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UV-Inks, Substrates and Wetting

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ABSTRACT

Presently, it is desirable that one type of ink be suitable for printing on various substrates with different properties. Hence, the emphasis on new models and methods of printability prediction is necessary. The main objective of this work was to study and find correlation between physical properties of printing ink and substrate and finally how these properties can affect printability. For this purpose, contact angle measurement, surface tension measurement, rheology, and various methods for surface characterization of substrates were used.

INTRODUCTION

Printability[1], or how well substrates perform with ink through the printing process, depends on a number of properties of the ink-substrate combination. Printability is affected by the physical structure of the substrate surface, as for example roughness, permeability, porosity and also by physicochemical parameters such as work of adhesion and surface free energy. Many other properties such as compressibility, opacity, whiteness, formation and strength also affect printability. Among major ink properties affecting the inkjet printing process are surface tension, rheological behavior, viscosity, and drop impact energy. With increasing smoothness of the substrate surface (i.e. plastic films and calendered-coated papers), the importance of the surface energy of a system during the ink-substrate interaction is predominant over other substrate surface properties. Wetting, as expressed by liquid-substrate contact angle, is especially important because it reflects the extent to which an ink drop will spread on the substrate. Such spreading, or lack of it, controls coverage in solid print areas and dot control in halftones.

In this work, we studied the correlation between ink and substrate properties. As a model ink we used a black UV-Curable Inkjet ink[2]. To change the state of UV-Curable inks from liquids to solid, exposition with UV-light is needed. There are two advantages of using UV-inks, environmental and physical aspects. The curing process of such inks is relatively fast and generates very low volatile organic compound levels. From a physical point of view, or end-use properties, “UV-ink-jet” inks also have improved rub and solvent resistance and high gloss[3].

In order to improve the wetting and spreading properties of an ink, the addition of various surfactants is used. However, as addition of surfactant leads to increased wetting, it has proved difficult to quantify wetting behavior of ink in terms of the competing forces of interfacial tension and adhesion[4]. The wetting process is essentially reflected by the contact angle, defined as the angle that a liquid makes with a solid surface. The equilibrium relation of a three phase system can be described by the Young[5]-Dupre[6] equation:

$$\gamma_{lv}\cos\Theta = \gamma_{sv} - \gamma_{sl} \tag{1}$$

where Θ is the contact angle and γ is the surface/interfacial tension at the liquid-vapor interface (*lv*), solid-vapor interface (*sv*) and solid-liquid interface (*sl*). The value on the right side of equation 1 is the expression for the free energy of adhesion between the solid and liquid. This equilibrium is fundamental to the determination of the surface tension of the components. There are two major schools of thought for estimation of surface energy of *v-s* systems. One is the surface tension calculation (Girifalco[7], Fowkes[8]) and the other is the approach via an equation of state for interfacial tensions (Neumann, Ward)[9].

In inkjet printing, drops of ink are ejected toward the receiver surface at velocities in the range 1-5 m/s. Upon reaching the surface, the drops start to spread, driven initially by both inertia and capillary forces[10]. The initial spherical shape of the drop is forced into a pancake-like form, when contacting the substrate. The driving force for impact spreading is kinetic energy of the droplet, whereas flow resistance is provided by viscosity and surface tension of the liquid[11]. After impact of the ink on substrate, surfactants need a time for diffusion from the bulk solution to the subsurface, adsorption from the subsurface to the surface, and reorientation of the absorbed surfactant. For this stage of an ink-surfactant system, the time evolution of surface tension is diffusion controlled[12].

In the case of UV-curable inks, no solvent has to be evaporated and because of this, the printing process is determined by curing speed, which is much faster than the evaporation of the solvent base ink[13].

EXPERIMENTAL

Materials

As a subject of study, we chose a black UV-Curable Inkjet Ink, with no added surfactant (in this work denoted as "pure ink"). In order to study wetting properties, various surfactants were added (Table I). The surfactant types used were those suggested by the manufacturer of the UV-ink, having been found during the development and application process to improve the ink wettability and their composition.

Table I Addition of surfactants into the pure ink and (*their labels used in article*)

Identification	Brands	Addition / wt. %
BYK 377	BYK Chemie	0.1, 1.0, 2 (*Aa, Ab, Ac*)
BYK UV 3570	BYK Chemie	0.2, 1.5, 3.0 (*Ba, Bb, Bc*)
Zonyl	DuPont	0.3, 0.5 (*Ca, Cb*)

The amount of surfactant addition was decided based on the ink manufacturer's recommendation. Several coated papers and one coated polypropylene film were used as test substrates (Table II).

Table II List of tested substrates *and* (*their labels used in article*)

Brands	Identifications
Fasson 55# Cast Gloss Elite	subs15308 (*S1*)
Fasson 60# Cast Gloss	subs07602 (*S2*)
Fasson 60# Semi-Gloss Elite	subs17670 (*S3*)
Coated PP film	subs76911 (*S4*)
Matt Litho paper	subs14532 (*S5*)

Methods

In order to study the effect of substrate properties on wettability and ink spreading, several physical properties of the substrates were tested, such as porosity, roughness, thickness, and pore diameter. The AutoPore IV and Parker Print-Surf tester were used for this purpose. The viscosity of the black ink was studied using an advanced rheometer AR2000 from T.A. Instruments. Final results were calculated as an average of at least ten values of specific physical property for individual substrates.

Measurement of the "static" surface tension of inks was done using the contact angle analyzer FTA200 from First Ten Angstroms. The values of ink surface tension were calculated from the pendant drop[14] shape of the ink. For the measurement of "dynamic" surface tension, a SensaDyne Tensiometer was used. This test is based on the creation of air bubbles at the end of two different orifices, thus causing the dynamic behavior of the system. The surface tension of liquid is computed from the change of pressure conditions and the radius difference of orifices.

The measurement of contact angle was done using the FTA200 as well as in the case of surface tension by using the so called sessile drop[15] method. The ink in pure form and added surfactants were used as testing liquids on individual substrates. Results from FTA200 are averaged from at least ten values of contact angle or surface tension for individual drops. For the estimation of surface energy of each substrate the software FTA32 version 2.0 (by First Ten Angstroms) was used. The Girifalco-Good-Fowkes-Young[5,7,8] computational model was chosen and two standard testing liquids, Water and Methylene Iodide, were used. Minitab (release 14) was used to make statistical and mathematical calculations.

RESULTS

Table III shows the values of the physical properties of the substrates from the Parker Print-Surf tester and AutoPore IV. In the case of roughness and porosity measurements, the value of pressure used was 1 MPa. The permeability was calculated from the Parker Print-Surf porosity, using the Pal[16,17] equation;

$$K = 0.048838\ Q\ X \tag{2}$$

These results confirmed that PP film, as expected, has the lowest values of permeability and porosity as a result of its uniform and non-porous surface.

Table III Results from substrates property measurements

Substrates	S1	S2	S3	S4	S5
Porosity ml min^{-1}	0.71	0.89	0.42	0.32	1.05
Permeability µm^2	3.42	4.68	1.87	1.35	5.41
Roughness µm	1.32	1.28	1.42	0.99	2.95
Avr. pore diameter µm	7098	552	686	613	919
Gloss (75°) %	90.2	77.3	80.1	98.8	14.5

The results displayed in Figure 1 are from viscosity measurements for all of the tested combinations. As it can be seen, there are changes of up to 25% in the ink viscosity. However, such changes can influence the ink jetting process, so the print head must be tuned accordingly to deliver the desired droplet size.

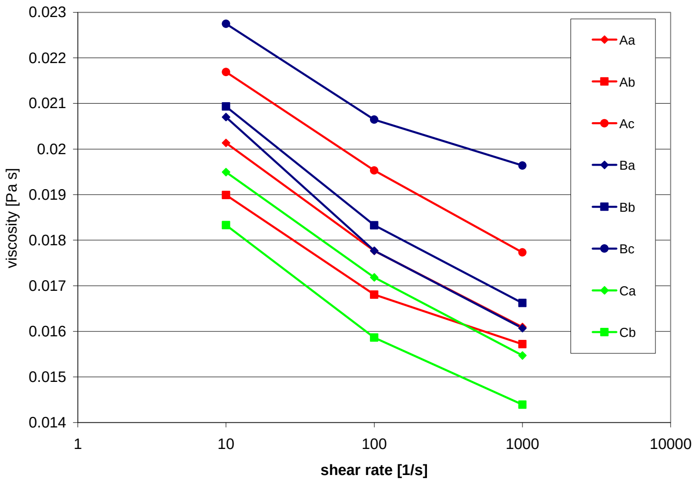

Figure 1 Plot of relation viscosity of inks *vs.* shear rate

Surface tension was measured with FTA (static surface tension) and SensaDyne (dynamic surface tension). Figure 2 illustrates an example (Sample of ink A) of surface tension results. All samples of inks (A, B and C) have very similar trends, meaning that the surface tension of inks decreases with addition of surfactants. However, the drop of surface tension tends to level out at a specific percentage of surfactant content and do not further change significantly. Such a point is known as the Critical Micelle Concentration[18,19] (CMC). Similar trends were found for both, static and dynamic surface tensions.

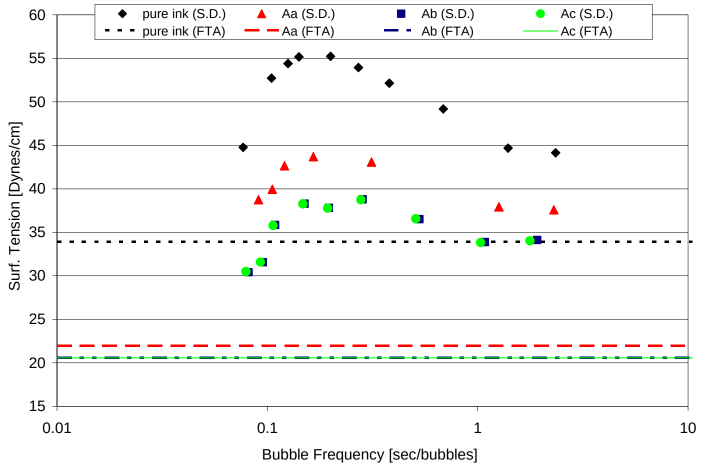

Figure 2 Values of static (FTA) and dynamic (S.D.) surface tension of inks

Contact angle measurements were performed on all substrates with all mixtures of ink and surfactants. Figure 3 and Figure 4 present examples of results for one of the coated papers tested and the PP film. These graphs show a general decreasing trend of contact angle with time and the same behavior can be seen in the drop of contact angle with addition of the surfactants. All remaining samples have similar trends. In spite of the fact that the CMC value was reached during testing, the contact angle still decreases with increasing concentration of surfactant. This indicates that with increasing surfactant concentration, the surfactant molecules increase their population at the liquid-solid interface, while their population at the liquid-vapor interface remains constant. This is turn causes further penetration of ink into the substrate and spreading over time, as predicted by the Lucas[20]-Washburn[21] equation.

A mathematical analysis of the contact angle *vs.* time relationship showed that all of these relations can be described with an exponential equation of second order

$$y \quad y_0 \quad A_1 e^{\frac{t}{t_1}} \quad A_2 e^{\frac{t}{t_2}} \qquad (3)$$

This is valid for all of the substrates studied independent of ink mixture. For every case, two times were required to give a good fit to the time data. This indicates that there are two rate processes governing the time dependence of both the contact angle and drop volume. The longer time is approximately two orders of magnitude longer than the shorter one. The times for the drop volume are not the same as the contact angle, but they are of the same order of magnitude.

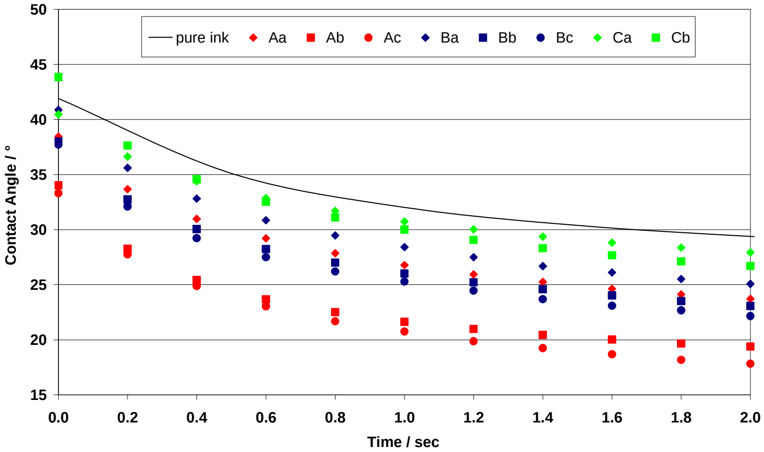

Figure 3 Plots contact angle *vs.* time. Picture shows result for substrate S3

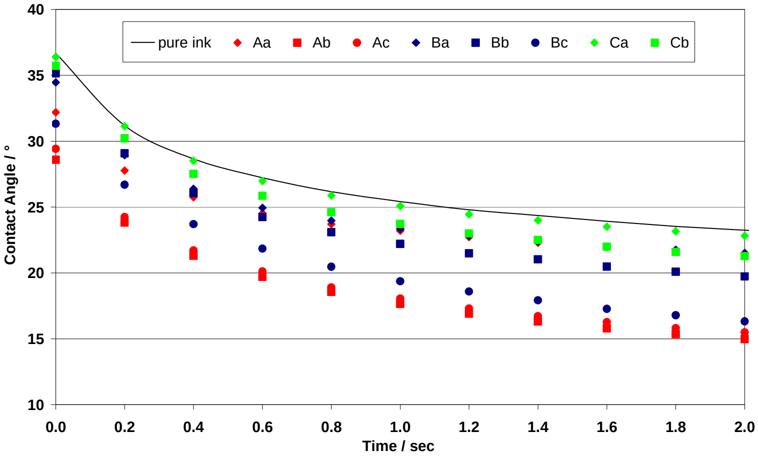

Figure 4 Plots contact angle *vs.* time. Picture shows result for PP film (substrate S4)

The final step in this work was to "model" the wetting process, meaning to find possible correlations between ink properties (contact angle, surface tension, viscosity, drop volume, etc.) and substrate properties (porosity, permeability, roughness, etc.) or ink interaction with substrate properties and their influences on printability. For this reason a statistical analysis was done using Minitab 14. Multiple linear regressions were performed with contact angle and asymptotic drop volume as responses and properties of all of the papers as independent variables. According to the results obtained, 80% of the variation of contact angle is explained by roughness, permeability and ink surface tension. When the Fowkes[8] surface energies of substrates are included into the analysis, the variation accounted for increases to 84%. The corresponding correlations for drop volume are 92%, and 94% respectively.

The numerical results of these regressions are:

$$\Theta_0 = 9.3 + 1.97\ K - 7.0\ \sigma + 0.39\ \gamma_{vl} + \varepsilon_1 \tag{4a}$$

$$\Theta_0 = -5.1 + 1.56\ K - 6.2\ \sigma + 0.39\ \gamma_{vl} + 0.41\ \gamma_{sv}^F + \varepsilon_2 \tag{4b}$$

$$V_0 = -0.13 + 0.173\ K - 0.88\ \sigma + 0.21\ \gamma_{vl} + \varepsilon_3 \tag{4c}$$

$$V_0 = -3.4 + 0.085\ K - 0.70\ \sigma + 0.21\ \gamma_{vl} + 0.096\ \gamma_{sv}^F + \varepsilon_4 \tag{4d}$$

where Θ_0 and V_0 are the long time values of contact angle and drop volume respectively from equation 2. K is permeability in μm^2, σ is the roughness in µm, γ_{vl} is the surface tension and γ_{sv}^F is the Fowkes surface energy of the substrate, both in dyn cm^{-1}. The root mean square of ε_{1rms}, is 2.2°. Likewise, $\varepsilon_{2rms} = 2.0°$, $\varepsilon_{3rms} = 0.42$ µl and $\varepsilon_{4rms} = 0.36$ µl.

These results are remarkable, considering that none of the independent variables directly reflect the chemistry or morphology of the substrate coating.

DISCUSSION AND CONCLUSIONS

We have examined the properties of a family of inks and different substrates, along with the properties of their interfaces. Addition of surfactants does not markedly change the viscosity of the ink, but it does change the contact angle significantly. This change is larger for the lowest concentration of surfactants (Sample A or Sample B) *vs.* middle concentration, than for the middle concentration *vs.* the highest concentration. This is because the surfactant concentration reaches the CMC near to the middle concentration. The continued decrease in contact angle above the CMC means that some surfactants may enhance wettability, even above the CMC.

We have seen that the approaches to equilibrium of the contact angle and drop volume of the various ink compositions on the different substrates represent complex rate processes, requiring at least two relaxation times, short time and long time. Short time constants for contact angle and drop volumes may be less than cure times and cure kinetics may not be fast enough for some substrates. Accordingly, ink drops may be significantly absorbed into permeable substrates before full curing has occurred.

A large portion of the variation of the equilibrium contact angle and drop volume can be accounted for from substrate properties and ink surface tension. Even though all of the substrates were coated to improve printability, the relatively accurate linear relations (4) with substrate properties take no account for coating chemistry or morphology of the coatings. This should be the next segment for research. Drops of the different ink compositions should be formed on coatings of known formulation. In addition to the substrate physical properties discussed above, the coating microstructure should be examined using scanning electron microscopy[22] or atomic force microscopy[23], for example. With further research and deeper analysis of all results, this work can be useful in prediction of printability and can be taken as "a guide" to the right choice of UV-ink for given substrate.

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