Study
of poly(vinyl alcohol) solution
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Doctoral Thesis Summary

Tomas Bata University in Zlín

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Faculty of Technology

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Study of poly(vinyl alcohol) solution for inkjet printing

Studium roztoku polyvinylalkoholu pro inkoustový tisk

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Keywords: *Poly(vinyl alcohol); solution; polymer; solvent; viscosity; surface tension; surface energy; rheology; viscoelasticity; relaxation time; ink; inkjet; Rayleigh breakup; velocity; drop; printability; stability; gel; digital printing; resolution; pattern; substrate;*

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ABSTRACT

The thesis is focused on the preparation and characterization of water-soluble polymer-based ink. The poly(vinyl alcohol) (PVA) was chosen for preparation of the suitable polymer inks for a Dimatix material printer DMP-2800 Series working in the drop-on-demand mode. Drop-on-demand mode is one of the two most frequently used ways in inkjet printing technology, which represents a promising technique for simultaneously patterning and material deposition without a need of any master form or masks.

The work is divided into theoretical background and experimental part. In theory, a brief introduction to inkjet printing technology is provided, and followed by a description of the main ways of drops generation together with the device arrangement. The next section of the theoretical part is focused on a description of the basic groups of inkjet inks as well as on their crucial parameters, for example, viscosity and surface tension. Further, the interpretational framework based on dimensionless criteria for ink property evaluation is discussed including viscoelasticity assessment. A brief description of the polyvinyl alcohol is provided in the last section of theoretical part. The main aim and goals of this work are defined in accordance with hitherto achieved results of research conducted in the laboratories at our institution and with the aid of information gathered from a literature review summarized in previous sections. The experimental part is arranged in accord once the sequence of the performed experiments. The core section of the work contains 10 chapters discussing obtained results. At the beginning of this section, a selection of polymer-solvent system is discussed. The rheological and viscosity studies of the prepared solutions are shown and discussed including the stability and aging issue. In the next step, discussion of surface tension measurements follows. According to the obtained results, the suitability of prepared solution for inkjet printing was performed by calculating and evaluating of dimensionless criteria to find optimum solution properties correlating with a processing window. It was shown that the analytical apparatus does not fully cover the studied case, in spite of its improvement. Therefore, the next section is dedicated to study drop formation and analysis of this process resulting in a study of viscoelastic properties and their analysis with respect to ink drop formation. In the last step, other parameters (waveform, drop velocity) were optimized with respect to the used digital printing cartridge and modified polyethylene terephthalate. Consequently, the prepared demonstration patterns are characterised and presented mainly in the form of images captured by optical microscopy and data obtained by AFM and mechanical profilometry.

Gathered knowledge and experience were summarized in the concluding summary section and in a short advice for practical ink development procedure.

ABSTRAKT

Práce je zaměřena na přípravu a charakterizaci inkoustu na bázi vodě-rozpustného polymeru. Polyvinylalkohol (PVA) byl vybrán pro přípravu polymerního inkoustu vhodného pro materiálovou tiskárnu Dimatix DMP-2800 Series pracující v módu „drop-on-demand", který je jedním ze dvou nejčastěji používaných v technologii inkoustového tisku, a který představuje slibnou metodu pro vzorování a ukládání materiálu současně bez potřeby použití tiskové formy anebo masky.

Práce je rozdělena na část teoretickou a část experimentální. Stručný úvod do technologie inkoustového tisku je popsán v teoretické části, za kterou následuje popis hlavních způsobů generace kapiček spolu s uspořádáním zařízení pro každý typ tvorby kapiček. Následující sekce teoretické části je zaměřena na popis základních druhů inkoustů, jakož i na jejich klíčové parametry, které jsou reprezentovány hlavně viskozitou a povrchovým napětím. Následně je diskutovaný interpretační rámec založený na bezrozměrných kritériích včetně posouzení viskoelasticity. Poslední sekce teoretické částí je věnována stručnému textu o polyvinylalkoholu. Poté jsou definovány hlavní cíle této práce v souladu s dříve dosaženými výsledky výzkumu prováděného v laboratořích naší instituce a s pomocí informací shromážděných v průběhu literární rešerše. Experimentální část je uspořádaná v souladu s posloupností provedených experimentů. Základní část práce obsahuje 10 kapitol zabývajících se získanými výsledky a jejich diskusí. Na začátku této části je diskutován výběr vhodného systému polymer-rozpouštědlo. Dále jsou uvedeny a diskutovány reologické a viskozimetrické studie připravených roztoků včetně záležitosti ohledně jejich stability a stárnutí. Poté následuje diskuse stanovení povrchového napětí. Na základě naměřených hodnot byla stanovena vhodnost připravených roztoků pro inkoustový tisk pomocí vypočtení a vyhodnocení bezrozměrných kritérii. Ty přes zlepšení mohou být využity pro nalezení vhodných vlastností inkoustu, které by odpovídaly zpracovatelskému oknu. Bylo prokázáno, že analytický přístroj zcela nepopisuje studovaný případ. Další sekce je proto věnována studiu tvorby kapičky a analýze tohoto procesu, který vyžaduje studium visko-elastických vlastností a jejich analýzu s ohledem na tvorbu kapičky. V posledním kroku byly optimalizovány ostatní parametry (waveforma, rychlost kapičky) pro použití digitálního tisku definované inkoustové kazety a konkrétní model flexibilního substrátu z poly(ethylentereftalátu). V návaznosti na to jsou připravené demonstrační vzory charakterizovány a prezentovány zejména ve formě obrázků zachycených pomocí optické mikroskopie a dat získaných z AFM a mechanické profilometrie.

Získané znalosti a zkušenosti byly shrnuty krok za krokem v části závěrečné shrnutí a v krátkém shrnujícím doporučení pro praktickou přípravu a vývoj inkoustu.

1. INTRODUCTION

Printing process has been known for a long period. The first written evidence came from the Far East. The earliest printed text, images and patterns were prepared by woodblock printing technique during the T`ang Dynasty (618 – 906) in China. The *"Diamond Sutra"* is the first printed book with illustrations and text. The writing ink was composed by lamp-black and gum dissolved in water. The modern printers were introduced in the second half of the 20th century by Xerox, Hewlett-Packard, Epson, and Canon. [1, 2]

The main types of printing processes include offset lithographic, flexographic, gravure, letterpress, screen printing, inkjet printing process and toner printing system. [1] The major part of the mentioned processes is based on roll-to-roll principle and each of them is specific for certain application. However, only a few of them are suitable for surface functionalization, especially for surface treatment of solid polymer materials or polymer deposition because of their thermal, mechanical, and functional properties.•

Although the inkjet printing seems to be relatively simple process of deposition, there are several important conditions that should be fulfilled for good printing performance. They include the requirements on inkjet ink, substrate properties, drop formation, and on the printing algorithm. Each part plays an important role in a whole inkjet printing process. Inkjet ink requirements include its properties, such as viscosity and surface tension; for substrate, the crucial parameters involve wettability, surface energy and surface structure; and the printing procedure, actuator type, drop size represent characteristic parameters of printing platform and drop generation.[4]

2. INKJET PRINTING

Inkjet printing (IJP) technology allows controlled material deposition and patterning without need of any master form or masks. Moreover, it is a non-contact deposition technique based on computer-controlled ejection of fluid (ink) drops from print-head nozzle to a pre-defined substrate position. [5, 6] The technique is suitable for preparation of several patterns, whose shape and size depend on a specific application. Although the IJP is still used for decoration, mainly, of textile substrates, the latest applications include preparation of printed

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• The term polymer is derived from the Greek words meaning "many parts." The polymer is prepared by a process known as polymerization, which involves the chemical combination of many small chemical units known as monomers. The repeating units may be either single atoms as in sulphur molecules or groups of atoms such as methylene units. Polymers have a linear, branched or cross-linked structure. [3]

electronics such as sensors [7, 8], partially or all-inkjet printed organic thin film transistors and capacitors [9, 10], or ionic actuators [11]; organic, or polymer light-emitting diodes (OLED or PLED) [12-14]; fabrication of polymer lenses [15]; and biological applications, e.g. cell-patterning [16]. Although inkjet printing may be used for preparation of different patterns or/and devices, this technique could be also used together with other deposition techniques to obtain a required functionalized device, such as a pixel-like capacitive vapour micro-sensor [17] or an organic thin film transistor [18]. Additionally, three-dimensional printing represents a method for rapid prototyping that aims to prepare a complex shape pattern directly from a computer by overprinting (slice after slice). Main advantages of inkjet printing are low ink consumption, possibility to manufacture very fine and precise structures, i.e. it is a cost-saving process. On the other hand, the technique is suitable for low viscosity inks (include polymer solutions, dispersions and others) [19]. Other limitations may come from thermal and chemical stability of device parts that are in contact with the used ink.

In practice, the resolution is characterized by abbreviation "DPI - Dots per Inch". The relationship between resolution and drop spacing is shown in Figure 1, which manifests that resolution is inversely proportional to the drop spacing. The drop spacing is a distance between centres of the two adjacent drops.
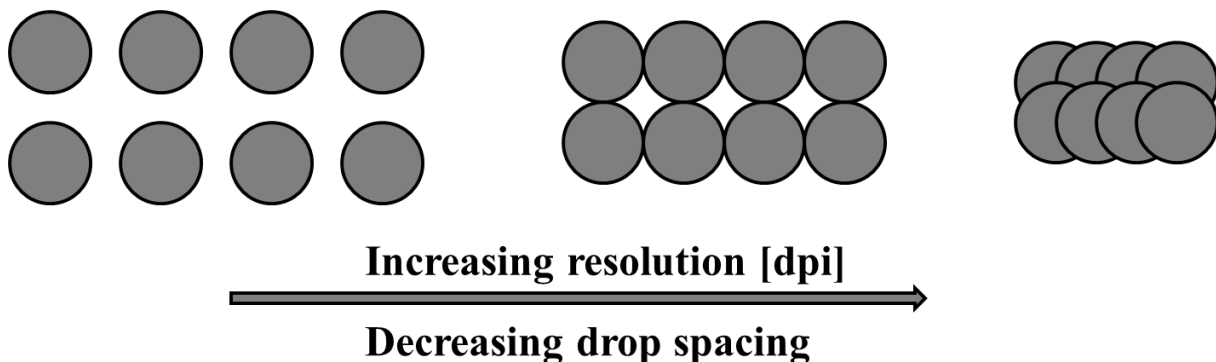
Figure 1. Scheme of relationship between resolution and drop spacing.

The inkjet printing methods can be divided according to drop generation modes into two groups, namely continuous inkjet printing (CIJ) and drop-on-demand (DOD). The DOD modes can be later divided into several subgroups. [6]

2.1 Drop-on-Demand Piezoelectric Inkjet Printing

The most important inkjet printing technology is drop-on-demand (DOD). In this case, the drops are generated and deposited only when required. Hence, drops are formed in dependence on the initial impulse, which is evoked by piezoelectric element.

The piezoelectric element (usually based on Lead Zirconium Titanate - PZT) is a material that exhibits a unique property - piezoelectric effect. It is the ability of certain materials to generate an electric field in a response to mechanical strain (applying pressure/stress), and more precisely, it is called *direct piezoelectric effect*. Oppositely, if this material is exposed to an external electric field, the asymmetric displacement or deformation of its crystal structure occurs, which is called *indirect piezoelectric effect*. [20]

The example of a waveform controlling the drop ejection process is illustrated in Figure 2-A together with the print-head nozzle with PZT located in the wall (Figure 2-B). The actual position of PZT corresponds to a "START" (or Standby) phase on waveform. In the phase 1, the voltage decreases to zero volts, which results in returning PZT back to a neutral position in the wall. In this phase, the chamber is filled with ink from a reservoir; moreover, the ink is also pulled from nozzle or meniscus at the same time, which results in maximum volume of the ink inside the chamber. Then, the applied voltage leads to compression of pumping chamber and also to drop ejection due to generated pressure (Phase 2). Consequently, the deflected PZT is returned back to the initial (standby) position. Thus, the voltage decreases back to the initial level (Phases 3 and 4). In this step, the motion of PZT is controlled during drop break-off.[21]
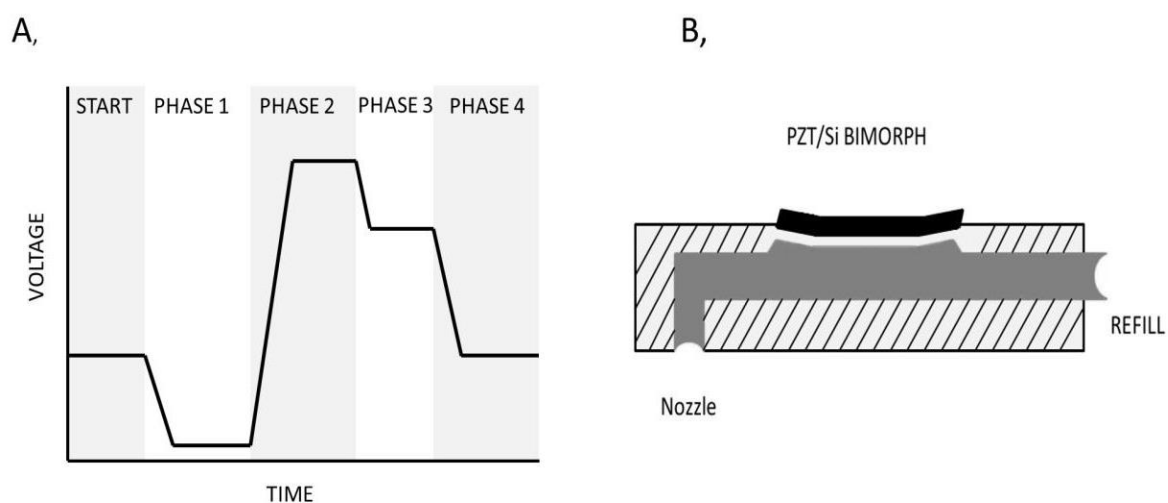
Figure 2. The proposed segments of pulse waveform (A), and the pumping chamber of piezoelectric print-head (B).[21]

Structure of waveform can be changed to obtain stable drops ejection and formation. Additionally, uniform drops velocity can be achieved by changing waveform parameters such as level, duration and slew rate. These parameters can be modified independently on each other in the case, when each nozzle (ink channel) contains its own piezo element (in the case of the Dimatix cartridges and print-head with 16 nozzles). [21]

3. INKJET INKS

The basic inkjet modes as well as drop ejections were mentioned in previous section. The inkjet printing process is not only about the printing modes. The other requirements come from ink properties. The inkjet inks classification and their basic composition will be described in this part.

3.1   Classification of Inkjet Inks

The inks suitable for inkjet printing can be divided into four major groups. Each group, except UV curable, can be found in alternative term in literature, for example water or aqueous ink, solvent or non-aqueous ink, and phase change or hot melt inks. Generally, the ink could be described as a system consisting of functional material and a liquid vehicle (carrier medium). The liquid vehicle usually contains different additives. Additives can improve the ink processing, visibility of prepared motives, ink adhesion, for example. These additives are surfactants, plasticizers, colorants, co-solvents, and other compounds. [22]

The appropriate ink formulation (composition) depends on final application of ink. The water-based and solvent-based inks include a solution or dispersion of functional material in carrier medium. The low viscosity inks are used in inkjet printing because of their transport through the nozzle, drop formation, and the drop integrity. The viscosity represents only one of the crucial properties of the inks. Other important properties are for example surface tension (SFT), density, and conductivity in the case of preparation of conductive patterns. In addition, the conductivity of inkjet ink is important in CIJ printing. [22, 23]

3.2   Crucial Ink Parameters

These properties include mainly viscosity and surface tension. Of course, specific applications may require inclusion of other ink properties, for example, conductivity in continuous inkjet printing.

3.2.1 Viscosity

The first important property of each printing fluid is its viscosity. However, the viscosity of ink can be affected by many parameters such as additives, surfactants, polymer concentration, and solvent composition and other. It can be also affected by other physical parameters, such as temperature, and pressure for a given fluid system. The viscosity of inkjet ink is usually very low, usually below 20 mPa·s, depending on a print-head. It is very important parameter for its performance during jetting and spreading on substrate. [24, 25]

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3.2.2 Surface tension and wettability

The next discussed crucial parameter of inkjet inks is surface tension (SFT). Surface tension is a reversible work needed to create a unit surface area in a substance. Sometimes it is also called the specific surface energy, the intrinsic or true surface energy [26]. All liquids are made up of molecules close to one another and exerting attractive forces. SFT is a result of a cohesive interaction (forces) in the liquid. The molecule in the bulk of liquid senses the same attractive forces in all directions, whereas these attractions are lacking in one direction for the molecules at the surface. Liquid with higher SFT (for example water) demonstrates a high intramolecular attraction and a strong tendency to form a sphere. On the other hand, liquids with lower SFT have a weak tendency toward sphere formation that is overcome by countering forces. The SFT for liquids is expressed in the units of mN/m.[27, 28]

Surface and interfacial tensions play important role in wetting, coating, corrosion and adsorption processes. A better wettability may be obtained either by modification of the SFT of liquids or by modification of a functional group on substrate surface.[29, 30]

To summarize, the role of surface tension of ink is twofold. First, it is important parameter influencing the printing process, namely the drop formation. Next, the lower surface tension of the ink results in better wettability of substrate.

3.3 Ink Jetting Characteristics

3.3.1 Ink drop formation

As has been already mentioned, the creation of patterns with precise shape and required quality is obtained by deposition of several hundreds or thousands of ink drops. Therefore, one of the important steps in inkjet printing process is ejection and formation of spherical drops without existence of any several smaller drops known as „satellite drops".

Controlling drop formation and break up of filament of ink is a complex process that depends on many factors including the rheology of ink. Besides properties of ink such as viscosity, surface tension and inertia, the phenomenon of viscoelasticity must be considered. Viscosity and elastic stresses resist a necking of liquid filament and the surface tension and inertia have also influence on the final shape and form of the drops. [31, 32]

Drop generation in DOD printing process is a repeated pulse process. Single pulse can be generally divided into five stages: (1) ejection and stretching of liquid, (2) pinch-off of liquid thread from nozzle exit, (3) contraction of liquid thread, (4) break up of liquid thread into primary drop and satellites, and (5) recombination of primary and satellite drops. In ideal case, no break up appears and the last (4 and 5) stage may be described as spherical drop formation and travel. [33, 34]

3.3.2 Dimensionless criteria

The drop formation is the key step of the process and its complexity can be characterized by a number of dimensionless groupings of physical constants, namely by the Reynolds (*Re*), the Weber (*We*), and the Ohnesorge (*Oh*) number. The number *Z* is defined as reciprocal value of the Ohnesorge number. [35, 36] The number *Z* was implemented by Fromm [37] who performed the fundamental work focused on understanding drops generation. Moreover, Fromm suggested that stable drop generation occurred for $Z > 2$ and that for a given pressure pulse the drop volume increases with an increasing value of *Z* as well. [5] This prediction was refined by many authors later. [35, 36, 38]

Although the *Z* number is widely used for the basic printability characterization of inks, there are also other dimensionless criteria that have to be considered because velocity "*v*" terms describing dynamic effects are cancelled in its fraction formula and only material constants and characteristic length remain.

Other approach relies on the introduction of another dimensionless number which includes velocity. The Capillary number (*Ca*) is one of these other numbers. Indeed, Kim and Baek [34] found that the *Z* number alone is insufficient for describing the drop formation dynamics. Hence, they used *Ca* taking into account the drop velocity during printing and demonstrated the printability window based on the Capillary number plotted against the Weber number.

3.3.3 Viscoelasticity in drop formation

The Rayleigh model holds perfectly for viscous liquids and it works with limited success for printable viscoelastic liquids as well. Further considerations are necessary for investigated solutions because the addition of small amount of polymer to the ink has significant effect on the break up dynamics. The polymer addition results in the formation of long-lived filaments (or thin threads), connecting the ejected drops with the nozzle of printer. Length and lifetime of filament increase with both molecular weight and concentration of polymer. Above a certain concentration, the capillary force is not able to break the filament resulting in elastic retraction of ejected drops back to nozzle by filament. [39, 40]

Morrison and Harlen [31] demonstrated the jet behaviour in their work. The break up dynamics of Newtonian jets was compared with non-Newtonian jets, in which the jet behaviour was varied with respect to different viscoelastic parameters such as concentration, Deborah number, and molecule extensibility. In Newtonian jets, the ligament is breakaway shortly from the nozzle. This ligament is then break up into several smaller drops due to Rayleigh instability that is attributed to grow of a capillary wave along the filament. In the presence of polymer, the breakaway from nozzle is delayed, moreover, the speed of primary drops is reduced and the distribution of satellite drops is different.

4. POLY(VINYL ALCOHOL)

The preparation of Poly(vinyl alcohol), (PVA), was firstly described by W. O. Herrmann and W. Haehnel in 1924. The stoichiometric saponification of polyvinyl acetate with caustic soda was used for preparation of PVA. [41] It cannot be prepared by traditional polymerisation way because its monomer vinyl alcohol is not stable and rearranges readily to acetaldehyde. Therefore, it is usually manufactured by hydrolysis of polyvinyl acetate. Hydrolysis of acetate groups involves partial or total replacement of the ester groups of vinyl acetate by hydroxyl groups, under defined condition (for example alkaline methanolysis). Then, the poly(vinyl alcohol) is precipitated, washed and dried. Properties of resulting product depend on the length of polymer chain (polymerisation degree, PD) and on the degree of hydrolysis (DH). Poly(vinyl alcohol) is an example of water-soluble semi-crystalline synthetic polymer. However, it is slightly soluble in ethanol and insoluble in other organic solvents. The higher degree of hydrolysis and polymerisation degree of prepared PVA, the lower solubility in cold water. [42]

It can be noted that DP and DH of polymer are the most important parameters, which affect the properties of prepared PVAs. Poly(vinyl alcohol)s are usually classified according to DH into fully (98-99 mol.%), intermediate (93-97 mol.%), and partially (85-90 mol.%) hydrolysed grades. The melting point of fully hydrolysed PVA grade (228 °C) is higher that melting point of partially hydrolysed grade of PVA (180-190 °C). [43, 44]

Concerning specific solvent system used in the presented work, very little is known. To date, two articles focused on inkjet printing of poly(vinyl alcohol) were released. In the first work, the printability of PVA was investigated by Yun *et al.* [45] for construction of 3D structures at micro-scale. In their work, the PVA was dissolved in mixture water/DMSO (4/1 v/v). In the second work, Salaoru *et al.* [46] investigated several numbers of inks composed from PVA with different both mass molecular weight and degree of hydrolysis. In this case, PVAs were dissolved in purified water at 60 °C in the first step. Then, the humectant (glycerine or mono propylene glycol) and pigments were added to prepared solutions.

5. AIMS OF THE THESIS

The thesis aims at a development of an ink based on water-soluble polymer for DOD digital printing for patterning of polymer surfaces. Besides that specific goal, the polymer system shall be treated as an exemplary case and lessons shall be drawn at each step of the work. It is possible to acquire not only new practical experience with material printing but also strengthen general knowledge in the field of polymer solution dispensing and improve the ink formulation development method. This aim has been defined in accordance with hitherto achieved results of research conducted in laboratories at our institution and with the aid of information gathered from literature review summarized in previous sections.

The aim of this Thesis may be achieved by pursuing following goals:

- Choice of proper solvent system and grade of Poly(vinyl alcohol) with respect to potential application for temporary patterns printing on polymer (PET) substrate.

- Research of PVA solution properties relevant to its use as an ink for DOD printing including stability (aging) issues including tuning of the solution properties by additives/co-solvents and finding optimum temperature for processing.

- Evaluation of prepared solution on the base of mainstream printability assessment methods with the use of dimensionless numbers. Critical reconsideration of these approaches and eventual improvement.

- Study of ink drop formation as the key step in printing process. What can be learned from it?

- Research in the field of specific features related with polymer solutions, namely viscoelasticity, if the Newtonian model does not apply. Critical reconsideration of these approaches and eventual improvement.

- Demonstration of the suitability of prepared ink for printing.
    - Research and development of printing method in laboratory scale on model substrate together with optimization of individual steps of printing process.
    - Preparation and characterization of testing patterns on model substrate (SiO_2 coated polymer substrate made from PET with surface energy of 49 mJ·m^{-2}).

- Summarization of practical advices for preparation of polymer based inks based on experience gathered during the work.

6. EXPERIMENTAL PART

6.1 Materials and Sample Preparation

A commercial poly(vinyl alcohol) (PVA) that represents a water-soluble polymer was purchased from Sigma-Aldrich under trade name Mowiol®. The experimentally investigated material in this work was Mowiol® 4-98. Degree of hydrolysis (DH) of this PVA was in the range from 98.0 to 98.8 mol %, polymerization degree (PD) around ~ 600 and weight-average molecular weight (M_w) around ~ 27,000 as declared by the producer. Also other PVA brands were tested at the beginning of the preliminary material selection for ink formulation, namely Mowiol® 6-98 that had DH in the range from 98.0 to 98.8 mol %, DP around 1,000 and weight-average molecular weight around ~ 47,000. Other initially tested materials was Mowiol® 8-88 that had weight-average molecular weight around ~ 67,000, DH ~ 86.7-88.7 mol %, DP ~ 1,400.

Dimethyl sulfoxide (DMSO) for UV spectroscopy grade, ≥ 99.8 % (GC), was also purchased from Sigma-Aldrich. Demineralised water was used as a major solvent. Laboratory grade of Triton™ X-100 surfactant was also purchased from Sigma-Aldrich. Polymer PET substrate selected for printing (NOVELE™ IJ-220) was supplied from Novacentrix (USA).

6.2 Experimental Methods

Measurements of the rheological properties of prepared solutions were carried out using a rotational rheometer (Bohlin Gemini, Malvern Instruments, UK), with coaxial cylinder geometry (controlled shear rate mode). Intrinsic viscosity, $[\eta]$, was determined by measuring the relative viscosities. The measurements were carried out by using a Lovis 2000 M/ME viscometer (Anton Paar) based on the rolling ball made from steel. Density measurements of liquids were performed at required temperatures by density meter DMA5000M (Anton Paar). The surface tension (SFT) was estimated using force tensiometer K100 from KRÜSS (GmbH Germany) by plate method (also called Wilhelmy plate method). All solutions were passed through a syringe filter with pore size 0.24 μm to eliminate insoluble impurities. Solution with suitable properties were printed by Dimatix Materials Printer DMP-2800 series (Fujifilm Dimatix) onto coated PET foil (NOVELE™ IJ-220). The cartridge and substrate temperatures were controlled. The print-head nozzles were purged for 1 μs after every 8 run. The surface energy of coated PET foil was determined using Surface Energy Evaluation System (See system) (Advex Instruments) by a Sessile drop technique. Printed demonstration patterns were analysed by optical microscope LEICA DVM2500 Digital Camera (LEICA MICROSYSTEMS) and by atomic force microscope (AFM) Dimension ICON (Bruker) under ambient condition. The mechanical profilometer (Bruker) was used for determination of high profile of prepared motives.

7. SUMMARY OF RESULTS, DISCUSSION AND CONCLUSIONS

Inkjet printing represents a promising technique for patterning and material deposition simultaneously without need of any master form or masks. However, the printing process depends on the type of inkjet printer as well as on the ink formulation. This Thesis provides description of experience and findings gathered during the work on preparation of water-soluble polymer inkjet ink. Poly(vinyl alcohol) (PVA) was chosen for preparation of the suitable polymer ink for the Dimatix material printer DMP-2800 Series working in drop-on-demand mode. Viscosity, density, and surface tension are generally considered crucial physical properties of each inkjet ink. The main problem of each water-based ink is its high surface tension coming from water. Hydrophilic polymers decrease the surface energy of their solutions however, it was experienced in this case that it was not enough to match the solution with the surface energy of chosen flexible substrate. Another requirement on the ink composition was to keep the formulation as simple as possible, ideally without any additives. Therefore, the ink properties were adjusted by choice of co-solvent system water/DMSO. The polymer solution with the best properties was used for preparation defined patterns on a typical flexible substrate (coated PET foil).

Firstly, the conclusions relating to PVA solution preparation will be summarized. According to empirical experience gained in first performed experiments, the polymer with lower weight-average molecular weight is more suitable for printing than polymer with bigger one. Other important parameter includes the degree of hydrolysis (DH). Although, dissolution of PVA with lower DH in carrier medium was easier than for higher DH, the gel forming tendency of solution avoided the ink being properly ejected thought nozzle. Therefore, the almost fully hydrolysed PVA with lower M_W was chosen (Mowiol 4-98, $M_w \sim 27$ kg/mol, DH = (98.0-98.8) %, DP $\sim$ 600). However, SFT of simple aqueous PVA solutions was too high. Addition of an available surfactant was tried without success due to interactions of the surfactant with the polymer (precipitation). Anyway, the use of surfactants was reconsidered and abandoned due to their inevitable residual content in printed material. Therefore, the decrease of SFT was obtained via using co-solvent miscible with water. Ethylene glycol was tried in hope it will work as humectant simultaneously, however, its addition increased enormously viscosity of the ink. Ethanol was tried as an alcohol with possibly disinfecting effect and desired decrease of SFT was achieved. Nonetheless, its high volatility resulted into fast nozzle clogging making such solution impracticable. As the last solvent, DMSO was tried because of its capability to modify SFT, serve as a humectant and not increase the viscosity dramatically. The rheological study was performed on both aqueous and solvent based solutions. It was observed, that addition of DMSO into the solvent system influenced SFT of

the solutions in a positive manner while viscosity was increased to acceptable value only. Co-solvent composition water/DMSO (2:1 v/v) was selected as sufficiently performing and having positive implications towards PVA dissolution based on available literature too. Indeed, the mixture showed better solvation effect in comparison with aqueous solutions, which was evaluated according to the Huggins and the Schulz-Blaschke constants obtained by intrinsic viscosity evaluation. The temperature dependence of both viscosity and SFT was also determined because the optimum printing process temperature is not known at the beginning of ink development. Obtained results of analysis of the dependence of viscosity on temperature were in good relation with theoretical behaviour of polymer solutions. The viscosity increased with increasing polymer concentration and the higher temperature, the lower viscosity of solution is observed. Activation energy for viscosity of water based solution was in accordance with literature values, while the values for water/DMSO were obtained for the first time and both the activation energy and interaction parameter were found to be significantly higher which testifies for stronger polymer-solvent as well as for stronger polymer inter- and intramolecular interactions. Within this framework, study of aging and shelf-life of prepared solutions was interpreted. The use of PVA in water/DMSO co-solvent system is limited to three weeks before being deteriorated by microgel formation manifested by turbidity appearance of the ink. If stored longer, the solution may turn to gel – see Figure 3.

Time (days)	1	1.5	2	2.5	3	4
52	-	-	turb	turb	gel	gel
22	-	-	-	-	gel	gel
14	-	-	-	-	turb	turb
8	-	-	-	-	turb	turb
3	-	-	-	-	-	-

Concentration of PVA (wt%)

Figure 3. Turbidity of PVA solutions in water/DMSO obtained by naked eye observation. The "-" sign means no change, "turb" stands for turbidity and "gel" indicates formation of a gel)

The second most important parameter for ink formulation is its surface tension that was characterised for both water and water/DMSO solutions. However, detailed study of SFT temperature dependence in the range from 20 to 40 °C was performed for the latter system only, as it showed be worthy of choice for further ink development. It was found that higher temperature shifts SFT towards optimum. On the other hand, viscosity and vapour partial pressure increases with elevated temperatures. Therefore, the operating temperature 35 °C was chosen as the best condition to study properties of PVA water/DMSO system summarized in Table 1.

Table 1. Experimental values of viscosity (η), SFT (σ) and density (ρ) of PVA in water/DMSO all obtained at 35°C. Density is expressed with 5 valid digits as this precision is given by the specification of the producer (Anton Paar.)

PVA concentration [wt%]	Viscosity [mPa·s]	Surface tension [mN·m^{-1}]	Density [kg·m^{-3}]
1	3.74 ± 0.10	44.0 ± 0.4	1045.4
1.5	4.4 ± 0.3	48.4 ± 0.3	1046.0
2	5.07 ± 0.13	50.10 ± 0.12	1047.3
2.5	5.9 ± 0.2	45.3 ± 0.3	1048.2
3	6.2 ± 0.3	44.1 ± 0.2	1050.0
4	8.97 ± 0.17	43.09 ± 0.16	1053.0

Results obtained by viscometric and rheological studies were analysed within the mainstream framework which approaches the ink as Newtonian fluid (or just having small deviations from Newtonian behaviour). Dimensionless numbers Re, We, Oh, Ca, Z, and Oh^{-2} were used for characterization of the system with the aim to find proper ink concentration to achieve optimum or at least satisfying quality regime of printing. The drops ejection rate was considered as the drop velocity (also drop impact velocity according to [47], in this case 5.4 m·s^{-1}; it was determined by drop-watcher camera integrated in the printer machine. The characteristic length (A) was derived from the nozzle geometry as its equivalent diameter. Used nozzles have the side size around 21.5 µm. The size has been confirmed by electron microscopic analysis (images are not shown, 10 pL cartridges are commercially available by the supplier). The same value is used throughout the literature for this kind of equipment e.g. [45]. Calculated results are shown in Table 2.

Table 2. Calculated dimensionless criteria: the Reynolds number (Re), the Weber number (We), the Ohnesorge number (Oh), the Z-value and the Capillary number (Ca) of prepared solutions of PVA in water/DMSO mixture for 35 °C.

PVA concentration [wt%]	Re [-]	We [-]	Oh [-]	Z [-]	Ca [-]
1	32.4	14.9	0.12	8.4	0.46
1.5	27.5	13.6	0.13	7.5	0.49
2	24.0	13.1	0.15	6.6	0.55
2.5	20.6	14.5	0.19	5.4	0.71
3	19.7	14.9	0.20	5.1	0.76
4	13.6	15.3	0.29	3.5	1.12

Application of dimensionless groupings helps to better understanding of liquid ejection and drop formation which is the key processing step of liquid dispensing

and DOD printing. It can be said, that these approaches are highly developed for Newtonian fluids and have long history. Nevertheless, the main ink printability evaluation schemes (criteria) available from the literature were applied to our dataset and besides finding the best candidate solution concentration for printing also weak sides of these concepts were identified. Definitely, all triad of material-tool-process parameters must be taken into account and the use of material-property only developed approaches is limited, as they do not take fluid velocity into account. The most advanced recent approach of Kim&Baek's *Ca* vs. *We* plot mapping of DOD printability regimes [34] was adopted together with their definition of good printability when "a single drop is formed either directly without second pinch-off or the satellite drop merges with the main drop within its travel distance less than 20 times characteristic length forming thus a single drop". However, extension of their original graph in Figure 4 was found to be needed by extrapolation towards higher *We* values to cover both investigated solutions and processing window advised by the printer producer.
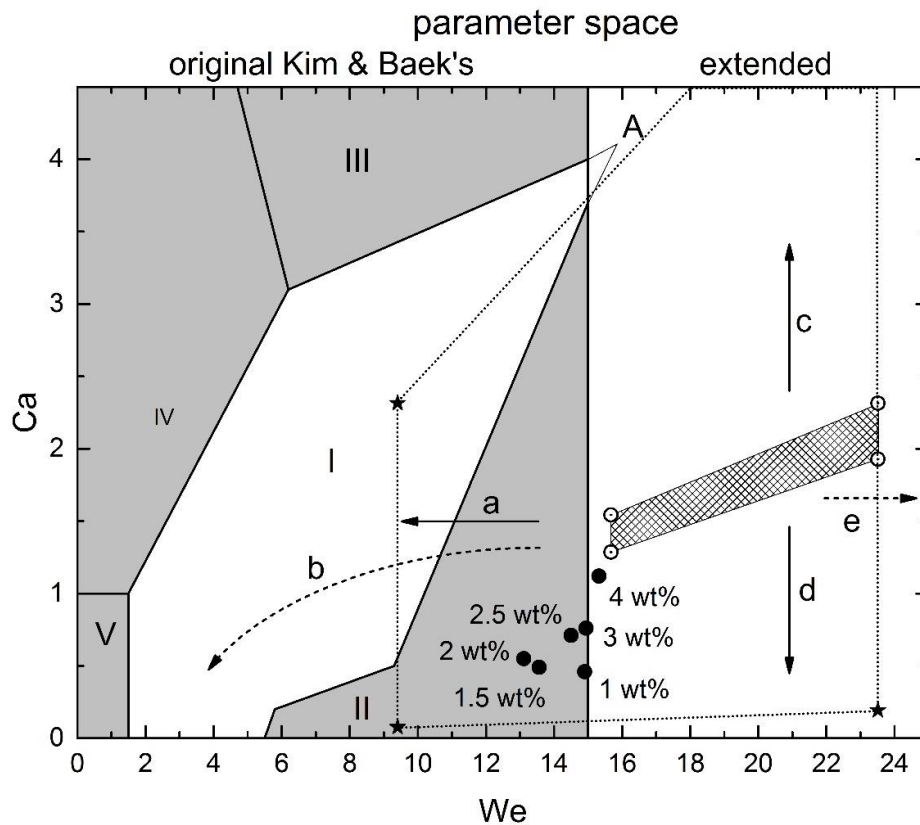

Figure 4. Capillary-Weber diagram showing the position of prepared PVA solution in water/DMSO.

The processing window of ink material properties and jetting velocity suggested by the printer producer outlies significantly the optimum printing area similarly as experimentally obtained positions for solutions prepared in this study. Nevertheless, good printing was achieved. To understand, why it is possible, main trends and pathways in dependence on variations of prepared inks (viscosity, SFT,

density) and change of processing (jetting velocity) parameters were described, while little (but still some) attention was paid to the tool parameter, as the nozzle size is fixed in studied case. It was found that the printing regime map can be replotted in other coordinates with advantage. *Re* vs. *Ca* graph covers the Kim&Baek's map [34] but also all criteria derived by their predecessors can be easily plotted into this space and printing regime evaluation systems can be easily compared. Using this plot shown in Figure 5, it may create feeling that velocity is somewhat cancelled from consideration, however, a series of *We* isolines and iso-Oh^{-2} straight lines conceptualize all necessary pathways in this graph.
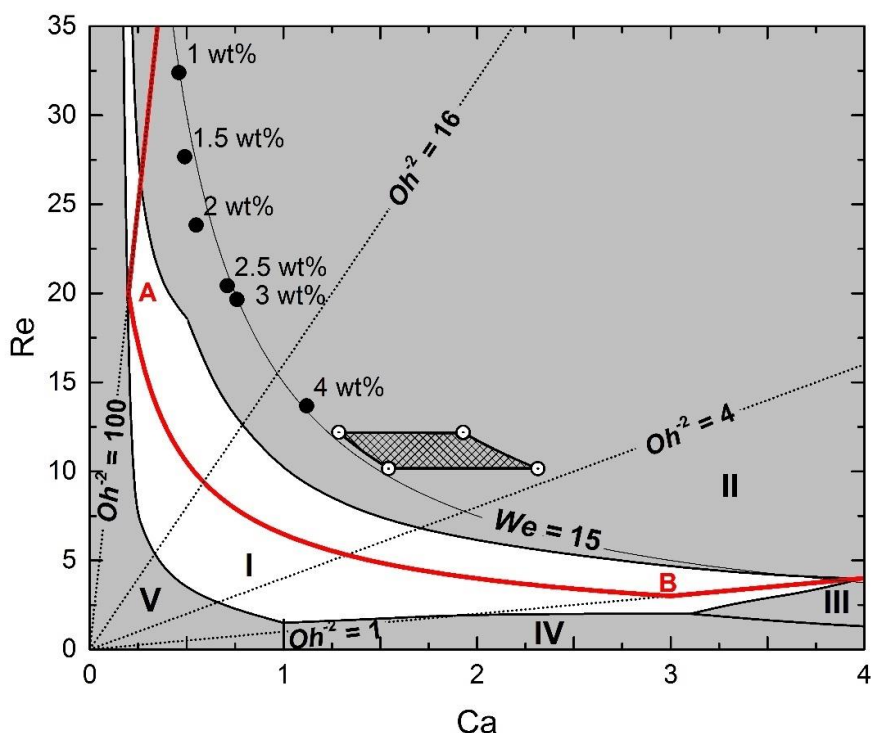

Figure 5. Reynolds-Capillary number diagram

Reinspection of this newly created graph revealed that the borderlines of optimum printing regime have more or less hyperbolic shape and that they may be roughly approximated by a pair of *We* number values, i.e. by two *We* isolines. To remind, the Weber number assesses the relative importance of the inertia of the fluid compared to its surface tension. This notice brought attention to the fact, that viscosity could be not necessarily the main parameter governing the ink behaviour from the point of printability but that it is SFT (surface energy) and relaxation time related to surface perturbation which governs the process. Indeed, the Rayleigh timescale does not depend on viscosity of the fluid. It was also observed, that good printability was achieved even fairly beyond the border predicted for viscous liquids in the sense of higher jetting velocities than should work properly. As one may expect, that the polymer solution of composition near to first critical concentration is not purely Newtonian fluid due to hydrodynamic screening and polymer interchain interactions, it was hypothesized that there is possibly another source of relaxation and the only plausible is the elastic energy.
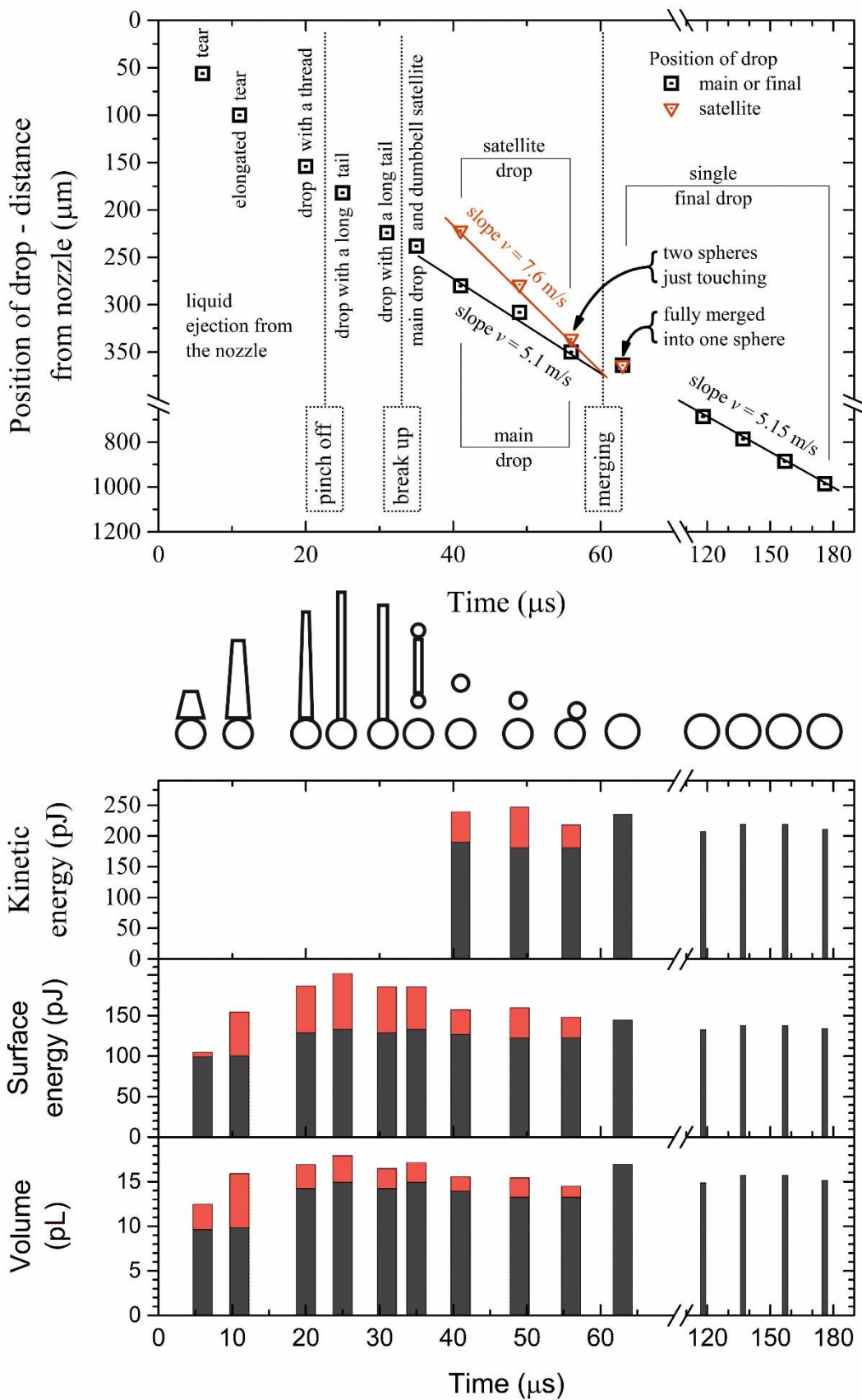
Figure 6. Analysis of drop ejection and formation based on captured images. Upper graph shows the position of the center of the main or final drop (open square with central dot) and satellite drop (open triangle with central dot) once formed. The middle gallery shows schematics of simplified geometric shapes used for image analysis. Lower

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graph: stacked bars show the volume and surface energy for the main drop (evaluated as a sphere, represented by grey bar) and its tail, thread, dumbbell or satellite (represented by red bar). The final drop property is than represented by the grey bar only after merging (from 63 μs). The kinetic energy is shown for main (grey bar) and satellite drop (from 41 μs, i.e. after its formation), the energy of the final drop is represented by the gray bar only after 63 μs. The time x-axis is common for both graphs.

Based on above described consideration of intermediate results, the drop watch camera integrated in the printer was used not only to empirical optimization of pulse driving voltage waveform to generate ink drop but a series of chronophotographic images was taken in order to analyse the process in more depth with the full awareness of the relatively low quality of that optical device. Therefore, the information extracted from the images was used to analysis of the process' dynamics in terms of energy balance and developing a basic scheme of acting forces. All steps of drop formation typical for weakly viscoelastic liquid were captured by the camera. Volume, surface and related surface energy and kinetic energy was obtained from image analysis using replacement of the liquid shapes by simple geometric shapes for dimension quantifications. Obtained results are presented in Figure 6. Velocity of the main drop and the satellite (once formed a sphere) was analysed from the time dependence of position from the nozzle. The kinetic energy of both the main drop and the satellite was calculated and their changes compared with the changes of surface energy. It was concluded that there is a significant yet not prevailing contribution of elastic energy to the recombination of the satellite with the main drop, which is the key of successful printing in the regime when Rayleigh break up occurs. The estimation of the elastic energy contribution has a relatively large error present already in the measurement but increased by its propagation during subtraction, therefore the result is of rather qualitative or semi-quantitative than quantitative character.

The clear evidence for presence of two driving mechanism of the satellite recombination with the main drop was given. Surface tension is the force causing relaxation of perturbed surface (related with the capillary time scale) working against the action of viscosity and the elastic force causes relaxation of tension present in liquids under stress due to interactions of polymer chains at the molecular level (related to the polymer relaxation time). This led to refinement of the dimensionless number evaluation; however, the state of the art of this analytical framework for printing of viscoelastic fluids is much less developed in contemporary literature. First, it must be noted, that adopted approaches using polymer relaxation time calculated according the Zimm theory failed and it must be so, because the Zimm theory was developed for evaluation of the longest relaxation time in infinite diluted polymer solutions only. (In other words, this approach can be useful for printing of trace amounts of polymer.) Instead, it was shown that relaxation time scale calculation based on the Kuhn segment length gives comparable values to those obtained for surface (interface) relaxation. Calculated Numbers are listed in Table 3.

Table 3. Calculated viscoelastic criteria: the Rayleigh time (t_c), the viscous time (t_v), the Relaxation time according to Kuhn segment (λ_K), the Deborah number (De), the Ohnesorge number (Oh), the Elasticity number (El), and the Elasto-Capillary number (Ec) of prepared solutions of PVA in water/DMSO mixture for 35 °C.

PVA concentration [wt%]	t_c [µs]	t_v [µs]	λ_K [µs]	De [-]	Oh [-]	El [-]	Ec [-]
1	15.4	5.5	5.2	0.336	0.12	0.040	2.82
1.5	14.7	5.9	6.1	0.415	0.13	0.056	3.10
2	14.4	6.5	7.0	0.485	0.15	0.073	3.21
2.5	15.2	8.4	8.2	0.538	0.19	0.100	2.91
3	15.4	9.0	8.5	0.553	0.20	0.108	2.82
4	15.6	13.4	12.4	0.793	0.29	0.228	2.76

Indeed, the value of *Wi* indicated the regime when stretched molecules rather than random coils are present in the liquid under stress which again point towards importance of molecular models based on polymer chain raptation. Also the value of *El* indicated moderate but still not prevailing contribution of elasticity. The relative importance of elastic component of viscoelastic liquid against capillary relaxation may be assessed with the help of plotting *De* vs. *Oh* which was conceptualised by McKinley [48]. However, the former approach does not include process dynamics and uses material-property based criteria only and cancels the Rayleigh timescale from consideration. The graph was improved by inclusion of *El* and *Ec* isolines although both are material-property groups also (See Figure 7).
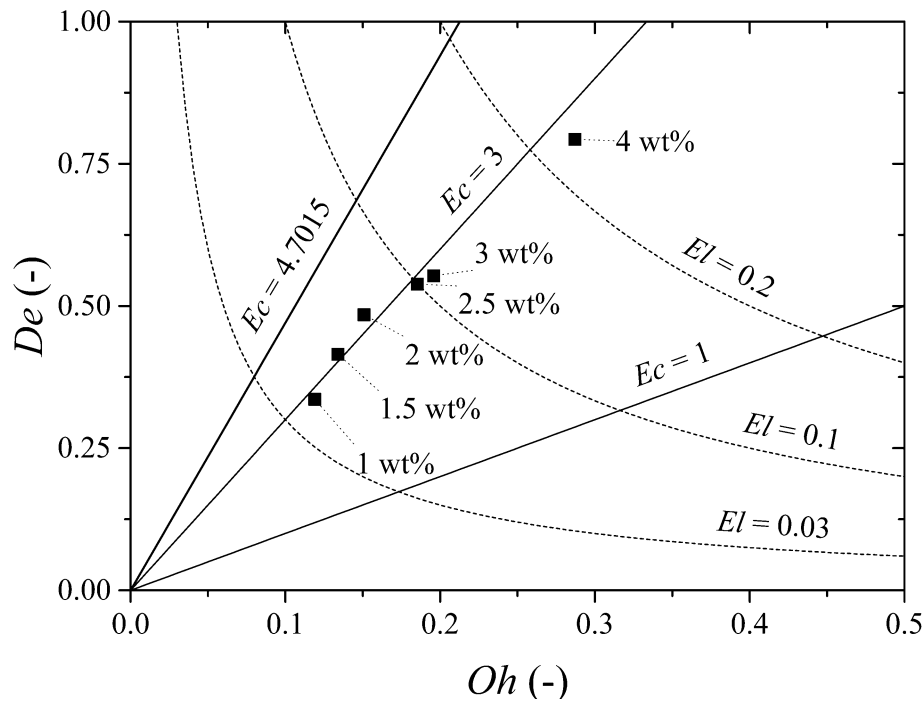

Figure 7. Replotted diagram of De number against Oh number showing the position of prepared solutions of PVA in water/DMSO.

Ec number shows the relative importance of elastic and capillary effects with respect to viscous stresses and *El* number compares the importance of elastic to inertial effects. In terms of physical quantities, it means, that for given solution, the nozzle dimension can only be varied as *El* and *Ec* numbers are quite tightly bound together through three shared parameters. However, sliding along the *Ec* isoline can be viewed as variation of the Rayleigh timescale as well if the polymer and capillary timescale are kept constant. Indeed, there is less freedom in moves along isolines in the graph than in the similarly appearing one (*Re* vs. *Ca* with *We* and Oh^{-2} isolines) developed for Newtonian fluids in this Thesis. The original McKinley's approach was further developed by Clasen *et al.* [49] who logically added a dynamic (velocity including) number because any dispensing operation can be fully described by any set of two material-property based and one dynamic non-dimensional groups while the remaining groups can be calculated (for example for known *Oh*, *De*, and *We* one obtains $Ca = Oh \cdot We^{1/2}$, $Wi = De \cdot We^{1/2}$, and $Ec = De/Oh$). The investigation was performed over a large range of involved parameters. The price for it is that they created a three dimensional space and their predictions estimate only the transition between dripping and jetting and are too coarse to catch and distinguish various printing modes. Construction of a plot of *Oh* vs. *We* or *Re* vs. *Ca* with *De* as a parameter for borderlines between printing regime areas would be therefore highly desirable but is beyond the scope of this Thesis.

In the last step of the work, testing patterns were printed to demonstrate the suitability of prepared ink for printing. A suitable general waveform was proposed for ejection of drops from nozzles of the printing head. However, the voltage at each nozzle was finely modified (tailored) to achieve uniform drop velocity. Other parameters involved the cartridge and substrate temperature, printing height (stand-off), the choice of substrate and its surface energy, and the angle of print-head that is attributed to certain resolution of printed patterns. The patterns were prepared in various shapes from basic elemental patterns (dots, dots array) up to rectangle or grid-shape patterns. The surface morphologies were studied by optical microscopy, AFM and profilometry. An example of AFM analysis is depicted in Figure 8.
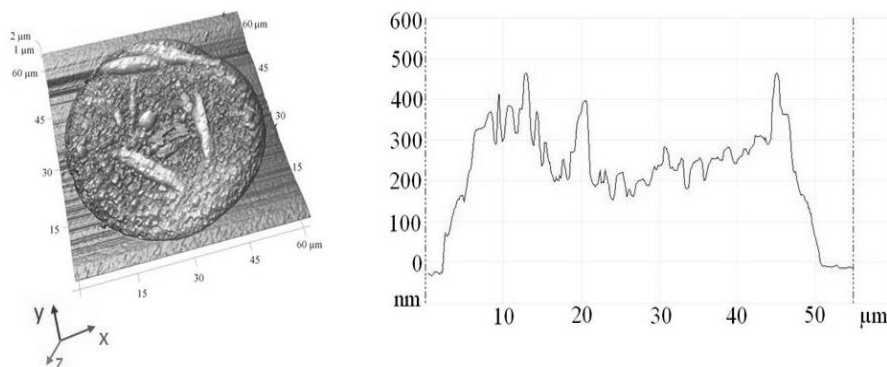

Figure 8. AFM topographic images of single drop of PVA printed on polymer substrate (left) with the cross-sectional profile (right) at 45 μm position in y axis.

8. CLOSING REMARKS

8.1   Contribution to Science and Practice

This study performed on exemplary water soluble polymer Poly(vinyl alcohol) contributed to science and practice mainly in following areas:

Properties of PVA solutions in the water/DMSO co-solvent system and its aging were studied and interpreted with respect to the solvent-solvent, solvent-polymer and polymer-polymer interactions on molecular level. The interpretational framework of ink formulation's impact on its printability was enriched in the field of both Newtonian and non-Newtonian fluid analytical approaches although there still remains a wide gap between them. Analysis of causes of recombination of a satellite with the main drop during printing which is one of the conditions for good printability demonstrated the importance of surface relaxation as well as elastic relaxation in the overall assessment, evaluation and development of polymer solution based ink and in engineering and control of printing process. Concepts using the Zimm relaxation time were dismissed in favour of real chain and raptation based models that hold best for parameter ranges applying in DOD printing. As the only future viable approach was identified joining of material-property and characteristic length based criteria including all relevant timescales with a dynamic criterion which includes (jetting) velocity of the fluid as the main parameter describing the printing process.

Other contribution includes the acquirement of useful skills in inkjet technology application, as printing can be considered perspective deposition technique that has already been implemented into various sector of industry. In many cases, the dispersions containing different nano-particles are investigated but there is relatively little number of published papers focused on preparation and characterization of polymer-based patterns and devices, especially based on water-soluble polymer. Therefore, this work described comprehensively the selection, preparation, characterization and deposition of chosen polymer (exemplified on PVA) for their processing by DOD inkjet technology.

Moreover, the work gives practical information and guideline for preparation of polymer solution based inkjet inks. The application potential of prepared inks includes patterning of flexible as well as rigid substrates and controlled modification of their surfaces.

Finally, obtained results of this work were presented in the international scientific journals and conferences and a manuscript covering yet unpublished work is in preparation too.

8.2   Ongoing Research and Future Prospective

In the field of theory

Definition and development of a practical map of printing regimes suitable for (weakly) viscoelastic liquids (namely polymer solutions) will be the paramount of ongoing activity, since the ideal goal has been already defined and prerequisite step stones have been laid. However, there is still a lot to be done to obtain a general evaluation framework applicable for viscoelastic fluids with Newtonian printability map as the limit case. Serious effort has to be spent both in the development of experimental techniques and theoretical work on interpretational framework of dimensionless groupings. A good sign is that all relaxation times playing role in expectable range of liquids for digital DOD printing are of similar magnitude and no extremes will need to be covered.

In the field of applied research

As was demonstrated, the patterns based on PVA were prepared. It is expected the proposed waveform could be used also for other water-soluble polymer-based inkjet inks. Thus, the printability of polyvinypyrrolidone (PVP) will be investigated in the next step. Moreover, the hitherto gathered knowledge can be utilised effectively to obtain the PVP ink faster as it was in the case of PVA. The PVP can be used as a dielectric layer during preparation of TFT(s) or capacitors. Moreover, it can be cross-linked in more controllable and simpler manner than PVA which represents an important feature for preparation permanent patterns.

Other potential research includes: preparation of permanent patterns from poly(vinyl alcohol) and their resistance tests (resistance to water, adhesion and abrasive tests and other); continuation in preparation and characterization of water-soluble polymer ink for DOD material printing; and preparation, characterization and testing of a new inks depending on the current needs of the research at the Centre of Polymer Materials of the Tomas Bata University in Zlín.

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LIST OF ABBREVIATIONS, SYMBOLS, DIMENSIONLESS NUMBERS AND UNITS

Alphabetically ordered abbreviations.

3D	Three-dimensional
AFM	Atomic force microscopy
CIJ	Continuous inkjet
DH	Degree of hydrolysis
DP	Polymerization degree
DMSO	Dimethyl sulfoxide
DOD	Drop-on-Demand
DPI	Dots per inch
IJP	Inkjet printing
OLED	Organic light-emitting diode
PET	Poly(ethylene terephthalate)
PIJ	Piezoelectric inkjet
PLED	Polymer light-emitting diode
PVA	Poly(vinyl alcohol)
PVP	Polyvinylpyrrolidone
PZT	Lead zirconium titanate
SEE System	Surface energy evaluation system
SFT	Surface tension

Alphabetically ordered symbols.

A	Characteristic length
c	Mass concentration
$c*$	Critical concentration
K_H	Huggins constant
K_{SB}	Schulz-Blaschke constant
M_v	Viscosity-average molecular weight
M_W	Weight-average molecular weight
T	Temperature
v	Velocity
v/v	Volume/volume ratio
w	Mass fraction
w/v %	Weight/volume percentage
wt%	Percentage by mass
$\dot{\gamma}$	Shear rate
δ	Solubility parameter
η	Shear viscosity
η_{sp}	Specific viscosity

$\eta_{sp}/c,\ \eta_r$	Reduced viscosity
$[\eta]$	Intrinsic viscosity
λ	Relaxation time
λ_E	Extensional relaxation time
λ_K	Kuhn relaxation time
λ_Z	Zimm relaxation time
ρ	Density
σ	Surface tension

Alphabetically ordered dimensionless numbers.

Ca	Capillary number
De	Deborah number
Ec	Elasto-capillary number
El	Elasticity number
Oh	Ohnesorge number
Re	Reynolds number
We	Weber number
Wi	Weissenberg number
Z	Z number, Reciprocal Ohnesorge number

Alphabetically ordered units.

°C	degree celsius
μm	micrometre
g	gravitational acceleration
g/cm^3	gram per cubic centimetre
kDa	kilo-Dalton•
kg/cm^3	kilogram per cubic centimetre
m/s	metre per second
mm	millimetre
mN/m	milliNewtons per meter
mol %	molar percentage
mPa·s	milliPascal second
nm	nanometre
s	second
s^{-1}	reciprocal second

• Although Dalton is a non-SI unit, it is widely accepted for use with the SI among units with experimentally determined values, better known as unified atomic mass unit (with the symbol u).

LIST OF PUBLICATIONS

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3.   PLACHY T., M. MRLIK, Z. KOZAKOVA, P. SULY, M. SEDLACIK, V. PAVLINEK, and I. KURITKA, The Electrorheological Behavior of Suspensions Based on Molten-Salt Synthesized Lithium Titanate Nanoparticles and Their Core–Shell Titanate/Urea Analogues. *ACS Appl. Mater. Interfaces*. 2015, vol. 7, no. 6, pp. 3725–3731, DOI: 10.1021/am508471f

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Conference contributions

1.   Jakub Ševčík, Pavel Urbánek, Pavol Šuly, Michal Urbánek, Jan Mašlík, Jan Antoš, Ivo Kuřitka, Preparation and characterization of nanostructured thin films applicable in polymer light emitting devices; 8th International Conference on Nanomaterials - Research and Application, NANOCON 2016, 2016, ISBN 978-808729471-0

2.   Pavol Šuly, Petr Krčmář, Jan Mašlík, Pavel Urbánek and Ivo Kuřitka; Poly(vinyl alcohol): Formulation of a Polymer Ink for the Patterning of Substrates with a Drop-On-Demand Inkjet Printer; 23rd International Conference on Materials and Technology, 2015, ISBN 978-961-92518-8-1.

3.   Petr Krčmář, Pavel Urbánek, Ivo Kuřitka, Jan Mašlík and Pavol Šuly; The preparation and characterization of CuO inkjet inks for gas sensors; Lopec 2014 7th International Exhibition and Conference for the Printed Electronics Industry

4.   Jan Mašlík, Pavel Urbánek, Ivo Kuřitka, Petr Krčmář, Pavol Šuly and Michal Machovský; The preparation and characterization of ITO ink for gas sensing; Lopec 2014 7th International Exhibition and Conference for the Printed Electronics Industry

5.   Pavel Urbánek, Jakub Ševčík, Jan Mašlík, Petr Krčmář, Ivo Kuřitka, Pavol Šuly, Barbora Hanulíková; The influence of ZnO nanoparticles content on the luminescence of the MEH-PPV in OLED devices; International Conference Plastko 2014, ISBN-978-80-7454-335-7.

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2.   Inorganic ink for material printing applications, comprises copper oxide nanoparticles, polymeric dispersant and rest of water. Krčmář, P, Kuřitka, I, Mašlík J, Šuly P, Urbánek P. Patent application: CZ201301022-A3

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CZ.1.05/2.1.00/03.0111 – Centre of Polymer Systems (2011-2015) - member of the research team

LO 1504 – Centre of Polymer Systems Plus (2015-2020) - member of the research team

IGA/CPS/2016/007 – "Preparation and characterization of functional polymer materials for thin films applicable in printed electronics and sensor technology" - member of the research team

IGA/CPS/2015/006 – "Preparation of functional inks for material inkjet printing and their applications in printed electronics and sensors"- member of the research team

IGA/FT/2014/006 – "The modification of polymer substrates and new materials for inkjet printing of sensors" - member of the research team

IGA/FT/2013/025 – "The material printing of polymeric and inorganic inks for advance applications" - member of the research team

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Study of poly(vinyl alcohol) solution for inkjet printing

Studium roztoku polyvinylalkoholu pro inkoustový tisk

Doctoral Thesis Summary