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# A novel method for the preparation of starch films and coatings

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**Abstract**

In this work, maize starch was used to demonstrate a novel method which enables the preparation of starch films and coatings with good thickness control. 5% starch in de-ionized water (w/v) was gelatinized at 120 °C for 30 min, subsequently small quantities of dispersant and ethanol were added and subjected to ultrasonic disruption to make a stable modified starch solution. Electrohydrodynamic behavior of this solution was studied and optimum conditions for film preparation were determined. The solution was then electrosprayed in the cone-jet mode and films were collected on a rotating plate. Film thickness was investigated by electron microscopy. Films of varying thickness were prepared by varying the electrospraying time and their characteristics are compared with solvent-cast films.


*Keywords:* Starch; Electrohydrodynamic atomization; Films; Coatings; SEM

## 1. Introduction

Starch is one of the most abundant naturally occurring substances. There is renewed interest in starch-based materials in recent years in order to exploit its biodegradability and mechanical properties. Starch is mainly composed of two homopolymers of D-glucose, amylose and amylopectin. Amylose is almost a linear polymer with α-D-(1→4) glycosidic linkages, while amylopectin is a highly branched polymer which also contains α-D-(1→6) glycosidic linkages at the branching points in addition to α-D-(1→4) glycosidic linkages (Karim, Norziah, & Seow, 2000). The molecular weights of the amylose and amylopectin have been estimated to be $\sim 10^5$ and $\sim 10^7$, respectively (Roger, Bello-Perez, & Colonna, 1999).

Starch films and coatings have been used for various food and pharmaceutical applications. Films prepared from starches are isotropic, odourless, tasteless, colorless, non-toxic and biodegradable. Edible films and coatings can be prepared from native and modified starches. The starch films have low oxygen permeability (Krochta & Mulder-Johnston, 1997; Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998; Forsell, Lahtinen, Lahelin, & Myllarinen, 2002). Starch coatings are nutritious, safe and economic and have been used in the storage and marketing of foods (Avena-Bustillos & Krochta, 1993; Avena-Bustillos, Krochta, Saltveit, Rojas-Vilegas, & Sauceda-Perez, 1994; Baldwin, Nisperos-Carriedo, Hagenmaier, & Baker, 1997). Their physical characteristics, chemical resistance and mechanical properties are similar to plastic films (Nisperos-Carriedo, 1994).

Starch can be modified chemically, physically, or enzymatically to suit various needs (Bemiller, 1997). Starch films are usually modified by the addition of plasticizers. Polyols (glycerol, sorbitol and polyethylene glycol) are commonly used as plasticizers (Goutard, Gulibert, & Cuq, 1993). These additives decrease the intermolecular attraction between adjacent polymeric chains, resulting in film flexibility and decrease in film strength (Donhowe & Fennema, 1993; 1994; Laohakunjit & Noomhorm, 2004). Fanta, Felker, Shogren, and Salch (2002) applied starch coatings to polyethylene films by immersing in starch solutions to impart hydrophilic properties. Palviainen, Heinamaki, Myllarinen, Lahtinen, Yliruusi and Forssell (2001); Krogars, Antikainen, Heinamaki, Laitinen, and Yliruusi (2002) have also reported the use of native starches films and coatings for the preparation of tablets and pellets for the drug release.

Electrohydrodynamic atomization (EHDA), also referred to as electrostatic atomization or electrospraying, is a process in which a liquid is forced through a capillary and a potential difference of the order of kilo volts is applied between the capillary and the collection electrode. This phenomenon was first systematically studied by Zeleny (1914, 1915, and 1917) and increased in technological importance over the last two decades after the discoveries of Fenn, Mann, Meng, and

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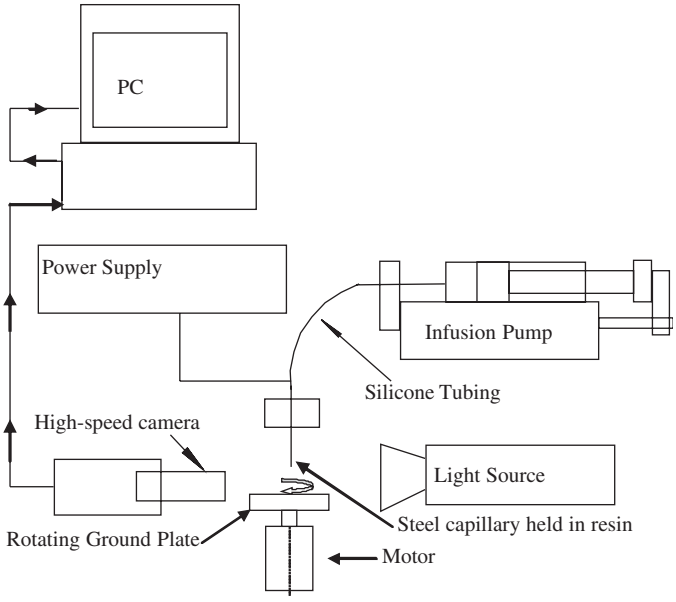


Fig. 1. Schematic representation of equipment set-up used for the electrohydrodynamic experiments.

Table 1
Physical properties of solvents and starch

| Sample | Density ($kgm^{-3}$) | Electrical conductivity ($Sm^{-1}\times10^{-4}$) | Surface tension ($mNm^{-1}$) | Viscosity (mPa s) |
|---|---|---|---|---|
| De-ionized water | 1000 | 2 | 68 | 1 |
| Ethanol | 800 | 0.03 | 20 | 1.3 |
| Gelatinized starch | 1040 | 225 | 73 | 3110 |
| Modified starch solution | 1010 | 110 | 43 | 3 |

Wong (1989) on its application to determine the mass of large biomolecules thorough mass spectroscopy. EHDA can occur in many modes but the stable cone-jet mode is most studied and desirable as it generates near-monodispersed droplets of a few micrometers in size (Clopeau & Prunet-Foch, 1989; 1990) and in this way the droplets size can be controlled by varying either the flow rate, applied voltage or the physical properties of the electrosprayed liquid (Ganan-Calvo, Davila, & Barrero, 1997).

If the electrical conductivity of the solution is too low, liquid cannot be sprayed in the cone-jet mode, while if it is high, the atomization mode depends on the liquid flow rate (Hartman, Brunner, Camelot, Marijnissen, & Scarlett, 2000). For the formation of stable cone-jet, the surface tension must be overcome by the resultant electric stress produced by the applied potential difference. A higher surface tension demands a larger potential difference and this increases the probability of electrical discharge (Ganan-Calvo, Davila, & Barrero, 1997). Viscosity influences the jet break-up process with high viscosity causing a significant increase in the size of the secondary droplets, and this is undesirable (Weber, 1931).

In the cone-jet mode, the electric field induces a surface charge in a drop, which forms at the tip of the nozzle and as a result of the electric field it is transformed into a cone. A jet with a high charge density emanates from the cone apex and subsequently breaks down into tiny droplets (Chen, Pui, & Kaufman, 1995). Compared with other atomization techniques of liquids, EHDA has some significant advantages, e.g. relatively easy generation of droplets and avoiding coalescence of droplets due to electric charge of same polarity in the droplets, achievement of a narrow size distribution of droplets by obtaining the cone-jet mode (Watanabe, Matsuyama, & Yamamoto, 2003). Also electrosprays have an intrinsic high deposition efficiency due to their guided deposition on the collection electrode due to the electric field (Siefert, 1984).

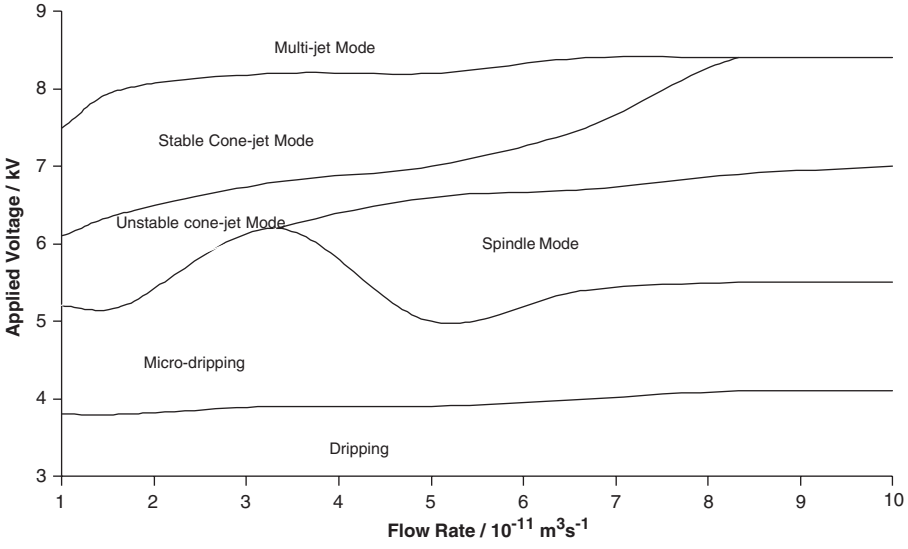


Fig. 2. Mode selection map for the 5 wt% modified starch solution.

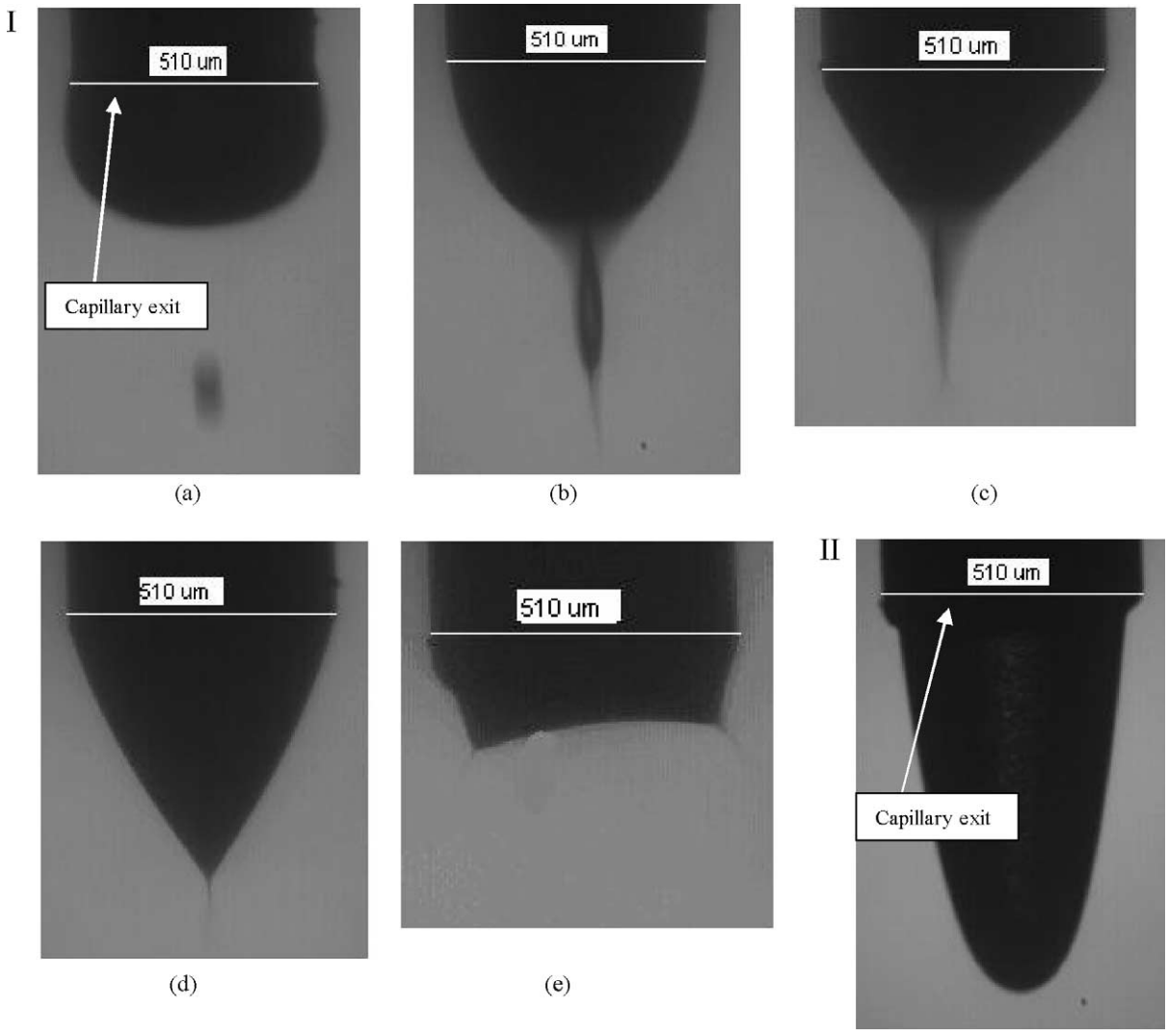


Fig. 3. (I) Atomization modes displayed by the modified starch solution at a flow rate of $5\times10^{-11}$ $m^3$ $s^{-1}$, (a) micro-dripping mode at 4.1 kV, (b) spindle mode at 5.5 kV, (c) unstable cone-jet mode at 6.5 kV, (d) stable cone-jet mode at 7 kV, and (e) multi-jet mode at 8.2 kV. (II). Electrohydrodynamic behavior of the gelatinized starch at $5\times10^{-11}$ $m^3$ $s^{-1}$ and 7 kV.

In general, EHDA is a very good processing route for forming thin films. Thin films of $LiMn_2O_4$ were prepared by Zomeren, Kelder, Marijnissen, and Schoonman (1994) for cathodes in rechargeable lithium ion batteries. Chen, Emond, Kelder, Meester, and Schoonman (1999) formed ZnO, $ZrO_2$ and $Al_2O_3$ nano-structured thin films from their precursors by EHDA. Nguyen & Djurado (2001) used EHDA to prepare yttria-doped nanocrystalline zirconia films for solid oxide fuel cells. Starch films have been traditionally prepared by casting (Wolff, Davis, Cluskey, Gundrum, & Rist, 1951; Mali, Grossmann, Garcia, Martino, & Zaritzky 2002) and extrusion (Shogren, Fanta, & Doane, 1993). The stiffness and strength of the films strongly depends on the film thickness (Jansson & Thuvander, 2004) and therefore it is of immense significance that while forming, the film thickness can be controlled. In this work, we propose a novel electrospray method to prepare starch films and coatings with nearly linear control over the film thickness with electrospray deposition time.

## 2. Experimental details

### 2.1. Materials

Maize starch (regular maize granules of 10–20 μm in size, donated by National Starch, UK) was used in this investigation.

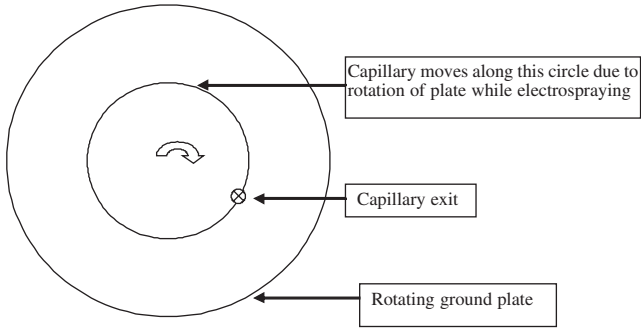


Fig. 4. Plan view of capillary and rotating ground plate set-up.

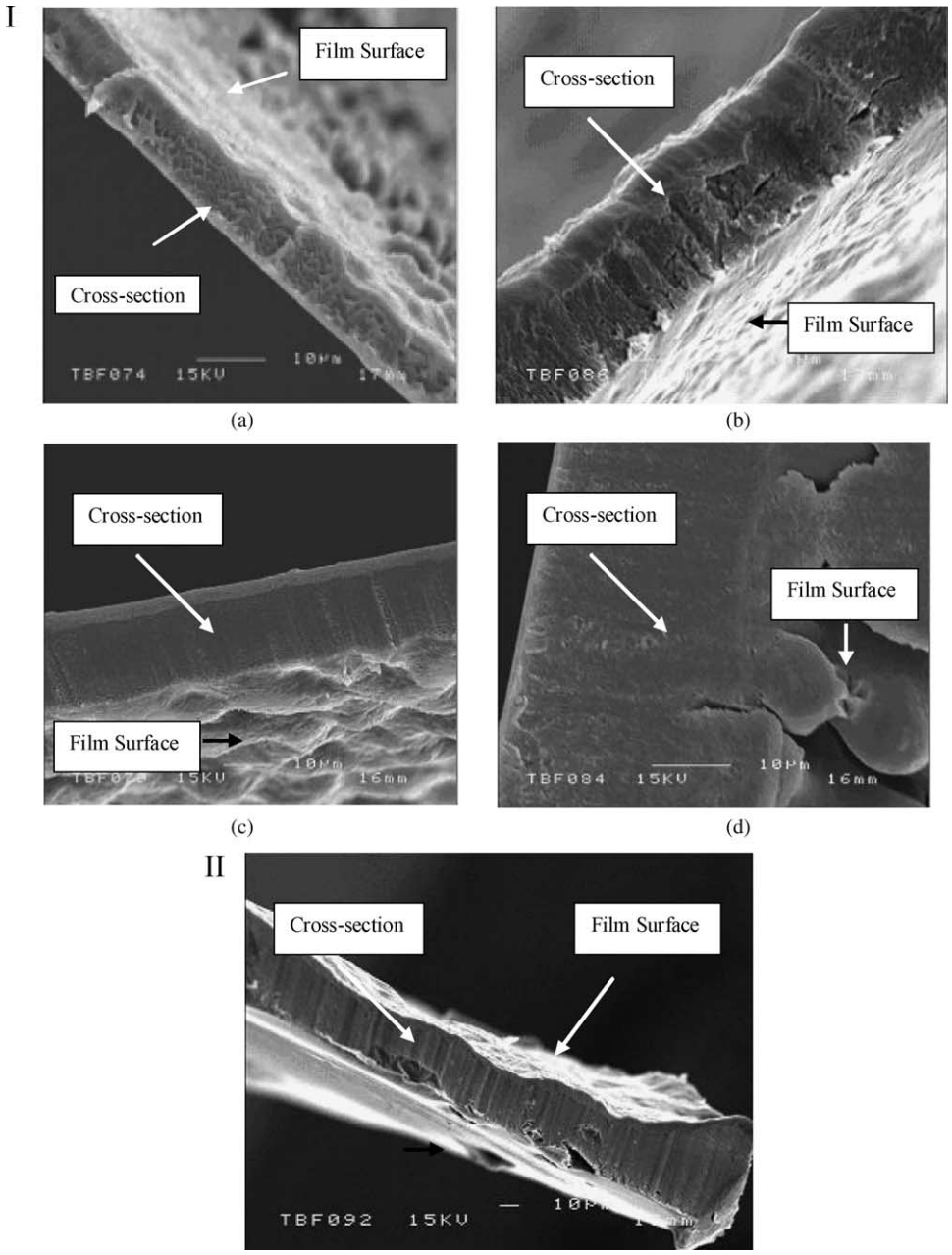


Fig. 5. (I) Scanning electron micrographs of electrospray deposited starch films showing cross-section and topography, (a) after 2 h, (b) after 3 h, (c) after 4 h, and (d) after 8 h, of electrospraying. (II) Scanning electron micrograph of solution-cast starch film, microscopy carried out after 3 days of casting 1 ml gelatinized starch.

According to supplier data the amylose/amylopectin ratio in this starch is ~27/73. De-ionized water was used in all the experiments. 5 wt% starch solution in water (5 g of starch in 100 ml of water) was subjected to gelatinization by heating to 120 °C for 30 min under constant magnetic stirring in an oil bath. Since this solution could not be electrosprayed, a modified starch solution was prepared in the following way so that its properties (like viscosity, surface tension and electrical conductivity) were suitable for electrospraying.

The gelatinized starch was left to cool to ambient temperature (~20 °C) under constant stirring and subsequently ethanol (HPLC grade) was added to it, to prepare a (80%) /(20%) water/ethanol (v/v) starch solution. After that EFKA-4580 dispersant (EFKA Additives, Heerenveen, Holland) amounting to 10 wt% of starch was added to suppress sedimentation of starch. Finally, the resulting solution was subjected to ultrasonic disruption (Branson Sonifier, 250 W) for 120 s. Modified starch solution quoted in this paper refers to this final solution obtained after addition of ethanol and dispersant, and then subjected to ultrasound disruption, in contrast to the original gelatinized starch.

### 2.2. Characterization

The physical properties of the modified starch solution and gelatinized starch such as viscosity, electrical conductivity,

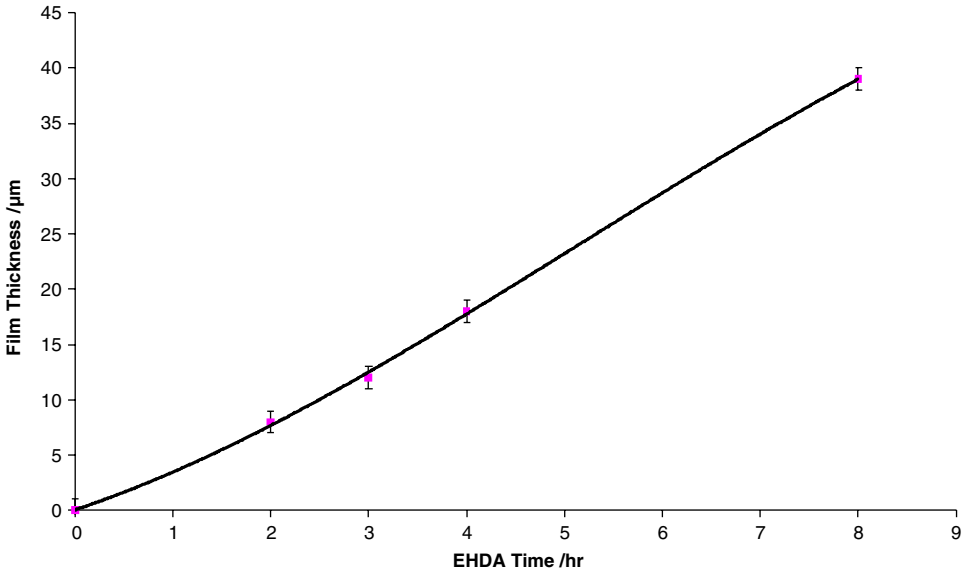


Fig. 6. Variation of starch film thickness as a function of electrospray deposition time.

surface tension govern the EHDA behavior and hence are important to this study. Thus, these properties were measured and all the equipment used for characterization were calibrated against reference data and performed at ambient temperature. DC electrical conductivity was measured using a HI- 8733 (Hanna Instrument) conductivity probe. Surface tension was measured using a Kruss Tensiometer K9 (Wilhelmy's plate method). Around 200 ml of solution was used and five consecutive surface tension readings were taken, and averaged. The plate was cleaned and dried after each reading to minimize error. The densities of the samples were estimated using the standard density bottle. A 25 ml density bottle was used for this purpose. 25 ml of solution was measured and weighed using a four decimal place balance. Average of three density readings is reported. Kinematic viscosity was determined by using a U-tube viscometer (BS/U type) in a water bath at 20 °C. This value was subsequently multiplied by density (in g/cm$^3$) to calculate dynamic viscosity.

### 2.3. Electrohydrodynamic atomization

The experimental set-up used to perform EHDA is shown in Fig. 1. The solution was uniformly and continuously pushed by an infusion pump (Harvard Apparatus PHD 4400) through a 1 ml plastic syringe to a stainless steel capillary (outer and inner diameter of 510 and 250 µm, respectively). Silicone tubing was used to connect the capillary inlet and syringe outlet. A high voltage dc power supply (Glassman Europe) was used to generate the required potential difference (of the order of kV) between the outlet of the capillary and rotating grounded plate electrode. The plate was rotating with the help of an electrical motor. The distance between the tip of the capillary and rotating ground plate was 20 mm. A high-speed camera (Weinberger AG, Dietikon, Switzerland) was used to observe the elecrospraying modes and capture images.

Modified starch solution was subjected to EHDA at 7 kV and $5\times10^{-11}$ m$^3$ s$^{-1}$ in the cone-jet mode to prepare starch films using this novel set-up and to study the effect of electrospraying time on the film thickness with the ground plate rotating at 2 rpm.

### 2.4. Scanning electron microscopy

Thickness of the starch films was determined using a Jeol JSM-6300 scanning electron microscope operating in the secondary electron mode with an accelerating voltage of 15 kV and working distance of 15 mm. The films were carefully placed on aluminum stubs so that their cross-section was visible and were gold-coated for 120 s prior to microscopy.

## 3. Results and discussion

After gelatinization at 120 °C for 30 min, the starch starts to retrograde with time and hence precipitates out of water (Elfstrand, Frigard, Andersson, Eliasson, Jonsson Reslow, & Wahlgren, 2004; Farhat, Blanshard, & Mitchell, 2000). For successful electrohydrodynamic spraying, it is necessary to have a stable solution. Therefore, the EFKA dispersant, which is a water-based high molecular weight acrylic polymer emulsion, was added and, subsequently, ultrasonic disruption was applied to stabilize the starch solution. Table 1 shows the physical properties of the solvents, gelatinized starch and modified starch solution.

Ethanol weakens the intermolecular attraction between the polymer chains. It is also known to have very low electrical conductivity, and its surface tension is much lower than water. Thus, addition of ethanol in limited quantity lowers the electrical conductivity and surface tension of the starch solution and reduces viscosity by three orders of magnitude and, as discussed below, eventually helps to get the cone-jet mode of EHDA, which is the preferred mode of electrospraying for regular deposition of films.

The mode selection (M-S) map (Fig. 2), i.e. atomization modes for applied voltage versus flow rate in the regime 3–9 kV and $10^{-11}$ $m^3$ $s^{-1}$–$10^{-10}$ $m^3$ $s^{-1}$, was determined to establish the best spraying conditions for the modified starch solution. It also shows several electrospraying modes such as, microdripping, spindle, unstable cone-jet, cone-jet and multi-jet obtainable at various flow rates and applied voltages. Fig. 3(I) shows the different atomization modes exhibited by the modified starch solution at $5\times10^{-11}$ $m^3$ $s^{-1}$ at different applied voltages. Fig. 3(I)a does not show a continuous jet and exhibits the microdripping mode with small droplets coming out of the capillary. Fig. 3(I)b is a characteristic of the spindle mode with fragments detaching from the liquid. Fig. 3(I)c exhibits the unstable cone-jet mode, with the characteristic blurred appearance at the cone apex. The stable cone-jet mode (Fig. 3(I)d) was obtained for the modified starch solution at 7 kV in contrast to the gelatinized starch, which simply dripped in the applied voltage-flow rate parameter space investigated (Fig. 3(II)). Fig. 3(I)e exhibits the multi-jet mode with two jets coming out of the skewed cone.

The electrohydrodynamic atomization modes differ in the way droplets are produced, droplet size and size distribution. Increasing the potential difference from zero increases the droplet dripping frequency and decreases the droplet size. Extensive details of the modes have been published by Jaworek & Krupa (1999). During EHDA, in cone-jet mode, solvents evaporate significantly from the jet and droplet (Grigoriev & Edirisinghe, 2002), and therefore starch films and coatings can be obtained instantaneously using our processing procedure. This makes our work also suitable for practical coating applications. Coatings can be obtained in a similar manner by replacing the collecting plate by the material to be coated.

The starch films were deposited on a rotating ground plate in stable cone-jet mode. Spraying conditions of 7 kV and $5\times10^{-11}$ $m^3$ $s^{-1}$ were chosen, as these resulted in the best film forming conditions. A rotating plate was used to ensure the even spreading of droplets generated by EHDA, and a balance between sufficient bonding time and drying, which is key to obtaining of film instantaneously with uniform thickness. The center of rotation of the plate was slightly offset to the exit of the capillary (as shown in Fig. 4), so that all droplets do not get collected in the center while rotating, permitting formation of films with larger diameter (~40 mm). The diameter of the films can be increased further by increasing the distance between the capillary outlet and rotating plate.

Fig. 5(I) shows the cross-section and surface topography of the films prepared by EHDA. These are compared with film formed by simply casting the starch solution (Fig. 5(II)). Fig. 5(I)a shows the film obtained after 2 h of electrospraying. Fig. 5(I)b shows the film obtained after 3 h of electrospraying. Fig. 5(I)c shows the film obtained after 4 h of electrospraying. Fig. 5(I)d shows the film obtained after 8 h of electrospraying. While the films prepared by EHDA showed uniform thickness, cast film had irregular thickness. The film thickness of EHDA starch films increased almost linearly with electrospraying time (Fig. 6). The times involved were much shorter than in solvent casting (typically a few days). However, as the film thickness increased, it affected the stability of the cone-jet mode mode of as it acted as a dielectric layer in the electric field and this made thickness control difficult (e.g. comparing Fig. 5(I)c with Fig. 5(I)d).

## 4. Conclusions

A novel electrohydrodynamic atomization method has been developed to deposit starch films and coatings. In this method while electrospraying in the cone-jet mode, the solvent evaporates very quickly due to the large surface area of the droplets generated, resulting in instantaneous films. Films with different thicknesses were obtained by varying the electrospraying time. The procedure incorporated a new droplet collection method, which ensured even spreading of droplets and thereby uniform thickness starch films with ~40 mm diameter were prepared.

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