were reported as mean with standard deviation. Statistical analysis was performed to determine whether differences were significant.

4.3. Results and discussion

4.3.1. Droplet deposition behaviour

The three membranes (nickel, PES and cellulose) were coated by electrospraying. The results presented in this section concern electrospraying of sunflower oil-based coatings; the results for both sunflower oil- and butter-based coatings were similar. The droplet radius of electrosprayed sunflower oil-based coating was found to be 30 ± 5 µm. The droplet deposition was random, which was in agreement with our previous investigations for non-porous surfaces (**Chapter 3**).

The amount of coating material deposited on these membranes was different (e.g. 7 g/m^2 for cellulose & polyether sulfone and 10 g/m^2 for nickel after one pass); the results for multiple passes can be found in figure 4.4. The differences can be related to the conductivity of the membranes, which explains why the nickel membrane had the highest amount of deposited coating material. The other membranes (cellulose and PES) were nonconductive and apparently charge accumulation occurred, therewith partially hindering the deposition of newly incoming droplets (back corona) (**Chapters 2** and **3**).

Figure 4.4 shows the film thickness as function of sunflower oil-based coating amounts deposited on the three membranes. The film thickness on the cellulose membrane increased linearly with the amount of deposited material. This indicated that the coating material accumulated on the membrane surface and thus directly contributed to the increasing film thickness. In contrast to cellulose, for PES and nickel membranes film thicknesses did not increase linearly with the amount of coating material deposited.

Our observations indicated that coating material had penetrated into both membranes. For the PES membrane, oil initially penetrated into the pores, but since the pores were small they seemed to be filled up fast, and additional material was deposited as a layer on the top of membrane. The slope of layer thickness versus deposited amount of coating material on PES (> 10 g/m^2) was less than that observed for cellulose. This indicated that oil was still partially absorbed into the membrane upon reheating during the next passage. The PES membrane pores needed about 75 g/m^2 to be filled up. However, at as low as 10 g/m^2 oil was already accumulating on top of the membrane indicating that the pores were blocked rather effectively.

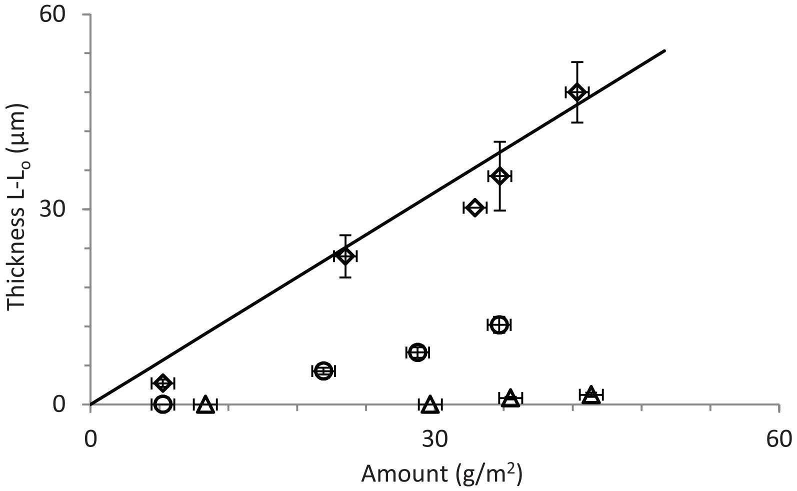

Figure 4.4. Film thickness of sunflower oil-based coating as a function of deposited amount on different membranes (◊ cellulose, o PES and Δ nickel membranes, – predicted values for cellulose membrane).

The film thickness of the coated nickel membrane only increased slightly after deposition of large amounts of the coating material. This suggested that nearly all coating material penetrated into the pores due to large pore size of nickel membranes that enabled fast ingression. Moreover, the nickel membrane surface was hydrophobic, thereby facilitating oil penetration. When considering only the layer with the smallest pores, a relatively small amount of material (8 g/m^2) would be needed to fill these pores. Given the deposited amounts (permeation behaviour is discussed later), it was clear that the oil penetrated further into the supporting structure of membrane which has a much higher porosity (Table 4.1). These findings illustrate how the target properties contribute to effective use of coating material.

The oil penetration and film formation on the membranes were examined by CLSM analysis. On the top surface of the nickel membrane, a very thin layer of coating was observed (Figure 4.5a). At the rear of the membrane (Figure 4.5b) the pores of the sub-layer were completely filled (Figure 4.6a). Oil penetration was most likely driven by a combination of capillary forces and gravity. One should note that the pore volumes of nickel membranes were larger than the droplet size generated by the electrospray nozzles.

For the PES membrane, the oil penetrated uniformly into the membrane structure down to a certain depth (Figures 4.5c and 4.6b). This indicated indeed that the small pores of the PES membrane was plugged early in the coating procedure, which led to partial filling and subsequent build-up of a film on top of the membrane (Figure 4.4). From our results, it may be concluded that the effectiveness of a coating would greatly depend on the pore size, pore geometry, and overall porosity of the target surface.

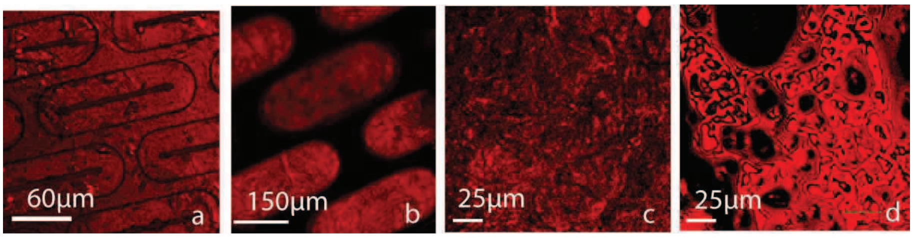

Figure 4.5. CLSM images of electrostatically coated membranes with sunflower oil-based coating, a) nickel membrane top view, b) nickel membrane rear view, c) PES, and d) cellulose membranes.

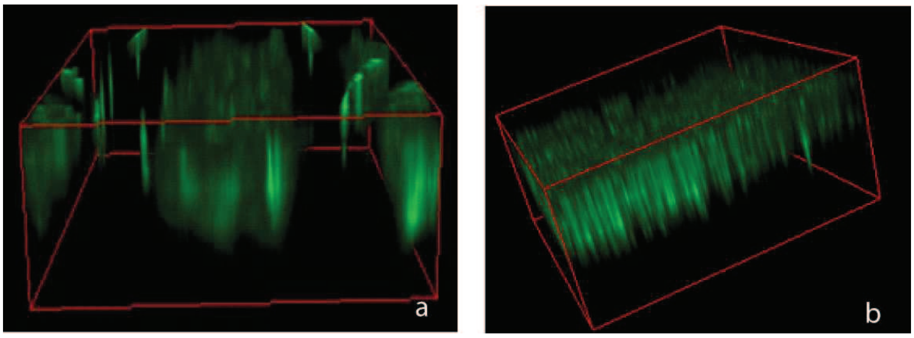

Figure 4.6. 3D representation of sunflower oil-based coatings penetrated inside the pores of a) nickel and b) PES membranes analysed by CSLM.

Oil was unable to penetrate into the hydrophilic cellulose membrane due to the small pore size (<1nm). Thus, droplets accumulated on the cellulose surface and a film formed on top of the membrane (Figure 4.5d). The different coating behaviour for these three model membranes correlated to different vapour permeation behaviour, as will be discussed in the following section.

4.3.2. Water vapour permeability

4.3.2.1. Calculated and experimental flux reduction

We related the deposition behaviour to the water vapour permeation, using a number of scenarios that we expect to occur based on the previously observed film formation (Figure 4.4). Three different types of coverage behaviours are assumed which are described as;

a) Complete pore filling

All pores are completely filled, after which a layer is formed on top of the membrane. In this case the permeability is determined by the filled pores and the layer on top of the membrane (Figure 4.7a).

b) Partial pore filling

All pores are partially filled, after which a coating layer is formed on top the membrane. The partial filling may be due to the complex geometry of the pores in the membranes. In this case the permeability is determined by the partially filled pores and the layer on top of the membrane (Figure 4.7b).

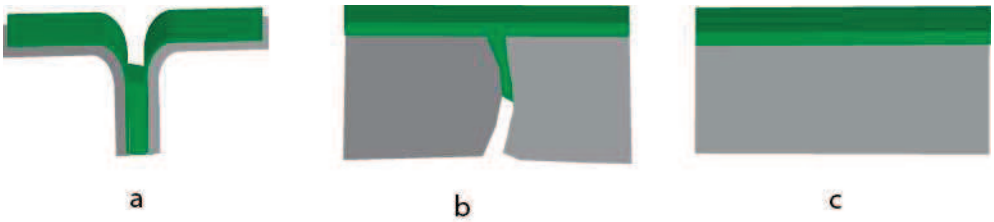

Figure 4.7. A schematic representation of film formation behaviours: a) pore filling, b) partial pore filling, and c) surface coating. Green colour represents the coatings on targets surfaces.

c) Surface coating based on uniform thickness of the applied coating

All coating material applied remains on top of the membrane and forms a layer, which also determines the permeability (Figure 4.7c).

Based on these scenarios, model lines were constructed assuming that when pores were completely filled, the permeability was reduced to zero (Figure 4.8). In practice, the residual water vapour permeability was observed which was very low compared to the situation with a film on the top of membrane.

Complete pore filling is most efficient in flux reduction. In case of partially filled pores followed by film formation, decrease in relative flux depends on the membrane porosity and on the moment at which subsequent film formation starts (Red, Green, and Blue lines in figure 4.8). As expected, for surface coating only, larger amounts of material are needed to achieve effective flux reduction since a larger surface area needs to be covered.

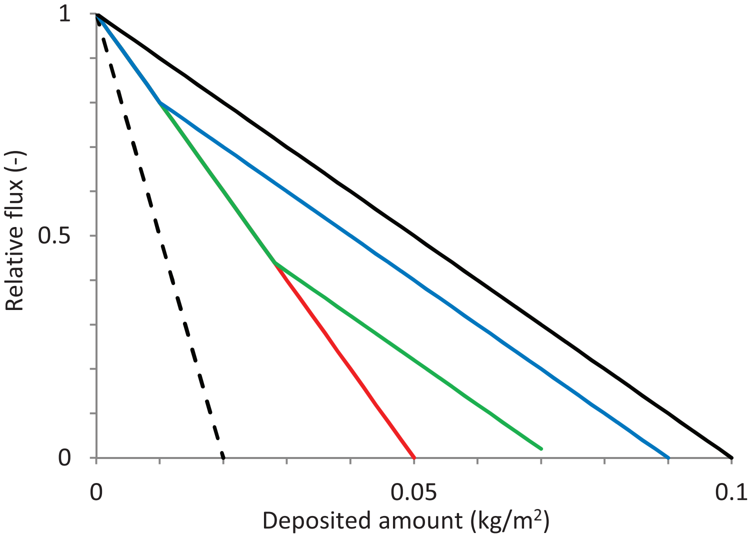

Figure 4.8. Calculated flux behaviour for various coating scenarios ranging from pore filling to surface coating. (dashed black line 0.04 porosity with 100% pore filling, Red line 0.5 porosity with 100% pore filling, Green line 0.5 porosity with 60% pore filling, Blue line 0.5 porosity with 20% pore filling, and solid black line surface coating behaviour).

In figure 4.9, the experimentally determined vapour flux reduction values are shown for the three model surfaces. The complete pore filling scenario explains the flux reduction for nickel; however, a residual flux of approximately 6% remained. As these values did not change significantly even at larger amounts of coating material applied, this can be interpreted as permeation through the coating material itself. The flux reduction for the PES membranes followed the partial pore filling behaviour; more coating material was needed for the same flux reduction compared to the nickel sieve. For cellulose membranes, the flux decreased proportionally with the amount of coating material applied, which indicated the build-up of a layer on top of the membrane. It was expected that the deposition behaviour and actual size of the droplets would affect the properties of the layer and also its functionality.

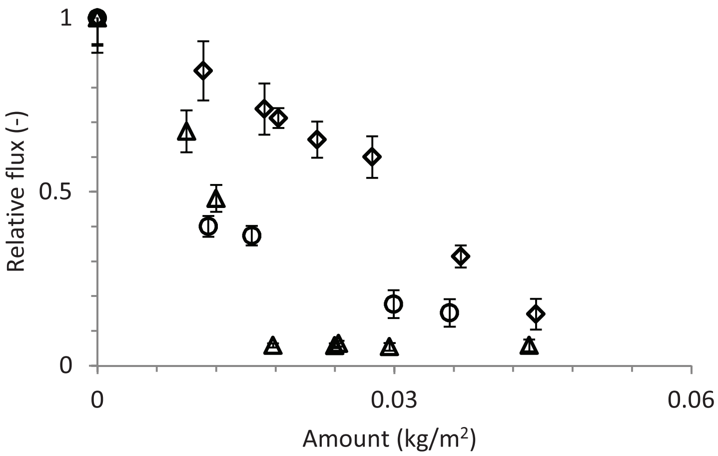

Figure 4.9. Water vapour flux through sunflower oil-based coatings on three different membranes (◊ cellulose, ○ PES and Δ nickel).

The spreading behaviour of droplets was further investigated by Monte Carlo (MC) simulations. We emphasized that the current simulations were performed for a non-porous surface, i.e. similar to situation for the cellulose membrane. The results of these MC simulations using the random and gap-filling deposition mechanisms are shown in figure 4.10, and gap filling deposition exhibited an even spread of droplet as expected. The results of the MC simulation for both gap filling and random deposition were converted into expected flux reductions based on the presence of droplets and differences in droplet height (Figure 4.11) as described in the materials and methods. At lower amounts of coating material, results for both models were found in closest agreement with the experimental data; however, the actual flux reduction was even larger than predicted by both models for larger amounts of deposited material. Possibly, deposited droplets (solidified after the first pass) were melted upon reintroduction in the heated cabinet, in which the coating was applied, leading to droplet fusion and more effective coverage of the surface.

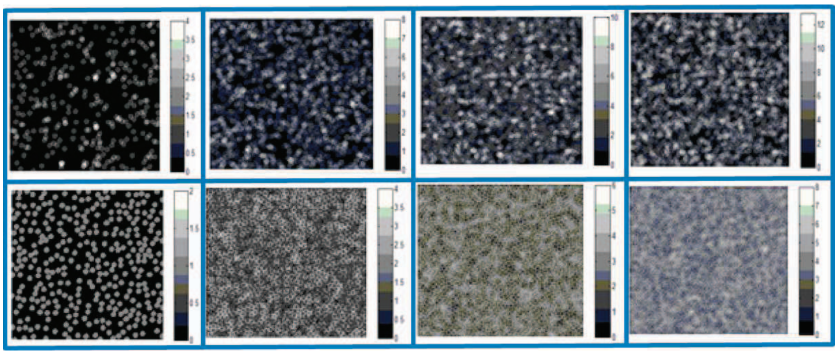

Figure 4.10. Graphical representation of Monte Carlo simulation of height profiles with increasing number of droplets resulting from two droplet deposition mechanisms (upper row of pictures represent the random deposition and lower row of pictures represent the gap filling deposition). Scale colours represent the numbers of droplet deposited over each other, resulting in varied film thickness.

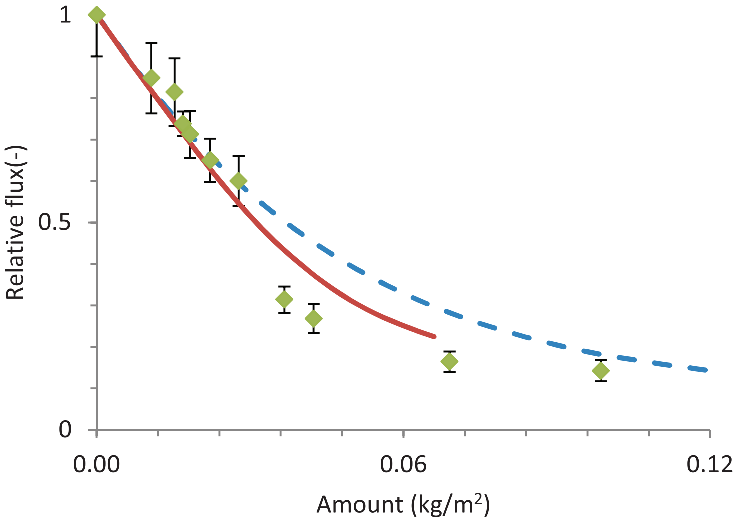

Figure 4.11. Water vapour flux through cellulose membranes coated with sunflower oil mixture (◊) compared to predicted flux for two deposition mechanisms (– – random and —— gap filing).

4.3.2.2. Influence of coating material on water vapour permeability

The results of electrospraying of butter and sunflower oil-based coatings on cellulose membranes in terms of flux reduction are explained in figure 4.12. As described before, the flux reduced rather linearly with the amount of sunflower oil- and for the butter-based coating the initial decrease was similar, but followed by a relatively constant value at around 80%. This could be explained by crack formation, which occurred when applying more butter and this effect was more pronounced at longer storage time. The cracks provided easy access for water vapour permeation and dominated overall permeability. Crystallization of the butter, leading to the shrinkage and rendering the coating brittle, may cause crack formation. In the sunflower oil-based film, no cracks were observed (with the naked eye) and were also found to be less brittle.

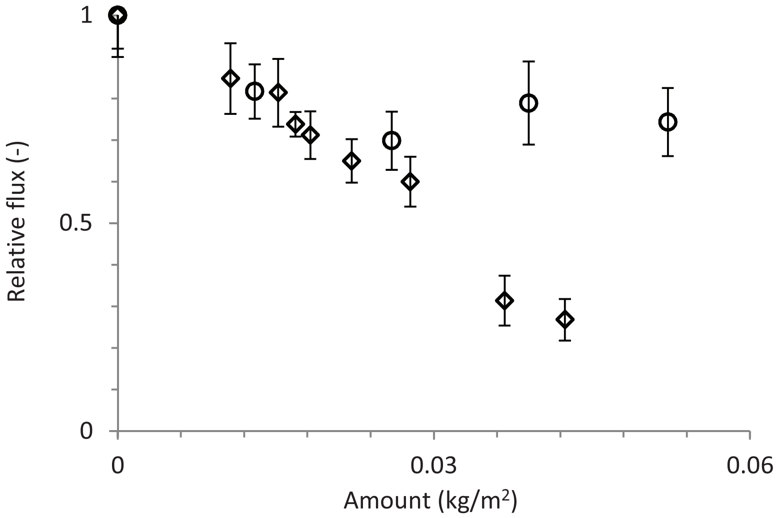

Figure 4.12. Comparison of flux reduction through coatings applied on cellulose membranes by electrospraying of butter (○) and SFO mixture (◊).

4.4. Conclusions

Coating material penetrated into the pores of nickel membranes having large pores. After (partial) filling of these membranes, a film was formed on top of the membrane. On cellulose membranes, a film immediately developed on the top surface, and it was concluded that microstructural properties (porosity, pore geometry) have large effect on coating behaviour and thus final coating properties.

Monte Carlo simulations were developed to predict water vapour flux reduction through the cellulose membranes. Actual measured flux reductions were higher than predicted which was ascribed to (partial) fusion of droplets after repeated application of material at elevated temperature. The small amounts of coating material can be applied sequentially with electrospraying, leading to better barrier properties.

Finally, it can be concluded that the combination of target (product) properties and coating material should be chosen carefully to produce effective thin films, which can play an important role in various applications. It is recommended that future work is directed toward development of electrospray coating strategies that consider the surface characteristics of foods or pharmaceuticals. For example, confectionary is expected to behave similar to the cellulose membrane, whereas bakery products are expected to have similarities with the nickel and PES membranes with their large (interconnected) pores.

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Chapter 5

Evaluation of lipid-based coatings on food product

This chapter has been submitted as: Muhammad Kashif Iqbal Khan, Maarten A.I. Schutyser, Karin Schroën, and Remko Boom. *Edible coatings on food surfaces prepared with electrospraying*.

Abstract

Electrospraying is a novel technique for the application of coating to foods. In this study, thin lipid-based coatings were prepared on tablets by electrospraying and evaluated for their moisture barrier functionality. Sunflower oil- and chocolate-based coating materials were electrosprayed at elevated temperature using a multiple nozzle system. Sunflower oil coated the sides and top surface of the tablets, while chocolate-based coatings deposited primarily on the top surface of tablets. In chocolate-based coatings, larger droplet size and lower charge to mass ratio explained the limited "wrap-around effect". Sunflower oil-based coating was penetrated into the tablets, which could be reduced by the addition of stearic acid (up to 15%). However, this addition resulted in crystallization and crack formation during storage, which ultimately reduced the barrier functionality. Conversely, chocolate-based material produced thicker coatings (up to 0.3 mm), which were stable during storage.

5.1. Introduction

Electrospraying is an effective technique to atomize liquids, in which an electric potential difference is applied across a droplet emerging from a capillary. The electrical field induces accumulation of charge near the surface of a nascent droplet, and destabilises the surface of a droplet which is disrupted into multiple diminutive charged droplets (Jaworek, 2007, 2008). These newly formed droplets do not coalesce in the air because of their charge and move along the electric field lines to the nearest grounded target surface. Electrospraying exhibits a higher transfer efficiency (80-90%) compared to conventional spraying methods which produce uncharged droplets (Jaworek & Sobczyk, 2008; Luo et al., 2012; Oh et al., 2008).

Ideally, in electrospraying, the charge of droplets leaks away upon contact with the target object. This is critical for smooth deposition of subsequent droplets. The capability of electrospraying to produce micron-size charged droplets with a small size distribution makes the technique promising for coating purposes. The droplet size, deposition rate, and layer thickness can be controlled by optimising process parameters such as flow rate and coating material properties (conductivity) (Jaworek & Sobczyk, 2008).

Coating materials for foods can be formulated from lipids, proteins, polysaccharides or any combination of these. Lipids are excellent barriers against moisture migration (Debeaufort & Voilley, 2009). Their use as a protective layer dates back to the 12th century, when wax was applied to citrus fruits to increase their shelf-life (Debeaufort et al., 1998). Lipids, combined with proteins and polysaccharides, produce coatings with better mechanical and barrier properties. However, these composite films may have higher moisture permeability compared to that of pure lipid (Bravin et al., 2004).

Lipid-based materials have been successfully electrosprayed (Gorty & Barringer, 2011; Luo et al., 2012; Marthina & Barringer, 2012). However, to our best of knowledge, electrosprayed coatings have not been investigated for their barrier functionality on food surfaces. Therefore, our study aims at formation of lipid-based coatings by electrospraying on a model food target and subsequent evaluation of its moisture barrier properties. For this, sunflower oil and chocolate-based coatings were electrosprayed on tablets (as model for a food material) moving on a conveyer belt. Initially, the coating and spreading behaviour on the target surface were studied with respect to the coating material properties. Latter, water vapour permeability of the coated tablets was investigated and compared to conventional 'dip'-coating. Finally, an assessment was made on the influence of coating thickness on water vapour permeability.

5.2. Materials and methods

5.2.1. Film preparation

Sunflower oil and dark chocolate (Verkade Zaandam, Holland) were obtained from a local supermarket. Due to the low melting point of sunflower oil, stearic acid (Sigma-Aldrich Co.) was added to ensure solidification at room temperature. Alcolic-S Lecithin (American lecithin company, Oxford, CT, USA) was used as an additive to increase the conductivity of coating materials in order to facilitate electrospraying. Polyglycerol polyricinoleate (PGPR) (Givaudan, Vernier, Switzerland) and butter (SOP int. Ltd., UK) were added to the chocolate to reduce the viscosity. A summary of the compositions of sunflower oil and chocolate-based coatings is presented in table 5.1. The viscosity of coating material was measured with a rheometer (MCR 301, Anton Paar, Graz, Austria) with a DG 26.7 geometry. A shear rate sweep was applied from 1 to 3000 s^{-1} and 3000 to 1 s^{-1} at a controlled temperature of 60 ^{o}C.

Readily available tablets (brand name 'zwartwit', Fortuin Dokkum, The Netherlands) were used to evaluate the coatings applied by both electrospraying and dipping (as reference). The water activity (a_w) of a tablet directly from the package is approximately 0.4 and thus it absorbs water when exposed to relative humidity values > 40%. The tablets were coated by electrospraying on a conveyer belt, moving at a velocity of 1 mm/s; the mass of applied coating material was measured after multiple (1-6) passes.

A multi-nozzle electrospraying system (Terronics Development Cooperation, USA) was used to prepare films at 60 ± 5 ^{o}C in a temperature-controlled cabinet (Figure 4.1). The nozzles were subjected to an electric potential of 20-25 kV using a high voltage source (Heinzinger electronic GmbH). The coating material was supplied at a rate of 0.9 ml/min via a syringe pump (Harvard 11 plus, Harvard Inc., USA). As a reference, a set of tablets were dipped in the coating material; the applied amounts ranged from 0.1 - 0.9 kg/m^2. The coated tablets were subsequently cooled down at ambient temperature to solidify the coatings.

Table 5.1. An overview of the different compositions that were used as coating material and corresponding values of their viscosity.

Lecithin %w/w	Stearic acid %w/w	PGPR %w/w	Butter %w/w	Sunflower oil %w/w	Chocolate %w/w	Viscosity (mPa.s)
20	10	-	-	70	-	20±5
20	15	-	-	65	-	30±6
20	-	15	0	-	65	420±150
5	-	15	15	-	65	200±7
5	-	15	30	-	50	140±7

5.2.2. Film analysis

Coated and uncoated tablets were analysed for moisture uptake as a function of time at 60% relative humidity and 20 °C in a humidity chamber (Memmert GmbH). The moisture uptake was monitored daily by weighing the tablets (Section 4.2.2). A minimum three replicates were measured for each film preparation and the average results of relative water uptake were reported. The water vapour permeability (WVP) of the coatings was determined as follows:

$$WVP = \frac{ML}{A\Delta P_v}, \qquad (5.1)$$

where M is the mass increase as function of time (g/h), L is the film thickness (m), A is the film surface area available for water vapour migration (m^2), and ΔP_v is the vapour pressure difference across the film (Pa).

Sudan red was used to label the sunflower oil-based coatings, which were analysed with a confocal laser scanning microscope (CSLM) (Carl Zeiss Axiovert 200 microscope, Zeiss, Jena, Germany) equipped with a LSM 5 Exciter and He-Ne laser lamp operating at a wavelength of 633 nm. The tablets coated with a larger amount of coating material were broken into two pieces and images were taken with a camera (Canon Inc.) equipped with sigma lens (50mm 1:2.8 DG Macro). Further analysis of the images was carried out with “Image J” software. In addition, the film thickness on the tablet surface was measured by a micrometer (Heidenhain, USA).

5.2.3. Statistical analysis

All measurements were performed in triplicates and values were reported as mean with standard deviation. Statistical analysis was performed to determine the significant differences.

5.3. Results and discussion

5.3.1. Analysis of the film

5.3.1.1. Sunflower oil-based coatings

Tablets were coated with sunflower oil-based material by electrospraying at 60 °C. The coating material did not only deposit on the top surface but also on the side surfaces of the tablets (Figure 5.1). This can be explained by the presence of charge on droplets, which induces them to follow the electric field lines to the nearest grounded object (Bailey, 1998; Sumonsiri & Barringer, 2010), that may be horizontally or vertically oriented. This phenomenon is known as ‘wrap-around’ effect, which contributes to the coating efficiency and offers an advantage compared to conventional spray coating that does not show this effect (Maski & Durairaj, 2010). At 10 g/m^2 uniform and complete coating was observed on the upper surface, but the side surfaces still had some uncovered areas. Closure of the film on all sides of the tablet was visually observed at approximately 22 g/m^2. The film thickness did not increase significantly as a function of the applied amount. This can be explained by the presence of pores into which most of the coating material penetrated, thus leaving out a thin layer on the surface as confirmed by CLSM analysis (Figure 5.2). The penetration was facilitated by the lowered viscosity of the oil at 60 °C. The penetration depth was increased up to 0.8 mm with increasing amounts of coating applied till 100 g/m^2. After which a layer of coating started to develop on the tablet surface with a thickness of > 50 µm, which could partly solidify before being fully absorbed by the pores of tablet. This observation could be explained with partial pore filling, in which a film starts to build on filled pores (**Chapter 4**).

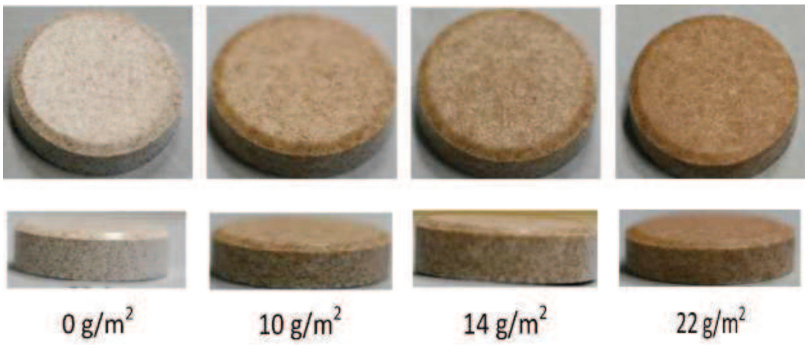

Figure 5.1. Visual representation of 'zwartwit' tablets coated with increasing amounts of sunflower oil-based coating applied by electrospraying.

Unlike electrospraying, a coating was applied by dipping that mostly remained on the tablet surface because of quick solidification of the coating material. We found limited oil penetration (max. 50 µm) and thicker film thickness on the top surface (50 - 900 µm). Thus, the properties of coating material and application method both determine the penetration depth of the sunflower oil-based coatings.

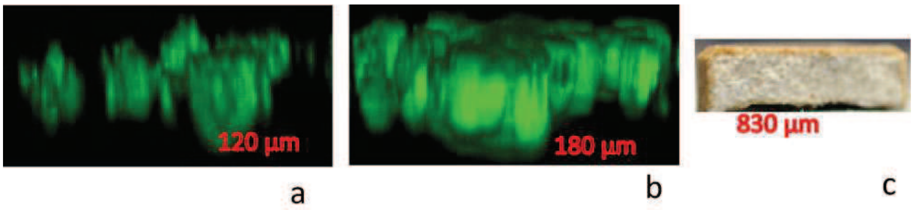

Figure 5.2. Visual illustration of sunflower oil-based coatings applied via electrospraying on tablets; a & b 3D CLSM pictures; c is regular picture of a broken tablet. The numbers represent the oil penetration depth.

5.3.1.2. Chocolate-based coatings

To investigate the influence of liquid properties on film formation, chocolate was selected as an alternative lipid-based model coating. During electrospraying of chocolate-based coating material, the wrap-around effect was less pronounced than sun flower oil-based coating (Figure 5.3). This may be attributed to the larger average droplet size (d_{50} = 88 µm) of chocolate, which gave droplets with about six times larger volume compared to the droplets of oil-based coatings (d_{50} = 49 µm). The larger droplets had a lower charge to mass ratio; therefore, paths of the droplets were determined by inertial and gravitational forces instead of the electric field lines. This leads to voids, uneven and thin films at lower deposited amounts and approximately three times more coating material was needed for complete coverage.

Besides the charge to mass ratio, the target surface conductivity was important: on less conductive surfaces the charge may accumulate, repelling new droplets and hindering their deposition (**Chapters 2** and **3**). Unlike tablets, in the coating of conductive aluminium cubes revealed that equal amount of coating material was deposited (28 ± 3 g/m^2) on all sides of the cube during the first pass. This indicated that chocolate can indeed be deposited uniformly on a well conductive surface. This difference in the coating behaviour of two target surfaces suggested that weakly conductive target surface did not allow the charge to leak away fast enough, which is prerequisite to achieve a uniform deposition, as previously mentioned in **chapters 2** and **3**.

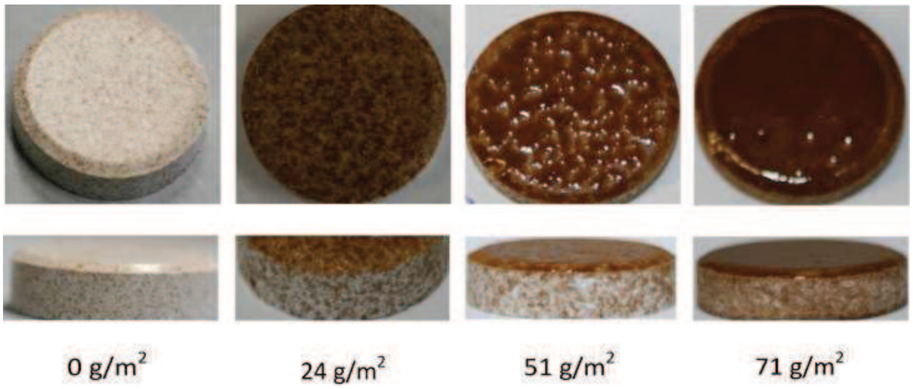

Figure 5.3. Film formation on tablets coated by electrospraying of chocolate-based coating material.

Unlike sunflower oil-based coatings, the chocolate-based coatings did not penetrate into the tablet and this resulted in a linear increase in the film thickness as a function of the applied amount (Figure 5.4). At low amounts of coating material applied (< 50 g/m^2), formed chocolate coatings were uneven due to limited spreading of the droplets, whereas application of increased amounts induced the fusion of randomly deposited droplets and resulted in an even film on the top surface (Figure 5.3). The above presented results revealed that film formation was greatly influenced by the type of coating material and target surface properties.

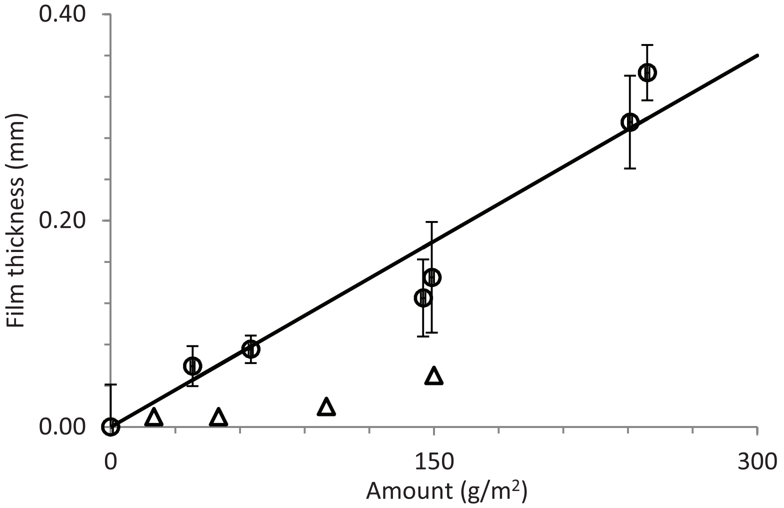

Figure 5.4. The film thickness as a function of the amount of (○) chocolate and (Δ) sunflower oil-based coatings applied by electrospraying on tablets (line, calculated film thickness for chocolate).

5.3.2. Barrier functionality

5.3.2.1. Sunflower oil-based coatings

Coated tablets were evaluated for their water uptake at 60% relative humidity and 20 °C as a function of time. The water activity (a_w) of these tablets prior to coating was 0.4, which means that water is readily absorbed by tablets from the surroundings in the absence of any barrier. The water vapour flux into the tablet was reduced with increasing amount of sunflower oil-based coatings (Figure 5.5). Until 0.2 kg/m^2, the water vapour flux decreased sharply, while at larger amounts of coating material applied, flux did not further decrease. Thus, the optimal coverage of the surface with the coating material was achieved at 0.2 kg/m^2, such that earlier non-covered pinholes were also covered. Similar behaviour was observed when investigating the permeability of coated membranes (**Chapter 4**); but more coating material is required to achieve similar flux reduction on the tablets, when stored under the same conditions. This may be due to the different morphology and water sorption properties of the membranes and tablets, the latter being relatively more hygroscopic.

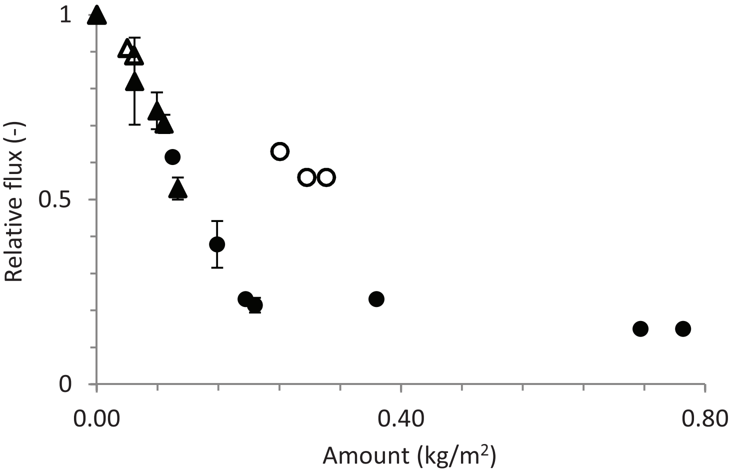

Figure 5.5. Water vapour flux into tablets coated with sunflower oil-based coatings applied by two coating methods: Δ electrospraying and ○ dipping. The coatings contain different contents of stearic acid 10% and 15% represented by filled and unfilled markers, respectively.

To reduce the penetration of the liquid coating material into the tablets, the amount of stearic acid in oil was increased from 10 to 15%. The increase in stearic acid content was expected to contribute in effective flux reduction (Fernández et al., 2007), since stearic acid has a lower water permeability. However, the water vapour flux was higher due to crack formation due to crystallization. The small droplets turn into crystals, resulting in crack formation during storage and a loss of barrier integrity (Figure 5.6).

In case of dip-coating, cracks appeared on the first day of storage and their size quickly increased, exposing the underneath surfaces to the environment (Jiménez et al., 2010). Thus, repeated application of small amounts with electrospraying is preferred over one large dose of coating material. Moreover, the composition of coating material should be formulated in such a way that crystallisation does not destroy the barrier functionality.

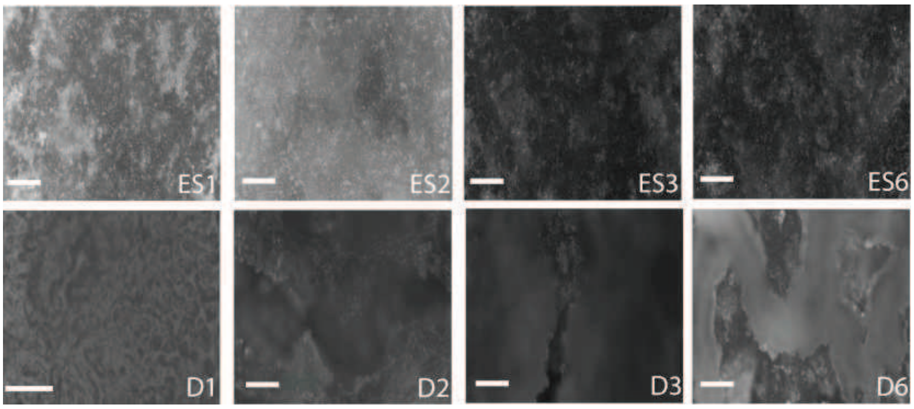

Figure 5.6. A series of microscopic images illustrating film stability of sunflower oil-based coatings containing 15% stearic acid. The films were produced by (ES) electrospraying and (D) dipping method. Numbers represent the storage days and scale bars represent 100 µm.

5.3.2.2. Chocolate-based coatings

The chocolate-based coating material has a relatively high melting point compared to sunflower oil, since the chocolate contains more stearic and palmitic acids. The water uptake behaviour of tablets coated with chocolate-based coatings was measured and results are shown in figure 5.7. The water vapour flux reduced rapidly with coating densities of up to 0.25 kg/m^2 applied by electrospraying. Beyond this value, no further decrease was observed for electrosprayed coatings which showed more variations. This was due to the incomplete coverage of the side surfaces, but may also be due to lower droplet fusion on these sides, leaving many holes in the coating.

When adding butter to the chocolate-based coatings, notable differences were found. The flux reduction was much higher at low deposited amounts of chocolate-based coatings containing 30% butter content. This is probably related to the better film formation on tablets and differences in fatty acid composition.

In dip coating, absolute flux reduction of chocolate-based coatings was larger than with the sunflower oil-based coatings. This illustrates the importance of complete coverage of the tablet's sides and the properties of coating material.

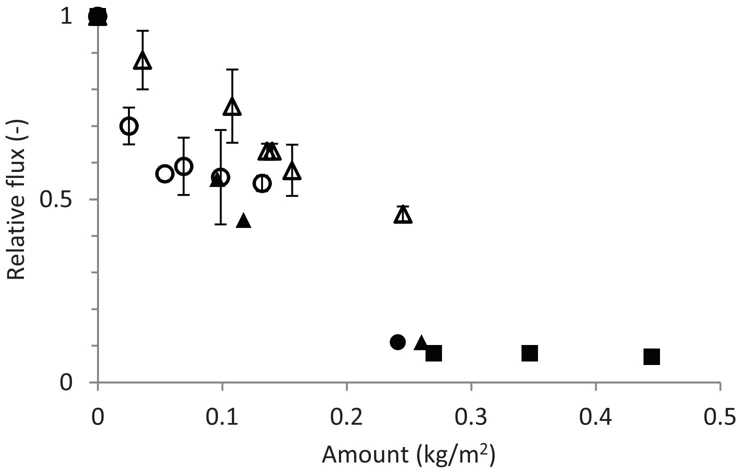

Figure 5.7. Water vapour permeation through chocolate-based coatings having different amounts of butter (□ 0%, Δ 15%, and ○ 30%) applied by electrospraying and dipping methods shown by unfilled and filled markers, respectively.

Microscopic scrutiny revealed that pinholes, which were present on the surface of chocolate-based coatings (Figure 5.8) and became larger with the passage of time. However, these pinholes remained on the surface of coating; the inner coating was not damaged significantly during storage (results not shown). Thus, the chocolate-based coatings were stable which may be attributed to the composition of chocolate-based material containing a mixture of saturated fatty acids, that are known to lower the water vapour permeability as reported by (Fernández et al., 2007; Jiménez et al., 2010; Nobrega et al., 2012), while fats that remain liquid may be able to repair small defects being caused by the contraction due to crystallization. Moreover, the fatty acids composition determines the crystal formation which ultimately defines the permeability of coatings (Debeaufort & Voilley, 2009).

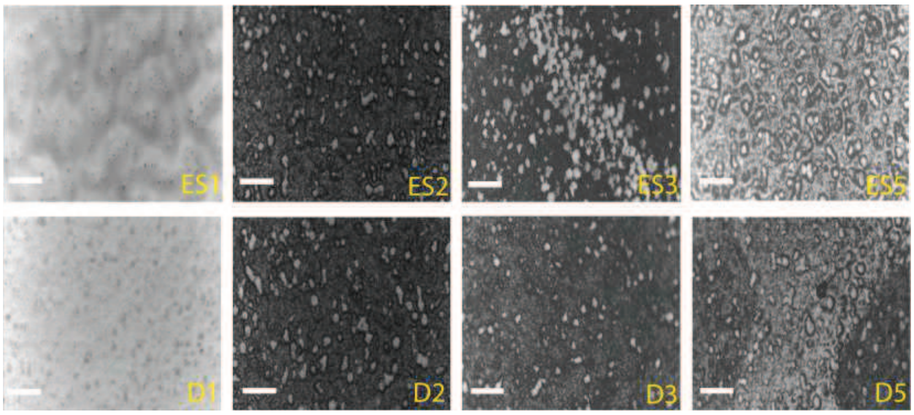

Figure 5.8. Microscopic pictures of chocolate-based coating material (30% butter) delivered with (ES) electrospraying and (D) dipping. The numbers represent the storage period in days and scale bars represent 100 µm.

5.3.2.3. Water vapour permeability

The experimental permeability values of sunflower oil- and chocolate-based coatings were 4.66 ± 1.75 and 2.67 ± 1 (10^{-14} kg/m.s.Pa), respectively. These values were comparable to that of pure myristic acid (3.47 10^{-14} kg/m.s.Pa) and are about twenty times higher than that of pure stearic acid (0.22 10^{-14} kg/m.s.Pa) (Debeaufort & Voilley, 2009). The permeability of the chocolate-based coating is ten times higher than that of dark chocolate, as reported in literature (0.24 10^{-14} kg/m.s.Pa) which can be partly attributed to the difference in formulation and storage conditions (Boom et al., 2011; Debeaufort & Voilley, 2009).

The measured moisture permeance as function of deposited coating materials are compared in figure 5.9. The chocolate-based coatings provide a better moisture barrier compared to sunflower oil, in spite of the fact that sides of the tablets were not covered completely with chocolate. This suggests that the moisture permeance may be further reduced by optimising the application procedure. The higher permeance of sunflower oil-based coatings may be ascribed to cracks, which grow with time. Thus, the stability of the deposited film as a function of time should be considered when selecting a coating material.

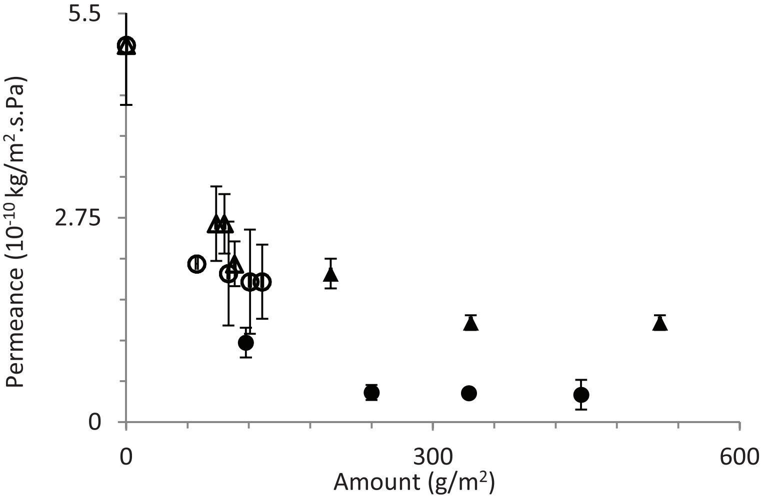

Figure 5.9. Moisture permeance through coatings of sunflower oil (Δ) and chocolate (○) produced by dip and electrospraying coating methods (filled and unfilled markers, respectively).

5.4. Conclusions

Moisture barriers were prepared on hygroscopic tablets with electrospraying of sunflower oil and dark chocolate-based coatings. The properties of the coating material influenced film formation behaviour. Smaller droplets resulting from a higher charge to mass ratio, gave better film formation on the tablets due to the 'wrap around' effect because these droplets will follow the electric field lines towards all sides of the target surface.

The sunflower oil-based coating material, which was relatively fluid, penetrated into the tablets, whereas chocolate-based coatings formed a film on top of the tablets. Pinholes and cracks were observed for both types of coatings, those in chocolate-based coatings were not throughout the film, and thus chocolate-based coatings were better barriers than sunflower oil-based coatings.

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Chapter 6

Electrospraying of water-in-oil emulsions

This chapter has been submitted as: Muhammad Kashif Iqbal Khan, Abid Aslam Maan, Maarten A.I. Schutyser, Karin Schroën, and Remko Boom. *Electrospraying of water-in-oil emulsions for thin film coating.*

Abstract

Electrospraying of water-in-oil emulsions into thin edible barrier films was investigated. A reproducible model surface was used, namely cellulose membranes of which permeability is well-established. PGPR-based emulsions were stable during electrospraying and produced a fine stable jet spray; emulsions prepared with lecithin and span80 produced unstable jets and only sporadic sprays. The droplet size decreased to 50 ± 10 µm by the addition of water droplets until 3% but remained constant at higher water contents. On the other hand, the addition of protein and salt influenced the droplet size and radius values up to 200 µm were found. The addition of whey protein isolates (10% w/w) resulted in films with water vapour barrier properties that were at least 70% better than for lipid only, therewith showing that addition of protein enhances the integrity of the films.

6.1. Introduction

Various strategies and technologies have been developed to maintain the quality and to extend the shelf life of (ready-to-eat) food products. In this paper, we focused on edible coatings that can be used for these purposes, since they act as barriers to water and to the exchange of gases. A range of ingredients such as proteins, polysaccharides, and lipids can be used either as single ingredient or in combinations to produce edible coatings with varying mechanical and barrier properties (Chiumarelli & Hubinger, 2012).

Polysaccharides and proteins based coatings are known to form good films having low oxygen permeability. These coatings mostly do not alter the taste and appearance of the product (Chiumarelli & Hubinger, 2012). Lipids are excellent moisture barriers due to their low affinity with water. (Debeaufort & Voilley, 2009). The films of pure components are mostly brittle which induces cracks in the films, resulting in poor food protection. This may be circumvented through combination of e.g. protein and lipid, which are known respectively as good barriers for oxygen and water vapour, ideally resulting in films with better moisture resistance, improved mechanical flexibility, and transparency (Hambleton et al., 2011; Monedero et al., 2009; Pereda et al., 2012). These blends are mostly applied through an emulsion in which both components can be well distributed (de la Caba et al., 2012).

Various coating techniques have been developed for preparing thin films. However, electrospraying has potential for thin and uniform coating because it is capable of producing smaller droplets. In electrospraying, applying a potential difference over a droplet emerging from a nozzle causes instabilities on the droplet surface which then spontaneously breaks up into smaller and relatively mono-dispersed droplets (Jaworek, 2007, 2008). The charged droplets follow a trajectory to the nearest grounded surface as a result of electrostatic attraction, leading to a high transfer efficiency compared to conventional spraying methods (Luo et al., 2012; Maski & Durairaj, 2010; Oh et al., 2008). Upon impact with the target surface, release of the charge needs to take place to allow following droplets to deposit on the surface and subsequently form a complete film.

Electrospraying of lipid-based coating materials has been well documented (Gorty & Barringer, 2011;Luo et al., 2012; Marthina & Barringer, 2012). Mostly lecithin, an ionic surfactant, is used to increase the conductivity of the to-be-sprayed lipid material; lipids are otherwise non-conductive and not suitable for electrospraying. Besides, we target at making barriers with a dual functionality as described earlier, making use of the combined properties of lipids and protein, and for this an emulsion needs to be the starting point. As information on electrospraying of emulsions is still lacking in literature, we explore here first the atomization behaviour of water-in-oil emulsions prepared with PGPR, span80, and lecithin, and later extend this to electrospraying of protein containing emulsions. Various formulations and process conditions were used to investigate droplet deposition behaviour in relation to film formation, and barrier properties.

6.2. Materials and methods

6.2.1. Materials

Sunflower oil purchased from a local supermarket was used as continuous phase and MilliQ water was used as dispersed phase. Span80 (Sigma-Aldrich, Germany), Alcolic-S lecithin (American lecithin company, USA) and polyglycerol polyricinoleate (PGPR) (Givaudan, Vernier, Switzerland) were used as surfactants. Whey protein isolates (Friesland Campina, the Netherlands) sucrose and sodium chloride (Merck KGaA, Darmstadt, Germany) were added to the water phase at different concentration (specified in respective sections).

6.2.2. Methods

6.2.2.1. Emulsion preparation

Water-in-oil emulsions were prepared using an ultra-turrax homogenizer (T18 basic, IKA-werke, Staufen, Germany). MilliQ water (0.5, 1, 3, 5, 7, 10, 20, 30, and 40% w/w) was gradually added to sunflower oil with 5% w/w surfactant. The conductivity of the oil phase and the resulting emulsion was measured using an electrometer (6514 system electrometer, Keithley, USA). A SevenMulti conductivity meter (Mettler Toledo International Inc. USA) was used to measure the conductivity of salt and sucrose solutions.

6.2.2.2. Electrospraying and film formation

A single-nozzle electrospraying system (Terronics Development Cooperation, USA) was used to prepare the emulsion films (Figure 3.1). The emulsions were supplied at a flow rate of 15 ml/h via a syringe pump (Harvard 11 plus, Harvard Inc., USA). An electric potential was applied to the nozzle by a high voltage source (Heinzinger electronic GmbH). It is important to mention that the spraying conditions (emulsion flow rate and applied voltage) were adjusted to get a stable jet spray. Table 6.1 presents a summary of the applied conditions for electrospraying as a function of water and salt content.

Table 6.1. Minimum electrical potentials applied to obtain a stable jet spray at a flow rate of 15 ml/h.

Water content		NaCl content in 10% water emulsion	
Amount %w/w	Applied voltage KV	Amount %w/w	Applied voltage KV
0	12 ± 1.5	0.01	14 ± 0.5
0.5	12 ± 1.5	0.1	10 ± 1
1-20	14 ± 0.5	0.3	11 ± 0.5
30	17 ± 1	0.5	9 ± 1
40	18 ± 0.5	0.7	9 ± 0.5

The emulsions were sprayed on two model surfaces: glass slides and cellulose membranes (dialysis membrane from Akzo Nobel N.V., the Netherlands). The surfaces were examined with a microscope (Axiovert 200 MAT, Carl Zeis B.V., Sliedrecht, The Netherlands) attached to a camera (MotionPro HS4, Redlake MASD Inc., San Diego, CA, USA), and the microscopic images were analysed for droplet size using image analysis software (Image Pro plus 4.5). The number-average droplet sizes of sprayed emulsion droplets were determined from the pictures taken. The permeability of the coated cellulose membrane was further tested as described in the next section.

6.2.2.3. Film properties

The emulsion films were analysed for water vapour permeability with a gravimetric method using a modified ASTM (1983) procedure (**Chapter 4**). The coated membrane was placed on top of a permeation cell containing MilliQ water (relative humidity inside the cell was 100%). The cell was tightly sealed and placed in a humidity chamber maintained at 20 °C and 60% RH. The cell was weighed daily; the weight loss as function of time was registered. Three replicates were measured for each film and the flux reduction was calculated as:

$$Flux\ reduction\ (\%) = \left(1 - \frac{M_c}{M_b}\right) \times 100\ , \qquad (6.1)$$

where, M_c and M_b are the rates of moisture loss as a function of time (g/h) through the coated and uncoated (bare) membranes, respectively. Moreover, barrier efficiency of the film was calculated as function of deposited amount (*M*) on the membrane surface as:

$$Barrier\ efficiency\ (\%/g) = \left(\frac{Flux\ reduction}{M}\right), \qquad (6.2)$$

6.2.3. Scaling of droplet size

The mechanism of electrospraying in the cone-jet mode has been studied by various authors (Fernandez de La Mora & Loscertales, 1994; Ganan-Calvo, 2004; Gañán-Calvo & Montanero, 2009; Hartman et al., 2000) who related the fluid properties and the operating conditions to the droplet size in air. The effective electric stress Δ*P* (due to the applied voltage) is defined as:

$$\Delta P = k_p \left(\frac{\sigma^2 K^2 \rho}{\varepsilon_0^2}\right)^{1/3}, \qquad (6.3)$$

where σ is the surface tension ($N{\cdot}m^{-1}$), *K* is the electrical conductivity of the liquid (S/m), ρ is the liquid density ($kg{\cdot}m^{-3}$), ε_0 is the permittivity of vacuum, and k_p is a constant in the order of unity. Based on analysis of the stability limits of the cone-jet mode, a scaling law for the cone-jet radius R_d was derived given certain process limitations that are summarized in the weber number *We*:

$$R_d = \left(\frac{Q^2 \rho}{2\pi^2 \Delta P}\right)^{1/4} \text{if} \qquad We = \frac{\rho Q^2}{\sigma \pi^2 R_d^3} \leq 20, \qquad (6.4)$$

where, *Q* is the flow rate. The droplet size on the target surface depends on the contact angle *Θ* of the droplet on the surface (**Chapter 3**), and can be calculated as follows:

$$a = R_d \left(\frac{4 sin^3\theta}{2 - 3cos\theta + cos^3\theta}\right)^{1/3}, \qquad (6.5)$$

where, 2*a* is the diameter of the falling droplet on the target surface. This equation was used to compare the experimental results of the study.

6.3. Results and discussion

6.3.1. Electrical conductivity

Electrical conductivity is an important parameter for electrospraying, which should normally be between 1×10^{-5} S/m and 1×10^{-10} S/m for successful atomization (Hayati et al., 1987). Lower conductivity limits atomization due to insufficient electrical stress build-up in the spraying material (**Chapter 3**), while higher conductivity leads to unstable cone-jets (Luo et al., 2012). The conductivities of the emulsions with 5% surfactant and 10% water in 85% oil are presented in table 6.2.

The results showed that all three surfactants increased the conductivity of oil (PGPR < span80 < lecithin). The measured conductivities were in the range reported above and considered suitable for successful electrospraying (Hayati et al., 1987). The conductivity of the emulsion was significantly lower than of just the oil phase except for the emulsion with PGPR, although it should be mentioned that this value was low to start. Most probably the surfactant molecules moved to the water-oil interface therewith effectively reducing the conductivity of the bulk of the continuous phase.

Table 6.2. Influence of surfactants on the conductivity of water-in-oil emulsions and sunflower oil.

Surfactants	Oil conductivity nS/m	Emulsion conductivity nS/m
-	0.00	Not measured
PGPR	0.07	0.08
Span80	0.89	0.30
Lecithin	1.19	0.04

Note: The measured conductivity of MilliQ water was 6.5 µS/m

6.3.2. Electrospraying

The electrospraying behaviour and the resulting droplet distributions on the target material were investigated with a single-nozzle spray system. The PGPR emulsion produced a stable and continuous jet spray with a relatively uniform droplet distribution

(Figure 6.1a). Emulsions stabilised with span80 initially produced a stable jet but not stable enough over prolonged processing. This ultimately resulted in an irregular and unstable jet, wide droplet size distributions, and uneven coating (Figure 6.1b). Also the spray cone formed by the lecithin emulsion was not stable; therefore only PGPR was investigated further at 5%.

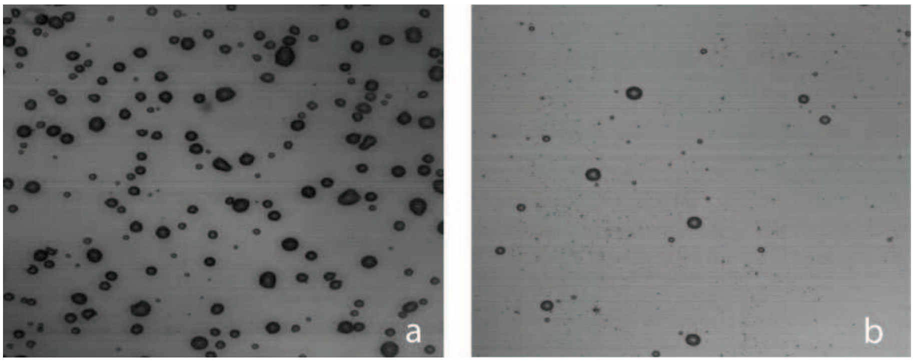

Figure 6.1. Micrographs of an electrostatically sprayed water-in-oil emulsion stabilized by (a) PGPR and (b) span80 presenting the size distribution.

6.3.3. Droplet size as function of liquid properties

6.3.3.1. Water content

The properties of emulsions (rheology, physical stability) are greatly influenced by the droplet size and volume fraction of the dispersed phase (Floury et al., 2000; Maan et al., 2011), and thus may affect their spraying behaviour. The emulsions with different water contents (0.5 – 40%) were prepared using 5% PGPR. For all the emulsions a stable jet and uniform droplet size distribution could be produced, although the spraying conditions (emulsion flow rate and applied voltage) needed to be adjusted to get stable spraying as shown in table 6.1.

The results revealed that until 3% water resulted in a significantly smaller droplet size (Figure 6.2); further at higher volume fractions no significant change was observed. The initial effect of the water content may be explained by the similar conductivities of the emulsions as a function of water content (0.02 - 0.09 nS/m for 0 – 40% water). The fact that above 3% water the droplets are much smaller compared to the model (Gañán-Calvo

& Montanero, 2009), may be due to the presence of water droplets that are more conductive compared to the oil phase and therefore may influence jet formation and subsequent break-up into small droplets.

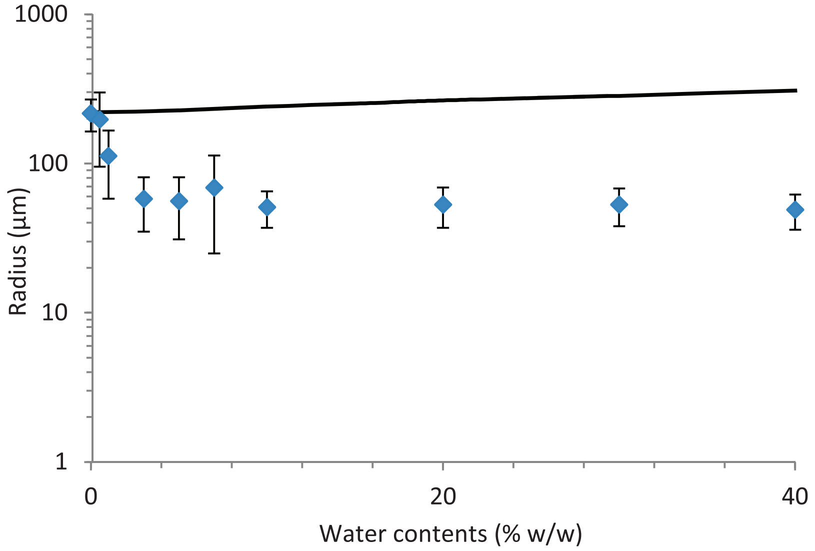

Figure 6.2. Effect of water contents on droplet radius of electrostatically sprayed water-in-oil emulsions prepared with 5% PGPR (dark line represents equation 6.5), 0% emulsion contain only PGPR in oil.

6.3.3.2. Dispersed phase conductivity

The influence of the aqueous phase conductivity on the droplet size was investigated by adding sodium chloride and sucrose. Sodium chloride significantly increased the conductivity of water (Figure 6.3) while sucrose did not affect the conductivity up to 30% (results not shown). The droplet sizes of salty emulsions, with various amounts of sodium chloride added, are shown in figure 6.3. The droplet size increased with the conductivity of the inner phase, while at 1% salt no stable jet was produced. The increase in droplet size may be attributed to corona discharge due to the high conductivity which resulted in insufficient charge build up on the interface to produce a stable cone-jet. Thus, the conductivity of the inner phase should not be too high since it will hinder the electrospraying process (Luo et al., 2012).

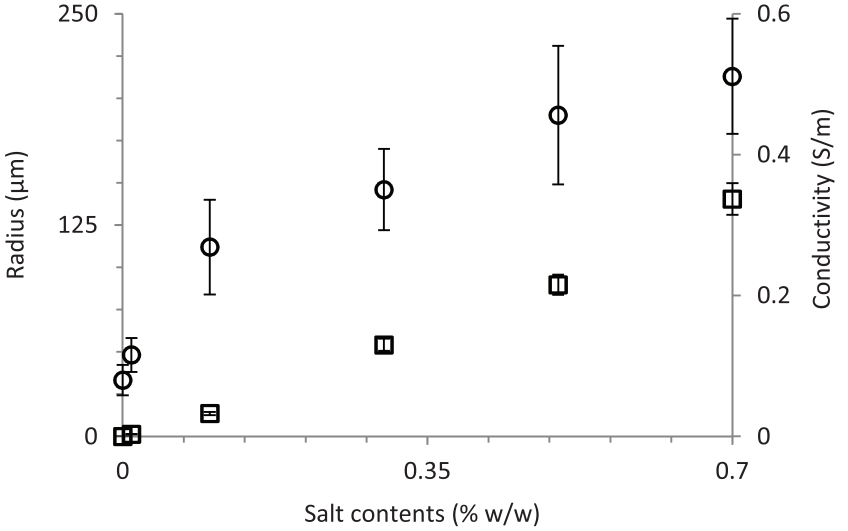

Figure 6.3. Effect of salt content on the conductivity of (□) water phase and (O) droplet size of electrostatically sprayed water-in-oil emulsions (5% PGPR and 10% water).

Inner phase conductivity now appears as a determining factor for the droplet size of electrosprayed emulsions. Addition of sucrose in the aqueous phase did not significantly influence the droplet size (50 ± 5 µm) as expected since the conductivity was not affected. However, the addition of sucrose seemed to increase the mono-dispersity of the emulsion droplets: the coefficient of variation decreased from 22% (without sucrose) to 15% (with 30% sucrose in the aqueous phase).

6.3.3.3. Protein content

Proteins are known to improve the mechanical properties and barrier properties of films (Perez-Gago & Krochta, 2000), and therefore their effects on droplet size were investigated. Addition of whey protein isolates (WPI) increased the water conductivity up to 0.08 S/m. All emulsions containing WPI (0-5% in the water phase) produced a very fine and stable jet spray. Figure 6.4 shows that the droplet size increases with the WPI contents. Larger droplet sizes were obtained as a function of protein contents, due to the increased conductivity of the inner phase.

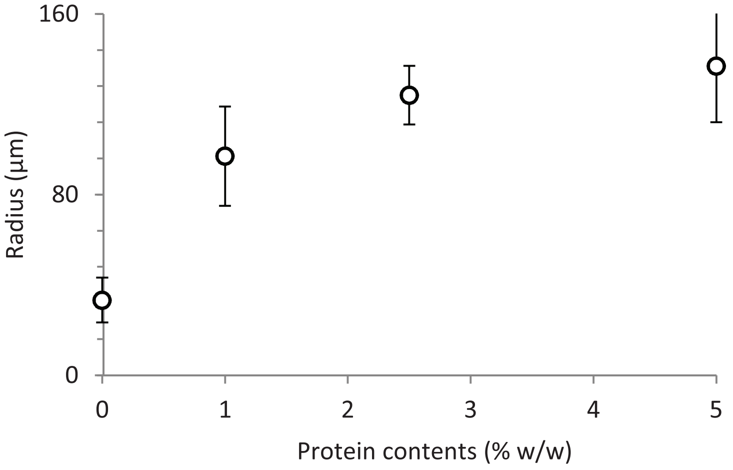

Figure 6.4. Droplet size of electrostatically sprayed emulsions as function of protein content in the dispersed phase (5% PGPR and 10% water).

6.3.4. Droplet size as function of applied potential

Salt containing emulsions produced a stable jet at a lower minimum applied electrical potential compared to emulsions that contain only water (Table 6.1). This may be another reason for the larger droplets. When increasing the electrical potential beyond the minimum value, smaller droplet sizes were observed (Figure 6.5).

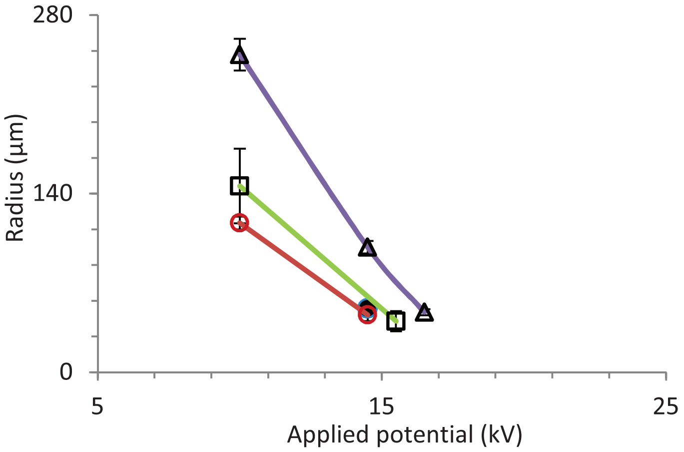

Figure 6.5. Influence of voltage on the droplet radius of electrosprayed water-in-oil emulsions containing different salt content in the aqueous phase (O 0.1%, □ 0.3%, Δ 0.7%, and ● no salt).

This was expected as charge to mass ratio increased significantly with the increase of applied voltage and resulted in smaller droplets (Bock et al., 2011; Xu et al., 2006). Obviously this is another way to control the droplet size without compromising (too much) on the composition of the emulsion that eventually will become the film.

6.3.5. Barrier properties of emulsion films

In this section, we investigated the barrier properties of the films that were electrosprayed using the emulsions that were discussed before.

6.3.5.1. Water content

PGPR containing emulsions were sprayed on cellulose membranes to produce thin films and their vapour permeability was determined. In all cases presented in figure 6.6, the same total amount of material (12 ± 2 g/m^2) was sprayed on the target surface. At 10% water, no significant difference in permeability was observed compared to the pure oil film (0%) water); while, at higher water concentration the flux was hardly reduced. Therefore, it was decided to take the 10% emulsion as reference for investigating the effects of having proteins in the emulsions.

6.3.5.2. Protein content

The emulsions containing various amounts of protein were electrosprayed on cellulose membranes to produce thin films. The reduction in water vapour flux was measured and the results are shown in figure 6.7. A higher protein concentration corresponds to stronger reduction of water vapour permeation per gram of sprayed material. It even proved to be possible to reduce water vapour permeation below the values of oil, using 10% protein. One may expect at least partial aggregation or fusion of the droplets at higher deposited amounts due to protein addition, yielding even films. Alternatively, the mechanical stability of such composite films (which cannot be independently tested) or prevention of crack formation e.g. by network formation may be possible explanations for the observed effects (de la Caba et al., 2012).

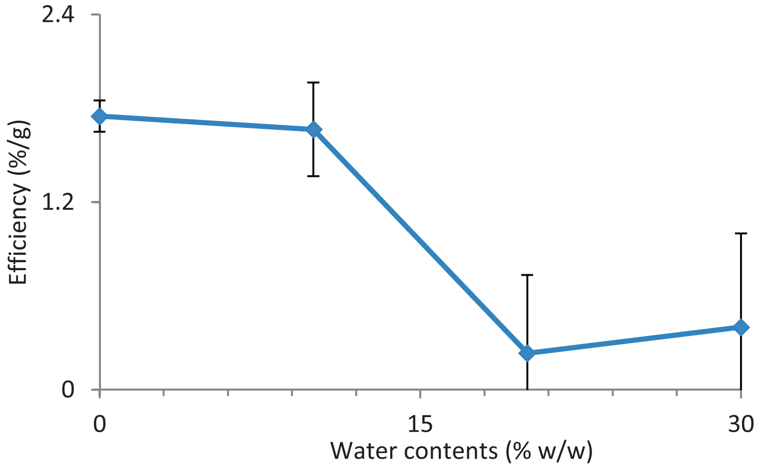

Figure 6.6. Effect of water content on the water vapour flux reduction efficiency of electrosprayed water-in-oil emulsion films (5% PGPR and 10% water).

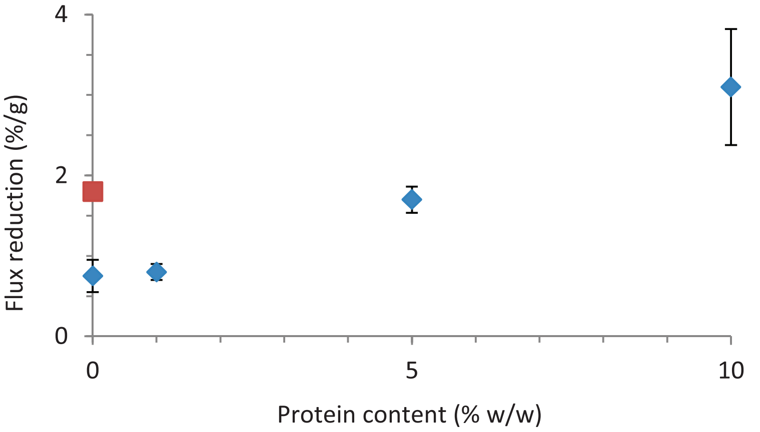

Figure 6.7. Efficiency of the emulsion film to reduce the water vapour permeation as a function of (◊) protein content in the aqueous phase compared with (□) pure lipid film (value taken from chapter 4).

6.4. Conclusions

Electrospraying of water-in-oil emulsions can be done with PGPR as additive, which resulted in stable operation and generation of small droplets in the cone-jet mode. The droplet size on the target surface decreases by the addition of water until 3%; at higher concentrations the droplet size became independent of the water content. However, the droplet sizes were smaller than expected on the basis of conventional theory. Moreover, higher conductivity of disperse (aqueous) phase resulted in larger droplet sizes produced by electrospraying, but also lowered the value of optimum electrical potential for stable jet spray. Further the addition of protein (WPI) to water-in-oil emulsions enhances barrier properties of the films relative to lipid films. From the results, it is clear that electrospraying of emulsions is feasible and can contribute to films with enhanced barrier properties, which is important for food applications.

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Chapter 7

General discussion and outlook

General discussion

In this study, electrospraying has been used to apply coating material on model surfaces and food products. This section reviews the findings of previous chapters, summarizing the main aspects that determine coating functionality starting from droplet generation to film formation, followed by an outlook towards various applications.

7.1. Overview of this thesis

Coatings, including edible coatings, are often sprayed onto a surface. Electrospraying has two advantages over other spraying methods:

1. It generates diminutive droplets, which is required in the preparation of thin, defect-free films. The droplet size depends upon the charge to mass ratio of the droplets, which is influenced by the flow rate of the atomised fluid, its conductivity, and the electric potential. These parameters should and can be tuned carefully to produce the droplets of a desired size.
2. In addition, the droplets are charged and will follow a trajectory along the electric field lines, towards the target surface; therefore, the fraction of material that ends up on the target surface is potentially larger than that with conventional (‘hydrodynamic’) spraying.

Electrospraying on less conductive surfaces initially resulted in more uniform droplet distributions compared to conductive surfaces, but droplets that arrived at later stages were repelled from the surface, limiting full coverage of the target surface. This was explained by limited charge leakage, resulting in charge accumulation and finally in repulsion of new incoming droplets (**Chapter three**).

In addition to the conductivity, structure of the target surfaces influences film formation by electrospraying (**Chapter four**). Porous membranes, having well defined characteristics, were used as model target surfaces. Smaller droplets penetrate into the pores of surfaces with large pores (nickel membrane; pore filling), or stayed on the surface of dense surfaces (cellulose membranes; surface coating), while an intermediate behaviour was observed for polyether sulfone membranes (having small pores 0.2 μm) leading to partial pore filling followed by accumulation on top of the membrane (Figure 4.7).

For the model surfaces, pore filling was the most efficient mechanism for reduction of the moisture permeability. Surface coverage was less effective: more coating material is required for complete coverage of the surface (**Chapter four**). However, surface coating was more effective in flux reduction when applying chocolate based coatings to crystalline and compressed tablets, compared to sunflower oil, which exhibited pore filling behaviour. This was explained by the mechanical instability of the coatings (crack formation) as a function of time: as soon as the coatings crystallized, the resulting shrinkage led to the creation of defects (**Chapter five**). Multiple electrospraying passes resulted in better film formation due to re-melting and fusion of the droplets, minimising the risk of cracks through the entire coating layer.

The applied coating material co-determines whether the surface of a three dimensional structure can be covered through the so-called wrap-around effect. This effect is caused by the electric field between the nozzles and the surface: as the field lines end at all sides of the product, the droplets will also end up at all sides of the product. This wrap around effect was more efficient for small highly charged droplets produced from sunflower oil based coating materials compared to chocolate based coating materials, which gave much larger droplets (**Chapter five**).

Composite films consist of different ingredients providing enhanced mechanical and barrier properties. One possible way to combine these ingredients is the use of emulsions (**Chapter six**). Since the conductivity of the electrosprayed fluid may not be high, we chose for the use of water-in-oil emulsions, to form a film that may attach well to the target surfaces. The presence of the aqueous phase in the electrosprayed emulsion resulted in smaller droplets, until 3% w/w and at larger volume fractions, the droplet size became constant. Increasing dispersed phase conductivity led to larger droplets. These effects cannot be fully explained by the conventional electrospraying theory. Addition of whey protein concentrate to the dispersed phase (10% w/w water) was effective in reducing water vapour permeability compared to lipid films, which was explained by improved mechanical stability of films preventing crack formation.

7.2. Scale up

The results of this study indicate that electrospraying is a versatile technique to produce thin films with edible materials. However, the total throughput of coating material through a single nozzle is quite small; typically 0.02 kg/h. Electrospraying using multiple nozzles and/or multiple passes could be an attractive alternative for conventional dipping or gas-assisted sprays suffering from poor transfer efficiency and material losses in an industrial setting. However, for the applications in which larger volumes need to be sprayed this will be a challenge, because much higher throughput per nozzle is not possible. A single nozzle (**Chapter three**) and a multiple nozzle unit (**Chapter four**) can coat an area[1] of about 2 and 10 m^2/h at flow rates of 20 and 120 ml/h, respectively.

At industrial scale, for example, cookies are produced at a rate of one tonne per hour which, we estimate, corresponds to the formation of a total surface area of 200 m^2/h that needs to be coated. For this, 120 single nozzles or 20 multiple nozzle units are needed which may be placed in series, parallel, and circular array. Here, a uniform distribution of the flow rates across all the nozzles, and a good design of the overall electric field to prevent interference between neighbouring spray nozzles are crucial factors to ensure good, even coating results (Arnanthigo et al., 2011).

Another option for up scaling of electrospraying could be the use of porous, metal membranes (Sato et al., 2010) in which the many pores will all act as nozzles. The number of pores and their distribution over the membrane will determine the throughput. The pore geometry and inter pore distance are crucial (Luo et al., 2012).

7.3. Applications

Electrospraying has already been applied in a range of applications (e.g., for analytical purposes in mass spectrometry, in air purification and for coating of various metal objects), but it is not well known in food industry. Therefore, this thesis specifically aimed at understanding the interplay between (electrospray) process and (food) product. Some

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[1] $A = \frac{3QW_sV_b}{4R_d}$, here A is the area covered during electrospraying of a liquid at a flow rate of Q, R_d is the radius of the droplet, W_s is the width of the spray, and V_b is the conveyer belt velocity.

specific strengths of electrospraying, that enable it to operate where other processes are not suited, are described as follows;

a. It can make very thin coatings, which are of interest for products that have a short exposure time to moisture.
b. Due to the ‘wrap around’ effect, electrospraying is suited for coating irregular products and products that are porous (**Chapters four and five**).
c. The ability to spray small amounts may also be used to dose specific active ingredients to a product surface; this in contrast to using it to produce dense, defect-free films.
d. By using a solvent that evaporates, one can encapsulate ingredients, which are then delivered to a surface.
e. By further exploring the effects of an electric field, one may produce fibres, which could be used for producing fibrillar products (e.g., meat analogues).

We will now discuss the types of food products that are potentially within the scope of the process.

7.3.1. Application of thin films on irregular products (a)

Many biscuits, snacks, and breakfast cereals have a crispy texture. However, during shelf life or consumer use the crispiness decreases due to moisture (vapour) absorption from its environment, which is governed by the difference in water activity and related mass transfer (Bravin et al., 2006). Coating of such foods with a suitable material can retard moisture migration and thus retain product crispiness for a longer period of time. A possible application could be the coating of products that are brought into contact with a liquid, during preparation by the consumer, and subsequent consumption. An example of this could be creating a thin, lipid coating around corn flakes to control water migration during submersion in milk. The porosity and varying shape and size, and large specific surface area of the corn flakes are complications in finding a good coating procedure; electrospraying may be a good option.

Suppose an oil in water emulsion is sprayed containing whey protein isolates having a water vapour permeability of approximately 1.32×10^{-13} kg/(m.s.Pa) (Quezada Gallo et al., 2000). A defect-free film of 10 µm thickness[2] would delay softening of the flake for twenty minutes, which would be ample for this application; even if the film has defects, it would retard softening for a few minutes.

7.3.2. Sensory attributes (b)

Besides for barrier functionality, chocolate-based coatings may be applied to enhance sensory attributes like taste and appearance. Coating of the top as well as side surfaces of cakes may be achieved with electrospraying in one pass. Flipping over of the cake is then necessary to produce an even coating on the entire cake which will reduce the coating steps and the processing cost (Figure 7.1). Here, the coating thickness will determine taste or appearance of the final product.

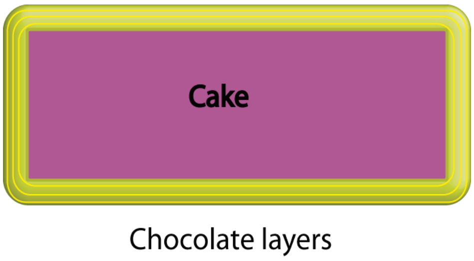

Figure 7.1. Schematic representation of chocolate-based coatings on cake applied by electrospraying.

7.3.3. Dosage of specific or active ingredients (c)

Electrospraying can accurately dose small amounts of active ingredients; an added advantage is that the method has very high yield, since the electric field lines from nozzles to target surface ensure that most of the droplets will end up on the intended target surface. Possible applications are here the dosage of micronutrients, colorants or preservatives, and antimicrobial agents (Falguera et al., 2011). Various other potential applications of edible coatings with electrospraying are summarized in table 7.1.

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[2] Time (t) was calculated as $t = \frac{\Delta M L}{A P \Delta p}$ where ΔM is the amount of water absorbed for the softening of the corn flake, A is the area of the corn flake, L is the coating thickness, P is the permeability and Δp is the vapour pressure difference across the flake.

Table 7.1. An overview of edible coatings which can be potentially applied through electrospraying (Bonilla et al., 2012; Cagri et al., 2004; Falguera et al., 2011; Rojas-Grau et al., 2009).

Functionality	Active ingredient	Products	Edible carriers
Texture	Calcium ions	Fruits and vegetables	Polysaccharides
Nutraceuticals	Vitamin, minerals, and probiotics	Fruits and dairy	Proteins and emulsions
Anti-browning, antioxidants	Ascorbic acids, sorbates, essential oils, and alginates	apple, peanut, and meat products	Oil, w/o, and o/w emulsions
Antimicrobials	Essential oils, fatty acids, and benzoates	Baked products, fish, and fresh meat	Protein, oil

7.3.4. Encapsulation (d)

Encapsulation is used for controlled release of active ingredients and for enhancing the shelf-life of food ingredients that may for example be susceptible to oxidation (e.g., fish oils). Conventional encapsulation techniques involve often conditions such as higher temperature (spray drying), pH shifts (coacervation or layer-by-layer deposition) or even use of organic solvents, which may be undesired for the active component and the consumer. Electrospraying can produce fibre or particles under mild conditions, for example encapsulated probiotic bacteria (López-Rubio et al., 2012; Schoenmaker et al., 2012).

7.3.5. Electrospinning (e)

Meat analogues are prepared to mimic meat in appearance, colour, flavour and texture. In particular the texture of meat consisting of a large network of protein fibres is critical to its taste experience. Electrospraying can be used, albeit in a different operational mode, to spin fibres from a protein solution, with a diameter of 10 - 240 nm (Kriegel et al., 2009; Stijnman et al., 2011). Not only can such fibres be applied in meat analogues, but the incorporation of bio-active compounds like enzymes, antimicrobials, colours, and antioxidants was achieved (Kriegel et al., 2010). It should be mentioned that for the production of larger amounts of a bulk material, the throughput of the process is still a major challenge. Future research has to elucidate the feasibility of this application for larger-scale food production.

7.4. Concluding remarks

In this thesis, electrospraying was investigated and evaluated for application of coatings on food surfaces. Results from experiments and simulations provided insight in electrospray coating, which was found influenced by the characteristics of both coating material and target object properties. These insights provide a solid basis for design and set-up of industrial applications with electrospraying, contributing to coating processes that deliver food products of high quality and at the same time operating at enhanced transfer efficiency and producing less waste.

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Summary

Summary

Edible coatings are thin layers of edible material applied on food products to improve quality and shelf life, or to add specific functionality to the product. To have optimal barriers properties, the films should be defect-free, and should be as even as possible. Electrospraying is a method that employs an electric potential over the interface, to create diminutive charged droplets. By applying the electric field, charged droplets can be 'steered' towards the target surface. Thus, it is very suited to create very thin coatings on complex, porous surfaces, which are typical characteristics of many food products.

Chapter 2 of this thesis deals with existing applications of electrostatic powder coating. In which, particles are charged in two ways: corona charging, passing the particles through an ion rich region, or tribo-charging, particles are charged due to collision with a surface. The charge on the powder particles is inversely related to the resistivity and the size of particles, which determines the transfer efficiency and particle adhesion to targets. Besides powder characteristics, target surface properties influence the deposition of charged particles (**Chapter 2**).

In electrospraying, the charge to mass ratio determines the droplet size, which decreases with increase in conductivity of the sprayed fluid and with the applied potential, while it increases with larger flow rates. The charged droplets that are small enough, follow the electric field lines to the target surface, and are deposited on the surface. They are uniformly distributed on surfaces if the charge of droplets is released fast enough to prevent accumulation of charge and under these conditions, the films are completed rapidly (**Chapter 3**). As many solid foods are porous, model surfaces (membranes with well characterised porosity, pore size and surface properties) were used that allow evaluation of permeability (**Chapter 4**). Afterwards, food products were coated (**Chapter 5**) and the results were compared with the model surfaces.

The electrosprayed coating material penetrates into the pores of model surfaces having relatively large pores, while it stays on the top of dense cellulose membranes with much smaller pores (**Chapter 4**). On surfaces with interconnected sub-micron-sized pores (PES membrane), the pores are first filled partially, after which a film develops on the surface.

For these model surfaces, the pore filling (blocking) mechanism is the most effective in reducing the moisture permeation; partial pore filling and surface coverage require more coating material to be equally effective in reducing moisture permeation. In general, multiple electrospraying passes result in fusion of droplets leading to more uniform coating which effectively reduces moisture permeation.

Since the electric field is present between nozzles and the target surface; electric field lines end on all sides of the product. Therefore, the sides and top surfaces of 3D objects may be coated due to the 'wrap around' effect, which is influenced by droplet size. The sunflower oil-based coatings coats the sides of the tablet more effectively compared to chocolate-based coating due to smaller droplet size. On a porous food surface (a crystalline tablet), sunflower oil-based coatings follow the partial pore filling behaviour. However, chocolate-based coatings exhibit the surface coating mechanism. Thus, the interplay of the process settings (electric potential, flow rate of fluid), the properties of coating materials (conductivity, viscosity), and the properties of target surfaces (conductivity, porosity, morphology) together determine the film formation behaviour on objects (**Chapter 5**). Besides the primary film formation, the morphological changes in the coating with time are of great relevance to the coating efficiency. Therefore, chocolate-based coatings retain their moisture barrier properties better than sunflower oil after several hours. This is ascribed to the crystal formation in the sunflower oil-based coatings, which induces the formation of cracks and defects which becomes progressively worse during storage (**Chapter 5)**.

In chapters 3-5, lipids-based coating materials are used and are targeted at reduction of moisture migration. In **Chapter 6**, the coatings are taken one step further and it is investigated whether other components can be incorporated. Therefore, emulsions are used to reduce the risk of defect formation and produce coatings with improved mechanical stability. In electrospraying of water-in-oil emulsions, the droplet size increases as a function of the dispersed (aqueous) phase volume (till 3%), and its conductivity. The barrier functionality of these coatings (till 10% water content) is similar to that of coatings prepared with lipid only, but indeed these films have better stability in time.

Chapter 7 consists of three sections. In the first section, the outcomes of the research described in this thesis are summarised. The second section discusses the out scaling of electrospraying with the use of multiple nozzles or membranes for higher productivity. In the third section an overview of possible food-related applications for electrospraying is discussed. The fact that electrospraying can accurately deposit small amounts of material to a large surface area, opens opportunities for various applications, ranging from barrier coatings, dosage of active ingredients such as micronutrients, antimicrobial agents or even medical components, to encapsulation and formation of fibrillar products.

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Kashif

Publications

Peer-review Journals

Butt M, Tahir-Nadeem M, Khan M, Shabir R & Butt M (2008). Oat: Unique among the cereals. European Journal of Nutrition 47(2): 68-79.

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Khan MKI, Maan AA, Schutyser M, Schroën K & Boom R. Electrospraying of water in oil emuslion for thin film coating (Submitted).

Khan MKI, Schutyser M, Schroën K & Boom R (2012b). Edible coatings on food surfaces prepared with electrospraying (Submitted).

Overview of completed training activities

Courses

Discipline specific

Nano-particle technology	2009
Reaction kinetics in food science	2009
Advance computer aided modelling	2010
Sustainability analysis in food production	2011
Food rheology	2012

General

Project Proposal	2009
Project Time Management	2009
Philosophy and ethics in Food science and technology	2009
Information literacy + EndNote introduction	2009
PhD competence	2010
An introduction to EDEM	2010
Techniques for Writing and Presenting Scientific Paper	2011

Conferences

Coated food seminar	2009
Delivery of functionality in complex food systems: third international symposium	2009
NPS 10 & 11	2010, 2011
1st international congress on food technology	2010
Novel approaches in Food industry	2011
Food balt conference	2012
FPE days	2009-12

Optional

Weekly Group meetings FPE	2009-2013
PhD excursion FPE	2010, 2012

About the author

Kashif Khan was born on 14th February 1985 in Narowal, Pakistan. In 2001, he completed higher secondary certificate and in the same year he started his bachelor degree in Agriculture (Food technology) at University of Agriculture, Faisalabad (UAF). After the completion of B.Sc. (Hons.), he got admission in M.Sc. (Hons.) Food Technology in the same university and graduated in 2007. During his stay at UAF, he has been an active scout and served as Group Scout Leader. Based on his achievements in scouting he was awarded by a gold medal. In 2008, he got the scholarship for MS Leading to PhD from Higher Education Commission (HEC) of Pakistan and joined the Food Process Engineering Group at Wageningen UR for PhD studies. The focus of his study was the optimization and scale up of an efficient coating technique (electrospraying), results of which are included in this thesis. Kashif can be reached through the email address: mki.khan@yhoo.com.

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