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Influences on spreading of Inkjet inks on coated cardboards

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Abstract

Well-known models to explain the interaction between liquids and surfaces include parameters as fluid viscosity, surface tension and density. Regarding the surface, the properties as porosity and roughness, and surface energy are relevant. In Inkjet printing this interaction can be influenced also by ink injection parameters. Several studies were published in the last years using these models to analyze different substrates for Inkjet as plain and Inkjet papers. The experiments here focus on this interaction but between Inkjet inks and coated cardboards. The main findings are related to an opposite ink spreading speed of pigment and dye inks with increasing of ink surface tension and viscosity. It is also demonstrated a high correlation between spreading speed and total surface energy of the cardboards.

Background

In Inkjet printing, when an ink droplet hits an absorbent surface several interactions can occur. Regarding the ink drop, there is a change in its shape as a function to the speed, ink viscosity, density, surface tension and the distance between print head and substrate. The Weber-, Reynolds- and Onhesorge-Numbers describe, based on these quantities, the conditions for ink injection and its behavior during flight. Also important, in the case of Inkjet inks, are the flow differences between both solutions and dispersions, respectively, dye-based and pigment-based inks.

When the drop hits the surface, its kinetic energy and inertia affect its initial shape and also the interaction with the surface. In addition to these influences, related to the deceleration of the drop movement, the drop spreading will be affected by ink physical quantities mentioned above. The characteristics of the substrate such as porosity (size, shape, accessibility, connectivity and pore distribution), humidity, polarity, roughness and the surface energy given by the chemical composition of the substrate are factors of high relevance in the interaction with the ink.

The quality of wetting, given by the contact angle between ink and substrate, affects the spreading speed of the ink. The physicochemical interactions between the ink and the substrate can change the structure of the substrate causing pore clogging, saturation and also increasing or decreasing wetting, absorption, diffusion and ink drying.

To describe the ink movement, also its spreading speed, on and inside a paper sheet there are several models developed experimentally and frequently modified, depending on the ink and substrate types. Bosanquet, Darcy, Fick, and mainly Lucas and Washburn and its several variations are some of the used models.

Motivation and problem

Based on these models several studies have been published in order to explain the interaction of Inkjet inks on and within porous surfaces.

Gane et al. used blocks of calcium carbonate mixed with latex or silica as substrate [1]. Gigac et al. used coated and uncoated Inkjet papers [2] as well as Oko et al. [3]. Clarke et al. studied this interaction by means of molecular kinetic theory using Millipore filters [4]. Desie and Van Roost use microporous Inkjet papers [5] and Daniel and Berg performed tests on photo Inkjet papers [6]. Rioux tested Inkjet inks with uncoated papers and coated papers [7]. Finally, Lamminmäki et al. used plan papers with modeled coatings from PVOH and SA-Latex [8] [9].

Industrially manufactured papers have an anisotropic character and highly random structure. The porosity distribution curve of a plain paper has pores with diameters that vary between nanometer and micrometer. Therefore, modeled surfaces are important to isolate poorly controllable variables such as porosity.

However, the surface of coated cardboards is less random and structurally different than plan papers. Figure. 1 presents an x-ray of the bulk and the coating of a cardboard. It is possible to observe and even measure the bulk cavities, but the coated surface is a continuous compact block in this resolution.

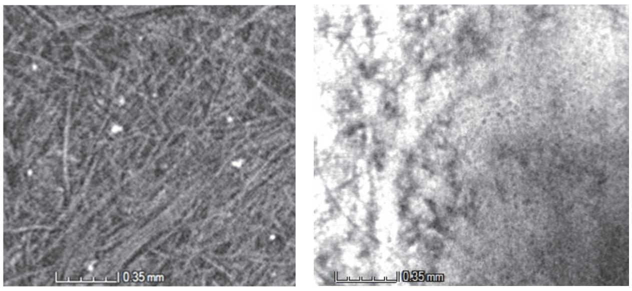

Figure 1. *Bulk (left), coated surface (right) of a coated cardboard (Image size about 1.75 x 1.75 cm)*

Images of a coated cardboard surface obtained with a SEM show that there is a surface structure at coated cardboards. But except for few points that can be understood as voids or pores, spaces, for ink flow cannot be observed, also between the visible particles – as minerals present in the coating (Figure 2). There is still the porosity on the coating minerals, but it is not visible by the SEM.

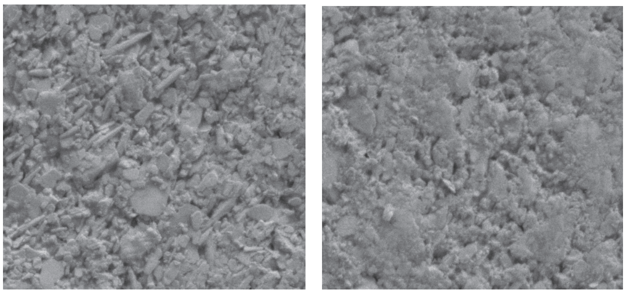

Figure 2*. SEM of coated cardboards surfaces (Image size about 9 x 9 µm)*

It is possible to affirm, that the structure of plain papers or Inkjet papers are not comparable with a coated cardboard and to best of our knowledge there is any study about the interaction of Inkjet inks using coated cardboards as substrate.

Therefore, the motivation for this study is to understand some points about this interaction i.e. the spreading of Inkjet inks on the surface of coated cardboards. For this, two essential parameters, present in several models mentioned above, were selected to be analyze: viscosity and surface tension of the liquid phase and surface energy of the solid phase.

The spreading speed of the Inkjet inks and water with different viscosities and surface tensions on cardboards with different surface energies are used to analyse this interaction.

Method, materials and experiment parameters

Materials and methods

For the experiments, two model Inkjet inks – one dye-based and one pigment-based – and water are mixed with polyethylene glycol (Table 1) in 3 different percentages by weight (Table 2) to increase the viscosity of inks and water. The surface tension of both inks is around 33 mN/m (without PEG). Water is used as a counterpoint for comparisons with the inks due to its high surface tension. Density, viscosity and surface tension of all 12, here called generically fluids, are measured, as also the surface energy (total, disperse and polar parts) of 7 coated cardboards (Table 1). Further informations about the measurement equipment are in the Table 3.

Materials	Data	
Coated cardboards	Seven commercial FBB and SBB 300 ±5 g/m2, identified as B01 to B07	
Polyethylene glycol	Average mol wt. 8000	
Water	High performance liquid chromatography water	
Dye ink	Major volatile components	[wt%]:
	Demineralized Water	72
	2-Methyl-1,3-Propandiol	22
Pigment ink	Major volatile components	[wt%]:
	Demineralized Water	76
	2-Methyl-1,3-Propandiol	18

***Table 1**. Materials data*

Fluid identification	Dye ink, pigment ink or water [wt%]	PEG [wt%]
0%	100	0
5%	95	5
10%	90	10
15%	85	15

***Table 2**. Fluids data*

Equipment	Measurement data
Tensiometer SITA Pro Line 115	Measurement: surface tension – fluids Bubble life: 200 ms Interval: 2s Result: average of 10 measurements per fluid
Pipette Roth and precision scale Mettler Toledo	Measurement: density – fluids Range volume pipette: 0.2 – 2 ml Volume used: 1 ml Weight measurement: precision scale Result: Average of 10 measurements per fluid
Rheometer MCR 101 Anton Paar	Measurement: viscosity – fluids Method: cone-plate Cone geometry: 50 mm (diameter), 1° (angle) Shear rate: 1 – 100 1/s Temperature: 21°C
OCA 30 Dataphysics	Measurement: Total, polar and disperse surface energy – cardboards Liquids: Water, Diiodomethane and Ethylene Glycol (3 measurements each liquid), Calculations method: OWKR Result: average of 3 measurements per cardboard Measurement: Contact angle over time – fluids and cardboards Video frame rate: 1000 fps Video length: 4 s Drop volume: 3 µl ± 0.5 Result: average of 3 measurements per cardboard

***Table 3** Equipments used in the measurements*

Drop volume definition and drop placement method

To visualize the fluid spreading on the surface of seven coated cardboard a high resolution camera (1000 fps) is used. An injection system (needles) dispenses a fluid drop with a predetermined volume. The drops are neither injected nor allowed to free fall, but caught from the injection needle. This method reduces the effect of kinetic energy on the droplet spread as also the influence of drop weight (about 3 µl) in free fall. This volume, when compared to the volume of drops in Inkjet printing, in the order of picoliters, is high, but necessary due to the experimental environment. Water, in particular, demands a high drop volume in this test. Due to the high surface tension of water, the droplets adhere strongly to the injection needle and remain an almost perfect sphere by low volumes. If caught, even with low volumes, the experiment would be invalidated. The force to break the strong adhesion between water droplet and needle surface increases the kinetic energy in the drop modifying the spreading. About 3 µl the drop forms a neck between the needle and the main drop volume and can be picked up (Figure 3).

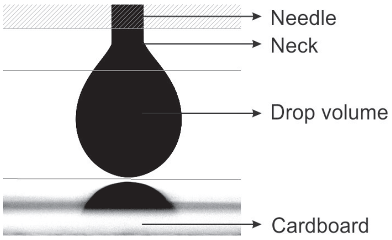

***Figure 3**. Water droplet shape before being caught*

Used parameters and time definition

Using videos it is possible to measure the contact angle, the drop height, drop base diameter and volume in each frame (Figure 4). Few seconds after the drop placement, the cardboard surface, due to the interaction with the fluid, tends to swell. The surface changes can invalided the test, for example, when the contact angle becomes higher over time. After some experiments the time interval was set to 3 seconds, an interval without significant swell. To analyze the drop behavior the first 30 (t0) as well the last 30 contact angles (t3) are used for the calculations as showed in the Equation 1 (where ms = millisecond).

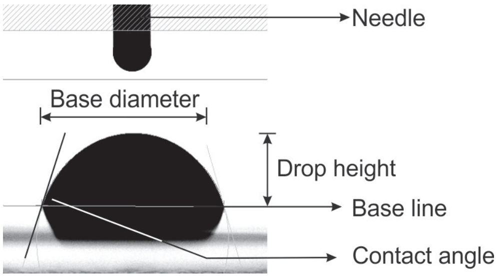

***Figure 4**. Measured parameters of a placed drop on the cardboard*

It was determined to use the contact angle to analyze the drop behavior due to the high delta (ΔCA) in the defined time interval (3 s) and also due to a little standard deviation in the results. Drop base diameter could also be used. The delta from drop height was too low, due to low drop volume.

$$\Delta \mathrm{CA} = \frac{\overline{X_{ms1:ms30}} - \overline{X_{ms2971:ms3000}}}{\overline{X_{ms1:ms30}}} =$$ Equation 1

$$= \frac{52.01-26.51}{52.01} = 0.49$$

Equation 1 also give a reference of the spreading speed. The contact angle average of the first 30 frames (30 ms) 52.01 degrees is subtracted from the average contact angles of the last 30 frames 26.51 and the result is divided by the first value to calculate the delta as a percentage.

The definition of the first frame to be used in the Equation 1 is done base in the drop shape. In the video sequence (Figure 5) the first 9 frames of a drop placement are shown. In the second frame the drop is still partially attached to the needle. In the third frame the shape of the drop, flattened at the top, indicates that it is under the effect of the detachment from the needle. The fourth frame could be considered the frame 1, however in relation to the later frames, there is still in frame 4 a strong vertical drop accommodation that is not seen in the following frames. The frame 5 is then considered the frame 1 and the measurement starts in this point. This evaluation process was proceeded for all sequences, in a total of 252 videos.

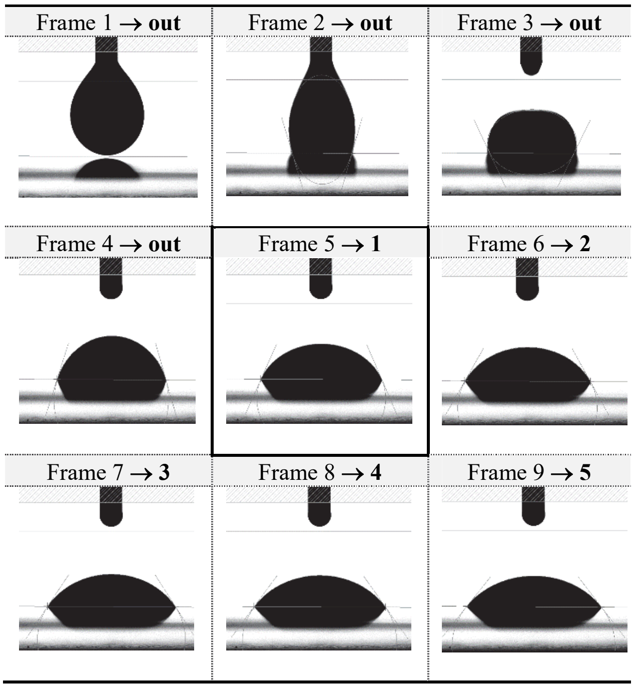

***Figure 5**. Video sequence of a drop placement, first 9 frames*

To calculate the correlation for selected results the well-known Pearson-Bravais correlation method has been applied. (Equation 2). The evaluation follow the scales and ranges presented in the Table 4.

$$r_{xy} = \frac{\sum_{i=1}^{n}(x_i y_i - n\overline{xy})}{\sqrt{\sum_{i=1}^{n} x_i^2 - nx^2}\ \sqrt{\sum_{i=1}^{n} y_i^2 - ny^2}} = \frac{cov(x,y)}{\sqrt{var(x)\ var(y)}}$$ Equation 2 [10, p. 76]

Values	Correlation´s strength
$0.0 \leq \lvert r_{x,y} \rvert \leq 0.2$	any to very weak
$0.2 < \lvert r_{x,y} \rvert \leq 0.5$	weak
$0.5 < \lvert r_{x,y} \rvert \leq 0.8$	medium strong / moderate
$0.8 < \lvert r_{x,y} \rvert \leq 1.0$	strong to perfect

***Table 4.** Values and correlation´s strength*

Results

The first analyze is about fluid spreading, viscosity and surface tension of the fluids. Here, fluid spreading is defined in terms of "spreading speed" or how fast the contact angle decrease in over time. As explained before, the difference between the contact angle in the drop placement moment and after 3 seconds is calculated and expressed in percent. Higher percent results corresponds fast fluid spreading, due to a high difference between contact angles as expressed in the Equation 1.

Figure 4 shows the interaction between fluids and cardboards. All fluids present the same trend independently of a particular cardboard. Water spreads much more slowly than the inks. Viscosity increase has a marginal effect in its spreading speed.

Water´s high polar surface energy slows the drop spreading. However, three seconds seems to be a too short interval of time to observe a relevant change in the behavior of different fluid viscosities.

The PEG-Water solutions show less surface tension than pure water. Nevertheless surface tension of the solutions (5%, 10%, 15% PEG is higher than 60 mN/m. Thus, the results remain almost the same for all cardboards and only by B01 the spreading speed can be notice as higher than for other cardboards. Dye inks spread faster than pigment inks. The higher the viscosity, the lower the spreading speed and this shows more intense at concentrations of 10 and 15% PEG by dye ink. Pigment inks show an opposite behavior. The higher the viscosity, the faster the spreading speed. By dye and pigment inks, the PEG increases the viscosity and also increases the surface tension. These physical ink proprieties change, due to increase from PEG, although similar, are differently evidenced in the spreading speed. At least, B04, a cast coated cardboard, is a well-known deviation in all experiments due to its low surface energy.

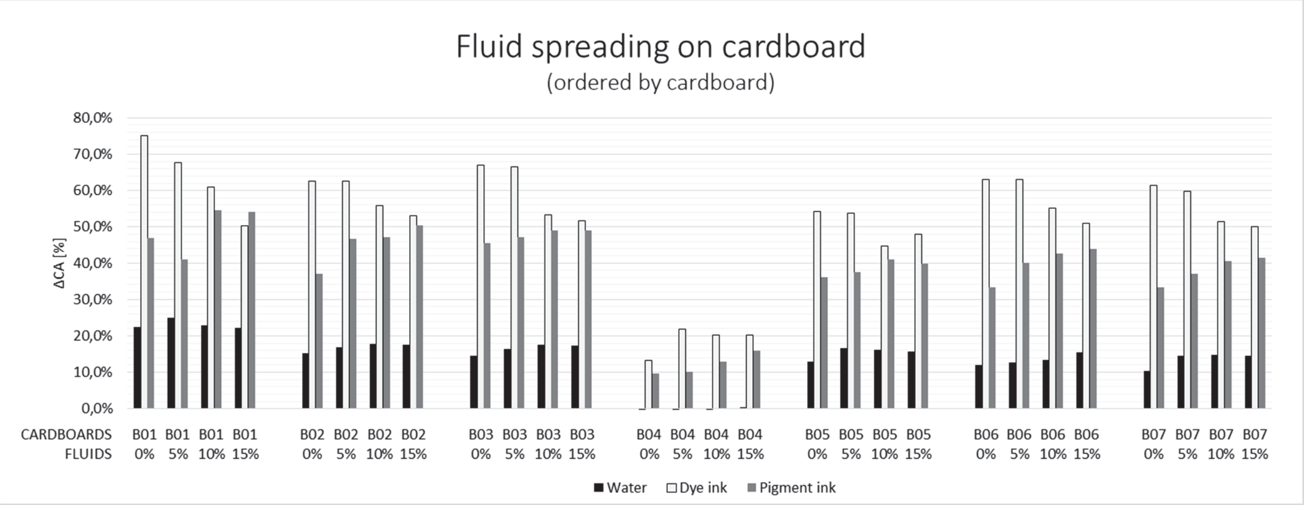

***Figure 4**. Fluid spreading by cardboard*

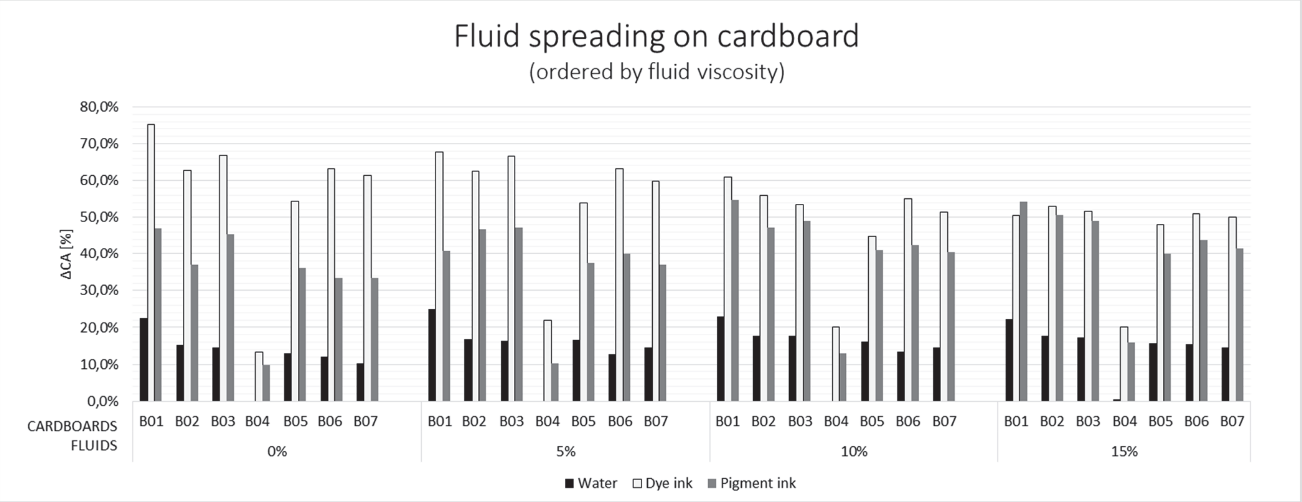

***Figure 5**. Fluid spreading by fluid viscosity*

To point out the differences between pigment and dye-based inks, the Figure 5 shows the same data set as of Figure 1, but order by viscosity and not by cardboard. It can be seen observe that for 10 and 15% PEG the delta from dye and pigment inks are almost the same, because the spreading speed of dye with PEG increase becomes lower and from pigment becomes higher.

Correlating the surface tension values of the fluids (all 4 variations) with the spreading speed these fluids over the 7 cardboards, the results are very similar and show the same trend per fluid (Figure 6). Both water and dye ink show a negative moderate to strong correlation. Decrease of surface tension corresponds with increasing of spreading speed. However, pigment-based ink show a moderate to strong positive correlation. Here, al all cardboards, spreading speed increases when surface tension increases.

As one example for cardboard B02 raw data of spreading speed and surface tension measurements are shown in Tables 5 and 6.

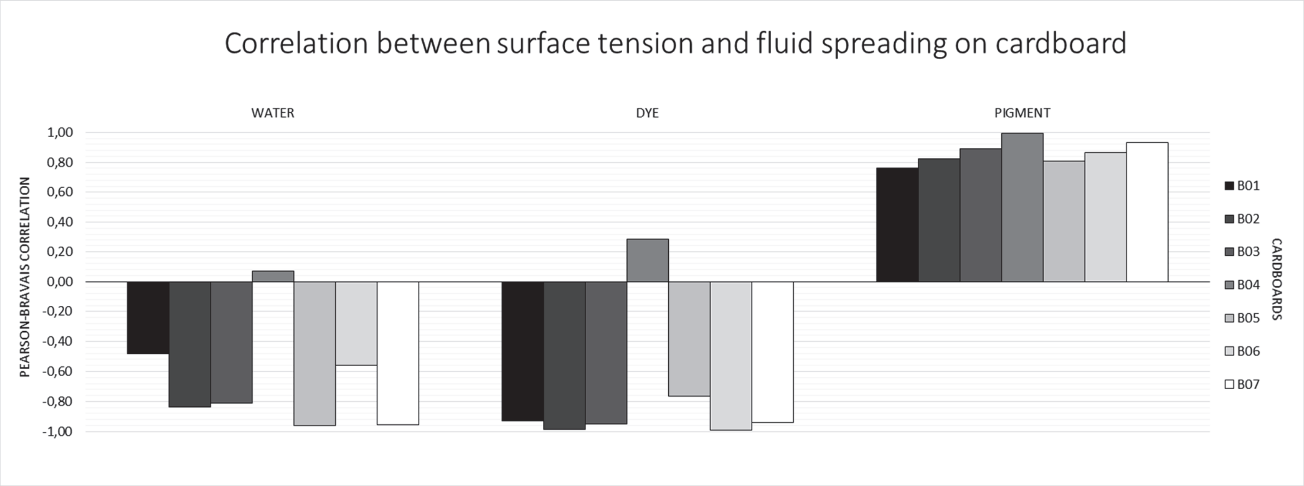

***Figure 6.** Correlation surface tension and fluid spreading*

	Water Δ CA [%]		Dye ink Δ CA [%]		Pigment ink Δ CA [%]	
	[%]	± σ	[%]	± σ	[%]	± σ
PEG 0%	15.3	0.6	62.7	1.9	37.1	4.8
PEG 5%	16.9	1.6	62.5	0.3	46.8	2.2
PEG 10%	17.7	0.6	55.9	1.2	47.2	0.4
PEG 15%	17.7	0.2	53.1	4.6	50.5	0.6

***Table 5**. B02 Spreading speed in % by PEG %wt*

	Water [mN/m]	Dye ink [mN/m]	Pigment ink [mN/m]
PEG 0%	72.73	32.40	33.58
PEG 5%	64.40	31.74	34.82
PEG 10%	66.80	35.76	37.60
PEG 15%	65.19	38.72	40.69

***Table 6.** Surface tension of fluids by PEG %wt*

The second analyze is about spreading speed and surface energy of the cardboards. Figure 7 shows the correlations between the cardboards surface energy (Table 7) and its fractions and the ΔCA (Table 8) of the fluids with different viscosities (Table 9). The dotted line marks the value above 0.80 where the correlation between the terms is considered highly positive and the dashed line marks the range where the correlation is moderate positive i.e. from 0.50 to 0.79 (Table 4).

Although this correlation method can present some distortions according to the data set, the correlations presented similar trends independent of the viscosity and fluid. There is a strong correlation between total surface energy (Table 7) and spreading speed, but for the dispersed and polar components the correlation is moderate or weak. Especially for the polar component was expected a higher correlation, because the increase in the polar component in this case can increase the wetting and accelerate the fluid spreading.

Cardboard	Total surface energy [mN/m]	Disperse surface energy [mN/m]	Polar surface energy [mN/m]
B01	42.67	27.89	14.78
B02	39.60	32.50	7.10
B03	35.33	28.52	6.81
B04	27.97	23.43	4.54
B05	32.99	24.81	8.17
B06	38.84	23.61	15.22
B07	35.65	29.93	5.71

***Table 7.** Total, disperse and polar surface energy by cardboard*

	PEG 0 %wt			PEG 5 %wt		
Cardboard	Water	Dye	Pigment	Water	Dye	Pigment
B01	22%	75%	47%	25%	68%	41%
B02	15%	63%	37%	17%	63%	47%
B03	15%	67%	45%	16%	67%	47%
B04	0%	13%	10%	0%	22%	10%
B05	13%	54%	36%	17%	54%	37%
B06	12%	63%	33%	13%	63%	40%
B07	10%	61%	33%	15%	60%	37%
	PEG 10% wt			PEG 15 %wt		
Cardboard	Water	Dye	Pigment	Water	Dye	Pigment
B01	23%	61%	55%	22%	53%	54%
B02	18%	56%	47%	18%	53%	51%
B03	18%	53%	49%	17%	52%	49%
B04	0%	20%	13%	1%	20%	16%
B05	16%	45%	41%	16%	48%	40%
B06	13%	55%	43%	15%	51%	44%
B07	15%	51%	40%	15%	50%	42%

***Table 8.** ΔCA - all fluids and cardboards*

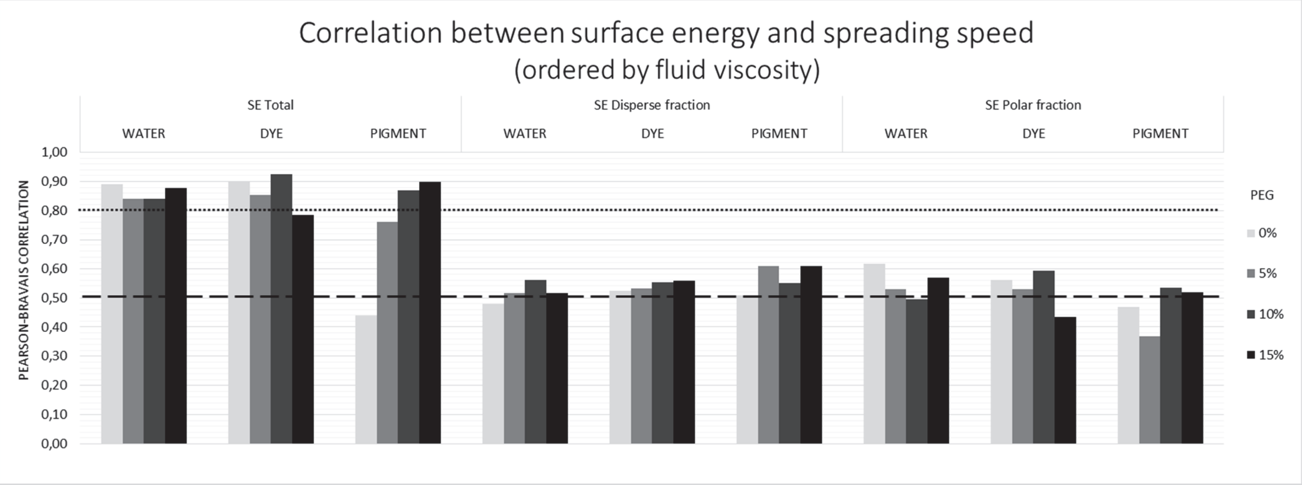

Figure 7. *Correlation between surface energy and spreading speed spreading*

	Water [mPa.s]	Dye ink [mPa.s]	Pigment ink [mPa.s]
PEG 0%	1.2	4.9	3.1
PEG 5%	2.5	14.4	8.0
PEG 10%	5.4	29.2	22.0
PEG 15%	11.2	38.2	40.1

Table 9. *Viscosity of fluids by PEG %wt*

Figure 8 presents this correlation graphically for 7 cardboard, here exemplarily for a concentration of 10% PEG. Increasing the total surface energy the delta increases. That means the spreading speed increases.

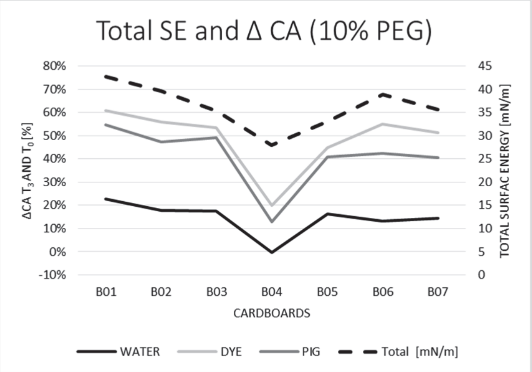

Figure 8 *Correlation surface tension and fluid spreading*

In resume,

- Increasing PEG:
  - Increases the viscosity
  - Increases the surface tension of dye and pigment-based inks
  - Decreases the surface tension of water-PEG solution

- During the first 3 seconds, the spreading speed of 3 µl droplet decreases, when:
  - Viscosity increases by water and dye-based, specially for solutions with 10 and 15% of PEG
  - Viscosity decreases by pigment-based inks
  - Every fluid shows its own particular trend, independently of the cardboards

- Dye inks spread faster than pigment inks.

- Between surface energy and spreading speed, there is
  - A high correlation with total surface energy of the cardboards
  - A moderate or weak correlation with both dispersed and polar surface energy fractions of the cardboards

Conclusions

Several factors influence the spreading of Inkjet ink on porous surfaces such as papers and cardboards. Inks and substrate characteristics and also the ink injection affect the interaction between them. The experiments presented in this study aimed to analyze the behavior of the ink drops in terms of their spreading speed. Well-known factors that can influence the spreading speed are the viscosity and the surface tension of the ink, as well as the surface energy of the substrate, corresponding with the contact angle of a liquid droplet on a solid surface.

An opposite behavior was identified between pigment-based inks and dye-based inks in relation to increased surface tension and viscosity. This phenomena could not yet be explain. It is however possible to observe a dependency of the results on the ink type and not on the cardboard type.

An expected and confirmed result is an increase in the spreading speed of the inks with an increase in the total surface energy of the cardboards.

These results can assist subsequent studies about the suitability models and equations to explain the interaction between Inkjet inks and coated cardboards, since well-studied plain papers and Inkjet papers have different morphological characteristics from coated cardboards.

Abbreviations

CA	Contact angle
FBB	Folding box board
PEG	Polyethylene glycol
SBB	Solid bleached board
SEM	Scanning Electron Microscope
DYE	Dye-based ink
PIG	Pigment-based ink

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