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NATTKLINIK

Innovations in Ink-Jet Technology

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Abstract

It is the scope of this Nordic R&D project on "Innovative development of the ink-jet technology" to utilise the outcome of national research programmes and to establish a Nordic network of research institutes, material suppliers, printer manufacturers and end users of the ink-jet technology.

The focus is on developing a normative specification and documentation of adequate measuring techniques for materials and process parameters for different application of the ink-jet technology. Special attention is paid to the influence of paper and ink properties on spreading and penetration, and hence, on print quality. Print quality is here seen in terms of image analytical factors, like dot size, darkness and roundness.

The first two steps of the project included an inventory of Nordic and international research results on ink-jet printing and a documentation of measuring methods, especially methods for drop formation, spreading and absorption when printing with different printer heads and substrates. These steps have been reported in a separate report.

The further work focused on practical material characterisation and interaction mechanisms in ink-jet printing. In these tests a representative selection of substrates and inks were further analysed on a laboratory level and test printed. Based on the results recommendations for material properties and process conditions, as well as measuring methods have been developed, and are reported here.

The project also discovered still remaining problem areas in the ink-jet method, where improvement can be achieved through a continued co-operation between scientists, material suppliers, equipment manufacturers and end-users. At the end we present preliminary plans for such a developing project.

Preface

This is the final report of a Nordic research project on "Innovative development of the ink-jet technology (NATTKLINIK)". The project was based on technical knowledge about the ink-jet printing methods achieved in national research programmes in Finland, Sweden and Denmark. It has utilised and further developed the knowledge about the ink-jet printing method and the materials used in different application. The work has been performed in a unique Nordic consortium enabling a direct implementation and utilisation of the results.

The project has been partly financed by the Nordic Industrial Fund, which is an official institution under the Nordic Minister Council. The fund initiates and supports research and development projects with focus on the Nordic innovation system. The project should per se improve the competitiveness of the Nordic business life, strengthen the Nordic culture, and contribute to a sustainable development of the Nordic society.

The project has been performed by three Nordic research organisations in co-operation – i.e. VTT Information Technology, Espoo, Finland, Ytkemiska Institutet, Stockholm, Sweden, and EnPro ApS, Copenhagen, Denmark. The project has been further supported by four industrial partners taking also an active role in the performance of the practical research work – i.e. Big Image Systems Sweden AB, Täby, Sweden, Stora Enso Research Centre, Imatra, Finland, Sun Chemicals A/S, Køge, Denmark, and Xaar Jet AB, Järfälla, Sweden.

The work has been governed by a Steering Committee with representatives for all the participating industrial partners and the Nordic Industrial Fund. The members of the Steering Committee have been: Mr *Oddur Már Gunnarsson*, Nordic Industrial Fund, Mr *Palle Chris Nielsen*, Sun Chemicals A/S, Mr *Werner Schäfer*, Big Image Systems AB, Mr *Risto Vesanto*, Stora Enso Research Centre, and Ms *Marie Wickman*, Xaar Jet AB.

The authors of the sub-report are greatly indebted to the members of the Steering Committee for their support, good co-operation and worthy comments.

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List of symbols

γ	Surface energy (mN/m)
γ_{sl}	Interfacial tension solid-liquid (mN/m)
γ_{sv}	Interfacial tension solid-vapour (mN/m)
γ_{lv}	Interfacial tension liquid-vapour (mN/m)
Φ	Integration function of the normal (Gaussian) distribution function
ϕ	Volume fraction of particulate
η	Viscosity (Pa s)
Θ	Contact angle (rad)
λ	Argument in the normal distribution function
λ_p	Argument value for the Gaussian function at the confidence level p
π	3,14
ρ	Density of a liquid (kg/dm ³)
ρ_{xy}	Correlation between the variables x and y
σ_x	Spread of the variable x
σ_{xy}	Covariance of the variables x and y
a_j	Regression coefficient for the independent variable j
dpi	Dots per inch
E	Energy; Work (J)
F	Force (N)
F_w	Wetting force (N)
g	Acceleration of gravity (9,81 m/s ²)
i, j	Running indecies
m	Mass (kg)
	Mean of a function
N	Number of observations in a test
n_i	Number of observations for calculating characteristics of the variable i
P	Dot perimeter (mm)
p	Level of confidence

r	Capillary radius (mm) Correlation coefficient; an estimate for correlation
R	Droplet radius (mm)
RI	Raggidness Index
S	Dot area (mm ²)
s	Standard deviation; an estimate for the spread of a function
t	Time (s) Argument in the t-distribution function
v	Speed (m/s)
x,y	variables
X_i	observation value for the variable x
$\overline{X}$	calculated mean value for the variable x
z	Height of capillary rise (mm) Residual term in the linear regression model

1 Introduction

During the last decade the ink-jet printing technology has developed rapidly, and new applications have been directed to produce both documents, publications, personalised advertisements, security documents, textiles, packages and cartonage. The method is suitable for both a wide variety of materials, frequently updated information, and for multi-colour high-quality products. The two main applications of the ink-jet technology – i.e. Drop-On-Demand (DOD) and Continuous Ink-jet (CIJ) – have been developed in parallel.

The method is strategically important for the Nordic industry, since the Nordic countries are important suppliers of paper and boards for ink-jet printing, an increasing share of the print market is taken over by digital printing, Nordic SMEs deliver printed products – such as cartonage, packages and high quality print – to a global market, ink-jet inks are basically imported an extremely expensive, and the Nordic countries also produce and export advanced printer heads.

For this reason the ink-jet technology has been the focus for several national research programmes. In Finland a national research programme called "Electronic Printing and Publishing" had been carried out in the years 1995-1999 with support from the National Technology Agency (TEKES). Research on high speed ink-jet had been carried out within this programme and continued in separate research projects after that. The focus had been on developing paper properties suitable for multicolor and high speed ink-jet printing and development of measuring methods. In Sweden YKI has focused the research on the interaction between ink and paper and surface energetic phenomena. The research work has been part of national research programs like PTF and S2P2. In Denmark EnPro has focused on the development of inks for the ink-jet technology.

This Nordic R&D project on "Innovative development of the ink-jet technology" utilises the outcome of the national research programmes and establishes a Nordic network of research institutes, material suppliers, printer manufacturers and end users of the ink-jet technology. The scope of the project is to present a normative specification and documentation of adequate measuring techniques for materials and process parameters for different application of the ink-jet technology. Special attention is paid to the influence of paper and ink properties on spreading and penetration, an hence, on print quality. Print quality is here seen in terms of image analytical factors, like dot size, darkness and roundness.

The first step in the performance of the project included an inventory of Nordic and international research results on ink-jet printing and its most important parameters in different applications. The second step provided documentation of measuring methods and routines developed by the research partners, especially methods for drop formation, spreading and absorption when printing with different printer heads and substrates. The outcome of these first two steps have been published in a separate report, but a short summary is given here in Chapter 2.

The experimental work includes laboratory tests and full scale test printing with a series of five substrates and four inks. The materials was selected to give maximum information about the impact of material properties on printing behaviour and quality formation. The

experimental has been described in Chapter 3 and the results and their interpretation in Chapter 4.

Based on the results recommendations for material properties and process conditions, as well as measuring methods have been developed, and are reported in Chapter 5. The chapter also contains recommendation for further development of the ink-jet process and its materials.

VTT Information Technology has been responsible for the parts dealing with the ink-jet technology itself, measuring methods for print quality and fast interaction in ink-jet, including measuring results. YKI was responsible for the parts dealing with contact angles and flow property measurements, and EnPro for the parts dealing with ink composition and ink properties.

2 State of the Art

2.1 The Ink-Jet Printing Technology

In ink-jet printing an impression is made through the use of separate ink drops. Drops are ejected onto the printing surface to generate a predetermined dot matrix. The size of the smallest drop determines the finest detail that can be reproduced in the ink-jet process. Dots as small as 3 picoliter (diameter about 18 microns) can be generated at the present level of ink-jet technology. Ink-jet printing is the only non-contact printing method and because of this it is the most ideal of all the printing methods. Also, multicolor printing can easily be carried out as the different process colors can be ejected directly onto the printing surface.

Ink-jet systems consist of three parts: printer, ink and printing surface. All of these elements must be taken into account when the system is developed. Ink-jet technologies are usually divided into continuous and drop-on-demand printing methods. Continuous printing methods are used in high-speed applications. Drop-on-demand methods were originally developed for office environments, but the technology has rapidly conquered the wide format printing area, where the screen printing method was formerly used.

There are three ways to raise the speed of a ink-jet printer:

- apply more ink-jet nozzles to each printing head
- apply more printing heads to a printer
- increase the drop generation frequency

In continuous ink-jet printing all these three methods can be used, but the drop-on-demand method limits the possibilities to the first two. At the moment the highest possible drop generation frequency in continuous ink-jet printing (1 MHz) is two orders higher than in drop-on-demand printing.

2.2 Measuring Interactions in Ink-Jet Printing

The research performed by YKI in the framework of the project Innovative Development of the Inkjet Technology mainly concerns the problem of ink-media interaction. The ink is considered as a complex liquid with appropriate hydrodynamic and surface-chemical properties and the ink setting dynamics are studied. By using high-resolution measuring equipment, the spreading and penetration of inkjet drops have been monitored for a number of common printing media including paper board and textile. The printing substrates, in their turn, have been characterized with respect to the surface energy and roughness, the two major factors determining the observed ink setting profile, ink adhesion, as well as the scuff- and rub-resistance of print.

2.3 Inks for Ink-Jet Printing

There are a number of ink types used for ink-jet printing. The different ink types are often used for different purposes and substrates, and they also have different drying performance. The main different ink types available are:

- Solvent-based inks - drying by evaporation and absorption (S)
- Oil-based inks (High boiling solvents) - drying controlled by absorption
- Water-borne inks - drying by evaporation and absorption (W)
- UV-curable inks- drying by absorption and UV-curing equipment (UV)
- Hot-melt inks (phase-change ink) - drying by solidification due to temperature decrease (HM)

Which type of ink that should be used, depends on the ink-jet technology as well as the substrate. Important ink parameters are viscosity, surface tension, and stability.

The ink-jet process is decisive for the surface tension and the viscosity of the ink. The ink has to be very fluid to pass through the fine nozzles. The requirements to the ink depending on the printing head technology can be seen in table 2.3.1. The surface tension is for all technologies except one only given by a minimum value, but the surface tension can also become too high which influences on the drop formation and hence the print result.

The performance on the substrate depends on the surface properties. A critical quality issue is the coalescence of the ink on the substrate, where important interaction parameters are the surface tension of the ink, the surface tension of the substrate and the ink absorption rate into the substrate.

Table 2.3.1 Inkjet ink requirements depending on the printhead technology.

Ink property	CIJ Bi-nary	CIJ Multi deflection	DOD Piezo	Valve jet	Office piezo	Office TIJ
Inks used	A; S	A; S	A; S; HM;UV	A; S	A; S; HM	A; S
Viscosity (cP)	~1,5	3-8	8-12	<2	~1,5	~1,5
Surface tension (mN/m)	>35	25-40	>32	>24	>35	>35
Particle size max. (µm)	1	3	1	5	1	0,2
Conductivity (µSiemens)	>500	>1000	No	No	No	No
Salt levels Chlorides (ppm)	<100	<100	<100	<100	<10	<10

It should be noted that the drop formation and jet stability are very important in most printhead technologies. Some of the most common problems are jet wander and foaming

for continuous inkjet; depriming nozzles, drying and starvation for piezo technology; and kagation nozzles, drying and starvation for thermal inkjet technology.

Generally an ink-jet ink can be described as a liquid medium (for hot-melts after heating) and a colorant (pigment or dye). In some systems a binder (polymer) is necessary to achieve adhesion, and in other systems the binder is a part of the liquid medium (UV-curing). Furthermore, can the ink dry by penetration to the substrate and/or by evaporation of the liquid medium and/or by curing of the binder system.

2.4 A Summary of the Survey

Based on the results collected from the literature and earlier studies at the research partners, the following general conclusions made be drawn about the known interactions in ink-jet printing:

- Absorption properties of the substrate and the tone value of the ink determines the intensity of the print
- Spreading dynamics depend on the amount of liquid in the ink, the kinetic energy of the droplets, rheology of the ink (ink dependent) and the surface energy and absorptivity of the substrate
- The inks are solvent-based, oil-based, water-borne, UV-curable or hot-melt or combinations of these; colorants are dyes or pigments
- Print quality is preferably evaluated by image analysis in parameters from dots, fonts, lines and solid areas
- Dynamic interactions are measured with a high-speed CCD camera for small drops
- Surface energy is evaluated using contact angles, dynamic wetting, surface energy composition, and profilometry
- The most important ink characteristics for the interaction with the substrate are rheology, surface tension and particle size distribution

3 Materials and Methods

3.1 Experimental Part, General

It was the aim of the experimental part to find most information about materials interactions and their impact on quality formation in ink-jet printing. The materials tested had to be restricted to 5 substrates (2 board, 2 textiles and 1 plastic) and 4 inks. The substrates and the inks were selected so that they represented a wide range in surface, absorption and rheologic properties. To find the inks for the final tests, EnPro and YKI performed a scan of seven ink samples delivered by Xaar Jet and Big Image Systems. The final selection of inks was made by EnPro and Xaar Jet.

Stora Enso delivered two board samples, Big Image Systems two textiles and one plastic for the final test. All the samples were tested by the three research organisations as described below. In addition Xaar Jet delivered 12 printer heads to VTT for the laboratory tests and Stora Enso delivered their Xaar printer for laboratory tests and full scale test printings.

Big Image Systems performed test printings in four colours and VTT in two colours. Print quality was evaluated by VTT.

3.2 Selection of Materials

3.2.1 Printing Inks

The inks used in this project are mainly received from the project partners. It is very difficult to get inks directly from the producers, due to the fact that most producers have an agreement with a printing head manufacturer and thus the ink should be delivered from the printing head supplier. It was the aim in this project to cover solvent-based, water-borne and UV-inks. As a printing head for water-borne inks was not available only solvent-based (including oil-based) and UV inks are included. The inks received are listed in table 3.2.1.

The solvent-based inks have some differences in flash point, which indicate that the evaporation profile is differing. The oil-based inks are evaporating even more slowly. All the inks are pigmented except for one, which is a dye-sublimation ink. Furthermore one UV-curing ink is included to get an indication of if there are any major differences with regard to physical properties compared to solvent-based inks. The UV-ink is not able to dry due to evaporation but demands UV-curing.

It was the goal to select suitable inks for printing tests from these 9 inks were the rheology, surface tension, particle size distribution and conductivity was varied as much as possible. It should be noted that M= magenta, C= cyan, Y= yellow and B= black.

Table 3.2.1. Ink types received.

Ink Code	Product type
SB-M1	Solvent-based (flash point approx. 47°C)
SB-M2	Solvent-based (flash point 63°C)
SB-M3	Solvent-based (flash point 63°C)
SB-M4	Solvent-based (flash point approx. 63,5°C)
SB-M5	Solvent-based (flash point approx. 68°C)
DS-SB-M6	Dye-sublimation ink (flash point 63-85°C)
OB-M7	Oil-based ink (flash point >120°C)
OB-M8	Oil-based ink (flash point >134°C)
UV-M9	UV-curing ink

3.2.2 Substrates

Two types of packaging paperboard (Ensocoat™, coated; Ensocup™, PE-laminated) supplied by StoraEnso and two fabric printing substrates provided by Big Image Systems were used in laboratory tests. Dynamic interactions between the substrates and (i) HP and Epson water-based ink-jet inks containing a dye-based colorant and (ii) Xaar-Jet solvent-based inkjet inks containing a pigment-based colorant have been studied.

3.3 Laboratory Test Methods

3.3.1 Ink Property Measurements

To evaluate the ink properties the following measurements have been performed:

- The viscosity is measured on a Bohlin VOR Millennium Rheometer according to ISO 3219-93: Determination of viscosity using a rotational viscometer with defined shear rate. The rheological properties were measured at 23°C. All measurements were performed with system C25 with the lowest torque element 1,31 gcm. The oscillation measurements were initially performed at a frequency of 0,001 Hz to 20 Hz. The most stable area was chosen on this background. The phase angle was then measured from low to high frequency and back again.
- The surface tension was measured at 23°C on a Krüss Tensiometer according to ISO 304-85: Surface active agents – Determination of surface tension by drawing up liquid films. The average of 3 values are given in table 4. The density according to ISO 2811/2-97: Paints and varnishes – Determination of density – Part 2: Immersed body method

- The particle size distribution was measured with a Malvern Mastersizer microPlus. The sample is diluted in a carrying media and the evaluation is based on a polydispers model to determine the particle size distribution. The refractive index should be known for the sample and the measuring range is from 0.05 – 500 μm .

Evaluating the data it can be seen that the variations generally are small. Still a number of inks should be chosen for testing. The inks suggested are marked in table 3.3.1. The intention is that as large a span as possible is achieved with regard to viscosity, phase angle and surface tension.

Table 3.3.1. Summary of data for technical properties

Ink Code	ρ Density [g/ml]	η Viscosity [mPas]	ΔE Phase angle	γ Surface tension [mN/m]	Particle size distribution peak	Particle size range	Particle size 90%
SB-M1	0,9783	17,6	87,2	29,8	0,36	0,17-0,78	<0,49
SB-M2	0,9331	11,3	87,8	28,1	0,36	0,15-0,78	<0,67
SB-M3	0,9382	13,1	88,1	27,9	0,36	0,17-0,67	<0,58
SB-M4	0,9908	22,8	69,5	29,4	0,23	0,05-0,58	<0,42
SB-M5	0,9903	15,9	87,8	27,0	0,36	0,13-0,78	<0,58
DS-SB-M6	0,8721	13,4	87,9	33,4	0,07	0,05-0,49	<0,31
OB-M7	0,8643	11,9	87,3	28,0	?	?	?
OB-M8	0,8645	10,2	86,7	30,7	0,36?	0,11-0,8?	?
UV-M9	0,9369	13,8	84,9	28,7	0,27	0,05-0,67?	?
OB-Y7	0,8538	12,0	87,3	27,9	0,36	0,17-0,58	<0,48
OB-C7	0,8530	12,2	86,4	28,7	0,07	0,05-0,49	<0,20
SB-B4	0,9965	16,5	87,5	26,3	0,08	0,05-0,49	<0,23
SB-M4	0,9910	13,1	85,8	26,9	0,31	0,15-0,58	<0,49
OB-B7	0,8850	13,6	86,1	28,7	0,06	0,05-0,31	<0,12
DS-SB-Y6	0,8888	9,7	77,9	30,4	0,36	0,20-0,58	<0,54
OB-M7	0,8632	11,2	86,1	28,5	0,36	0,17-0,58	<0,47
DS-SB-C6*	0,8875	6,4	78,4	29,7	0,49	0,36-0,91	<0,85
DS-SB-B6	0,8890	12,1	85,2	31,5	0,05	0,05-0,08	<0,07

*= Difficulties in the measurements

Furthermore, is the differences in composition evaluated using thermogravimetric measurements. These measurements are only performed on the magenta inks, but in duplicate:

- Thermogravimetric measurements can be used to determine the solvent/aqueous content (<250°C), the dry matter (approximately rest at 250°C), and the amount of inorganic material(>600°C). Approximately 30 mg sample is weighted on a microbal-

ance into a 70 µl aluminium oxide crucible with a lid. The sample is heated with 10°C per minute from 30°C to 620°C in nitrogen atmosphere (100 ml N₂/min). The results are recorded on a PC and each thermogravimetric curve is evaluated by means of the software programme METTLER TOLEDO STAR^e System. (ASTM E 1131-98: Compositional Analysis by Thermogravimetry)

Table 3.3.2. Summary of thermogravimetric data. The data given is the rest prof of the product in wt-% after heating to the given temperature.

Temperature	100°C	200° C	250° C	300°C	400° C	500° C	600° C
SB-M1, average	97,23	12,70	11,51	10,19	7,79	6,12	0,92
SB-M1, std.dev.	0,92	0,69	0,35	0,33	0,33	0,06	0,27
SB-M2, average	97,21	11,60	10,11	8,74	7,79	6,37	2,64
SB-M2, std.dev.	0,17	1,05	1,03	1,09	0,56	0,11	1,07
SB-M3, average	97,13	13,99	13,11	12,03	8,63	5,74	1,15
SB-M3, std.dev.	0,86	0,69	0,04	0,04	0,18	2,12	0,76
SB-M4, average	97,05	8,09	7,46	6,01	5,10	3,48	1,11
SB-M4, std.dev.	0,50	0,04	0,23	0,13	0,12	0,30	0,09
SB-M5, average	97,33	8,03	7,52	6,38	5,11	3,78	1,00
SB-M5, std.dev.	0,07	0,29	0,35	0,45	0,42	0,53	0,37
DS-SB-M6, average	99,84	81,82	46,47	17,16	4,11	1,35	1,23
DS-SB-M6, std.dev.	0,09	4,76	6,09	5,46	0,16	0,15	0,24
OB-M7, average	100,28	95,56	76,68	21,37	12,83	11,21	4,72
OB-M7, std.dev.	0,07	2,38	9,76	7,71	1,41	1,07	0,63
OB-M8, average	100,19	96,13	80,18	36,24	12,66	10,58	3,49
OB-M8, std.dev.	0,04	0,62	2,43	2,73	0,08	0,02	0,01
UV-M9, average	97,75	12,02	10,47	8,42	7,66	6,28	2,10
UV-M9, std.dev.	0,11	0,02	0,35	0,46	0,66	0,66	0,34

Evaluating the thermogravimetric data it can be seen that there are some composition differences also in the solvent-based products. The standard deviations for M6 and M7 are very high at some temperatures, but this is due to decomposition at the given temperature, i.e. there is a peak, which means that even small differences in weight might influence. The oil-based products have a dry matter of about 80 wt-%, while the solvent-based have about 10 wt-%. The dye-sublimation ink has a dry matter of approximately 50 wt-%. A magenta pigment will decompose from about 300°C, why the rest product at 600°C is the inorganic rest, but not equal to the pigment concentration.

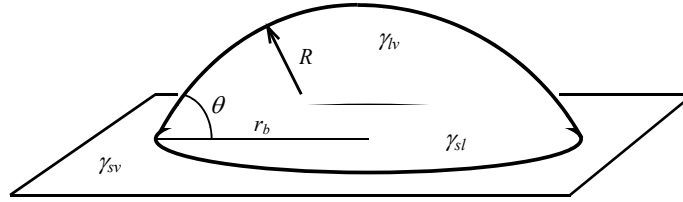
3.3.2 Surface Energetic properties

The wetting ability of a liquid with respect to a solid surface can be characterized by measuring the contact angle between by the liquid meniscus and the surface; a contact angle less than 90° indicates that the substrate is readily wetted by the test liquid, while an angle greater than 90° shows that the substrate will resist wetting.

The contact angle can be related to the surface tensions, or excess free energies, of the corresponding interfaces that intersect at the three-phase-contact line,

$$\cos q = \frac{g_{sv} - g_{sl}}{g_{lv}}$$

This relation is known as the Young-Dupré equation. This equation can be easily derived by analysing the equilibrium drop configuration corresponding to the minimum excess surface energy. Let's consider a small liquid drop sitting at a partly-wettable solid substrate,



The gravity effects can be neglected because of a small size of the drop. There are three interfaces contributing to the total excess free energy of the system shown,

$$E = E_{lv} + E_{sl} + E_{sv}$$

where

$$E_{lv} = g_{lv} S_{lv} = 2p R^2 g_{lv} (1 - \cos q)$$

$$E_{sl} = g_{sl} S_{sl} = p R^2 g_{sl} \sin^2 q$$

$$E_{sv} = g_{sv} S_{sv} = \text{const} - p R^2 g_{sv} \sin^2 q$$

It should be noted that there exists an additional contribution, E_{svl} , from the three-phase contact line where all the three interfaces intersect. However, the corresponding correction is only significant for sub-micron size drops. In ink-jet printing, the typical drop size is about $10 \mu\text{m}$, hence the line tension effects can be safely ignored.

The value of θ corresponding to the minimum E is then found from the equation,

$$\frac{dE}{dq} = 0$$

taking into account that the volume, V , of the drop is constant and the radius, R , of the drop is related to the contact angle,

$$R(q) = \sqrt[3]{\frac{3V}{\rho(2 - 3\cos q + \cos^3 q)}}$$

Then, after some basic arithmetics, one arrives at the Young-Dupré equation. Furthermore, the wetting force acting per unit length of drop perimeter is given by

$$F(q') = - \frac{1}{r_b} \frac{\gamma E}{\gamma_b} = - \frac{1}{r_b} \frac{(\gamma E / \gamma q)}{(\gamma_b / \gamma q)} = g_{lv}(\cos q - \cos q')$$

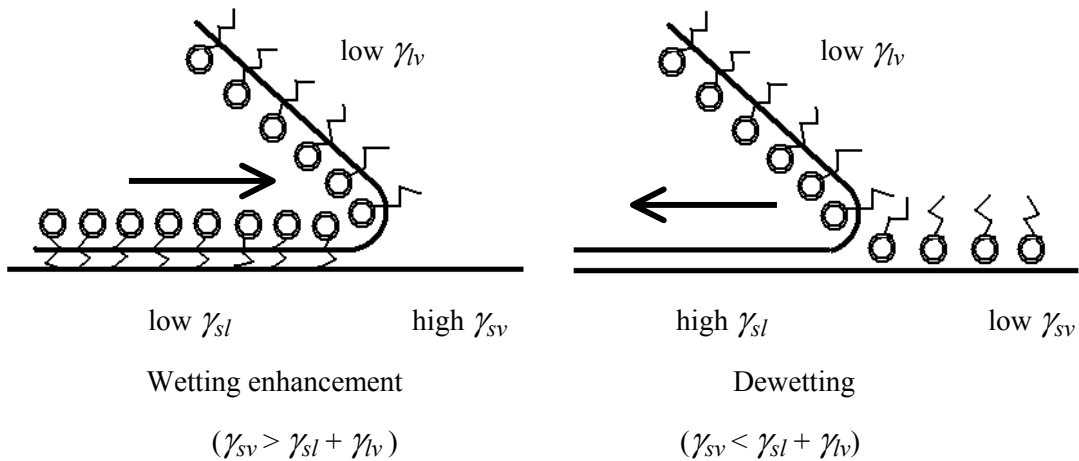
where q is the equilibrium contact angle determined by the Young-Dupré equation, q' is the out-of-equilibrium contact angle, and r_b is the radius of the drop base corresponding to a given value of q' .

It is clear that high energy substrates, which are characterized by a high value of γ_{sv} , will be readily wettable by most liquids. In contrast, low-energy substrates are only wettable by liquids whose own surface tension, γ_{lv} , is low enough. Since surfactants have been shown to reduce γ_{lv} , and probably γ_{sl} as well, they promote wetting. The equilibrium contact angle between a solid surface and a drop of a surfactant solution is a function of surfactant concentration, herewith

$$\begin{aligned} \cos q(c) &= \frac{g_{sv} - g_{sl}(c)}{g_{lv}(c)} = \frac{g_{sv} - g_{sl}(0) + RT \int_0^c \frac{dG_{sl}}{dc} d \ln c}{g_{lv}(0) - RT \int_0^c \frac{dG_{lv}}{dc} d \ln c} \\ &= \cos q(0) \left\{ 1 + \frac{RT}{g_{lv}(0)} \left[\int_0^c \frac{dG_{sl}}{dc} d \ln c + \int_0^c \frac{dG_{lv}}{dc} d \ln c \right] + \dots \right\} > \cos q(0) \end{aligned}$$

i.e. the addition of surfactant leads to a decrease in the contact angle, $\theta(c) < \theta(0)$. This is a thermodynamic interpretation of the wetting-enhancing effect of surfactants.

It should be noted that, depending on adsorption affinity of surfactant to various interfaces, either wetting enhancement or dewetting effect may prevail. These two scenarios are illustrated in the following drawing:



Dewetting will normally occur if there exists a strong specific interaction between the polar group and the substrate, forcing surfactant molecules to adsorb in a configuration where their hydrophobic tails extend towards the solution phase. The result of such a specific adsorption is that the substrate surface becomes more rather than less hydrophobic.

A few notes regarding applicability of the Young-Dupré equation should be stated. First, if $\gamma_{sv} - \gamma_{sl} > \gamma_{lv}$, there is no real contact angle that would meet the equation. In this case, referred to as the complete wetting, the liquid will spread to a monolayer film. Second, if γ_{lv} is always positive, γ_{sv} and γ_{sl} can in general be negative. In the latter case, the stability of the corresponding interfaces is ensured by mechanical hardness of the solid substrate. Although there is no direct methods for determination of the surface tension of solids, it is believed that many superspreaders can render the surface of the sl interface negative.

The wettability can also be characterized by the spreading coefficient,

$$S = \gamma_{sv} - \gamma_{sl} - \gamma_{lv}$$

positive values of S corresponding to the complete wetting. For $\gamma_{sv} - \gamma_{sl} < \gamma_{lv}$, the value of S can be found from the contact angle,

$$S = \gamma_{lv}(\cos \theta - 1)$$

and normally is negative.

Since there is no reliable method for measuring the surface energy of a solid substrate, it is advisable to carry out determination of the critical surface tension instead. A standard

procedure for determination of the critical surface tension of a solid substrate is as follows: Contact angles between the substrate and a number of test liquids with various surface tensions are measured, and the results are plotted in the contact angle vs. surface tension coordinates (see Figure 3). The plot is extrapolated to the zero contact angle, which from a thermodynamic viewpoint is equivalent to the condition of complete wetting. Any liquid with a surface tension lower than the critical surface tension of the substrate will spread over its surface and there will be a strong adhesion between the substrate and the liquid film. This also holds true for inks.

To investigate specific aspects of ink-paper interaction, the following physico-chemical methods were used:

- XPS analysis
- Profilometry

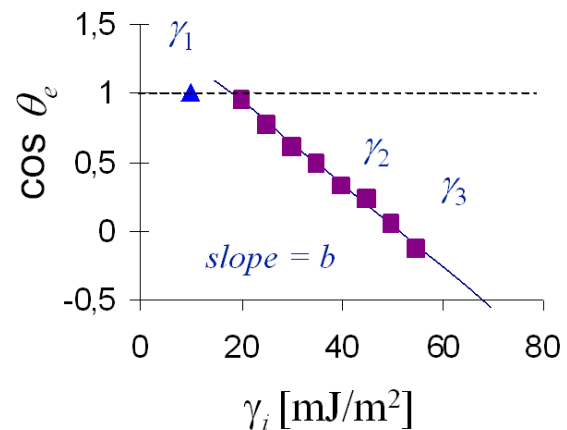


FIGURE 3.3.1 Determination of the critical surface tension of a solid substrate from wetting tests.

- Dynamic contact angle measurements
- Surface energy decomposition and critical surface tension measurements

X-Ray Photoelectron Spectroscopy (XPS) also known as Electron Spectroscopy for Chemical Analysis (ESCA) can be used to analyse elemental composition of a thin surface layer of printing substrates. The principle of XPS is in short explained below.

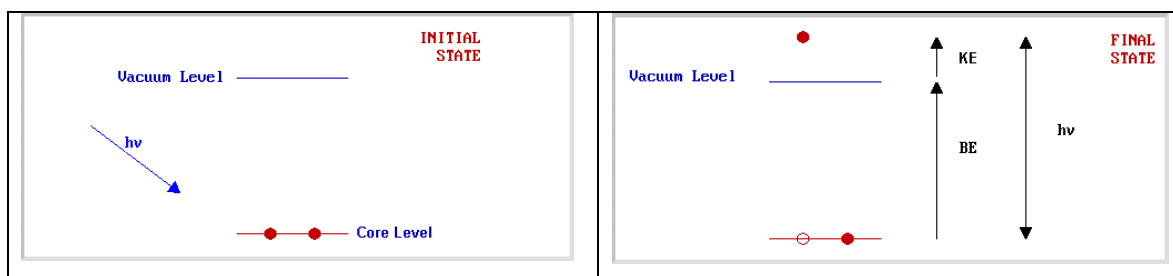


FIGURE 3.3.2 The principle of XPS. By irradiating the sample with X-rays (Mg $K\alpha$ radiation : $h\nu = 1253.6$ eV or Al $K\alpha$ radiation : $h\nu = 1486.6$ eV), core level electrons of constituent atoms are knocked out and their kinetic energy quantified.

Since each element has a unique pattern of energy levels occupied by electrons, the XPS spectrum can be used to identify chemical elements present in the surface layer. In a high-resolution mode, the oxidation states of constituent atoms can be differentiated, too. YKI has an ESCA AXIS-HS instrument from Kratos Analytical.

Surface topography of printing substrates can be studied by interferometric profilometry. ZYGO NewView 5010 profilometer available at YKI is a state-of-the-art instrument that allows one to reconstruct a digital image of the surface profile using the principle of white light interferometry. The instrument analyses interference between two beams of the light, one being reflected from the substrate and another from an internal reference surface. The principle of how the profilometer works is illustrated in Figure 3.3.3:

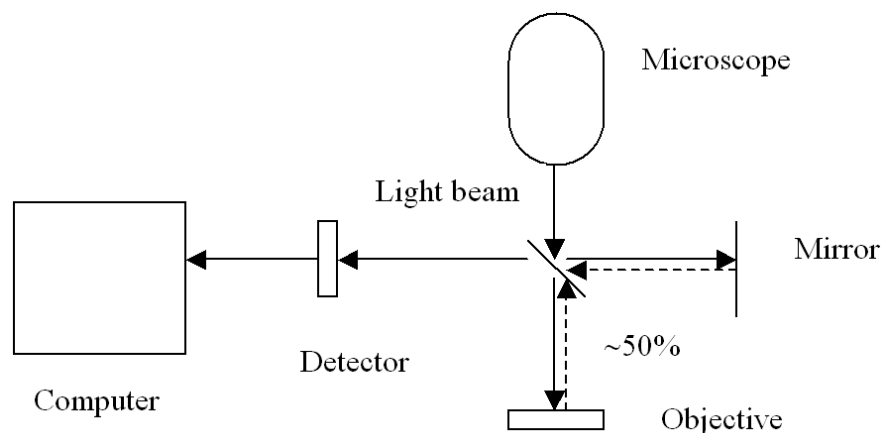


FIGURE 3.3.3 The work principle of the profilometer. The light beam from the microscope hits a filter and a mirror. About 50 % of the light is reaching the sample while the other part is hitting another mirror, which reflects the light and returns it to the detector

together with the light which has reached the sample. From the detector it goes to the computer where the picture of your sample is displayed.

The real power of the NewView system is in its MetroPro analysis and control software. The probe is scanned by vertically moving the objective with a piezoelectric transducer (PZT). As the objective moves, a video system captures intensities at each camera pixel. The maximum resolution is 307200 pixels per image. The grabbed images are displayed on a video monitor. The vertical resolution is of the order of 0.1 nm over a range of 100 μm . The lateral resolution varies depending on the optics and is about 2.7 μm when scanning an area of approx. 3.5 by 2.6 μm , or 0.9 μm over an area approx. 0.9 by 0.65 μm . When the so-called "stitching method" is used, the lateral range is extended allowing areas as large as 1 by 1 cm to be imaged and analysed without compromising the resolution. This provides an excellent means of obtaining statistically sound evaluations of the surface topography over macroscopic areas. The instrument can also be used to quantify the surface roughness.

Drop absorption and dynamic contact angle measurements are done using the Dynamic contact angle and Absorption Testers, models 1100 and 1129 DAT, from Fibro Systems AB. These devices give dynamic measures of the drop base, volume and height, as well as the contact angle with a time resolution of 10 ms. The measurements were started when the drop had been formed on the tip of a syringe. The drop was applied on the surface by a short stroke from an electromagnet. The time between the drop formation and the stroke of the electromagnet can be varied in order to study effects of surface pre-equilibration (see Figure 4). Experiments are performed under controlled humidity and temperature. The drop volume can be varied from 0.2 up to 5 μl .

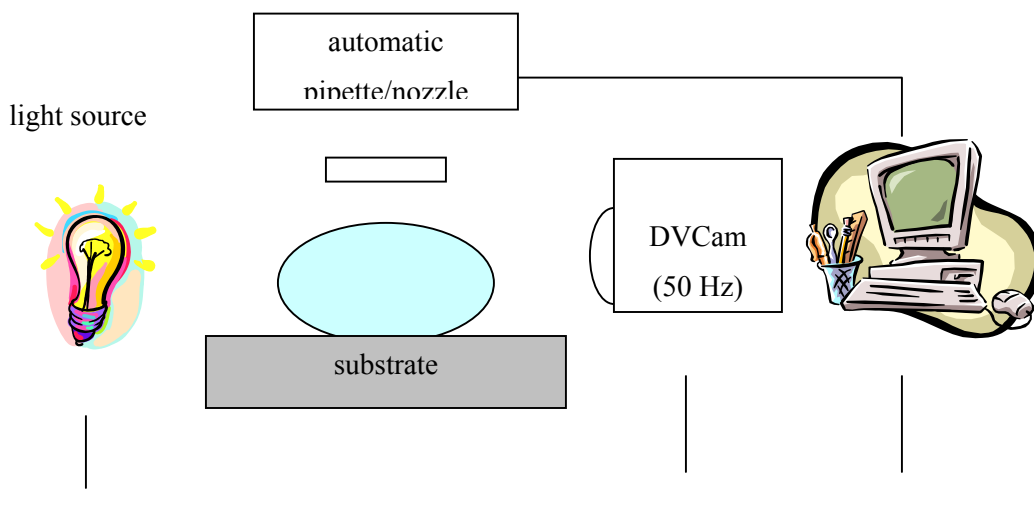


FIGURE 3.3.4 The operation principle of the dynamic contact angle and absorption tester. When applying an ink drop to a substrate, a sequence of images of the drop is being captured and the images are digitally processed using special software.

A typical example is shown in Figure 3.3.5.

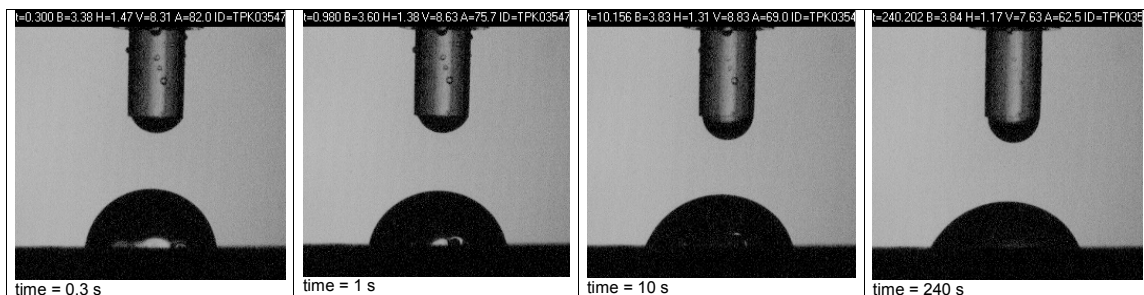


FIGURE 3.3.5 Penetration of a water drop into AKD/rosin-sized packaging board.

Thereby, the information about the contact angle, drop volume, and drop spreading diameter is retrieved.

3.3.3 Dynamic Interactions

Ink jet printing sets even stricter demands on the printing material, because the image is created directly onto the surface of paper, usually using solvent-based inks. The print quality will decrease dramatically, if ink flows on the surface of coated paper or spreads in the capillary network of uncoated paper.

These phenomena are especially crucial in high-speed ink jet printing where there is no time for evaporation of solvent. A better knowledge of the basic mechanisms of the dynamic interaction between ink and paper is needed to produce more reliable and appropriate quality specifications for printing surfaces. A unique approach to this problem is the laboratory-scale testing environment developed by VTT Information Technology for the high-speed imaging of ink jet drops. The impact, spreading, absorption and drying of the ink droplets on the samples can be observed and analysed in this testing environment on a time scale of milliseconds up to several minutes. Differences in spreading dynamics between paper grades can be noticed immediately after drop impact. In the absence of any other method to detect these high-speed phenomena, this research environment has proven to be a precise tool for the development of ink jet printing materials, inks and printers.

3.4 Full Scale Printing Trials

3.4.1 Test Procedure

Ink-jet printability was tested with Agfa testrig. Xaar's standard 360 dpi printheads were used. Print samples were held flat on a thin metal shuttle that runs across the heated platen, the temperature of which was held in 40 °C. The testrig is able to print either dot images or colour stripes.

- Dot images were printed with one colour in each series. Average dot sizes were measured from these images.
- Colour stripes were first printed at fixed resolution (360 dpi) with constant print angle and firing frequency (60 ° and 1764).
- Based on measured average dot sizes the resolution of samples to achieve full coverage was calculated. Print angle and firing frequency were also calculated. If this full coverage angle differed from 60 °, printings were done using also these settings.

Test printings are based on Xaar's test procedures.

During printings drying time was evaluated visually. Some approximate values were written down. Bleeding behaviour can be seen in printed samples where two colour stripes are overlapping each other. Optical density values were measured.

3.4.2 Print Quality Measurement

The print quality was evaluated using optical density measurements and visual comparison tests. The results are presented in Tables 4.4.1 and 4.4.2. The optical density of three dark areas were measured and an average was calculated. Each area was measured three times. In visual comparison cartons were compared with each other. Cloth, polyester and vinyl were compared with each other. The test persons had to rank the samples based on the overall visual quality.

3.5 Statistical Methods

Statistical analysis is usually applied to the results in order to estimate their confidence limits. In the case of a normal distribution (Gaussian distribution function) a variable X can be expressed by its mean value $\bar{X}$ and its confidence interval λ :

$$X = \bar{X} + \lambda_p s$$

where $\bar{X} = \frac{1}{N} \sum_{i=1}^N X_i$ is the mean value of X

$$s = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (X_i - \bar{X})^2}$$
 is the standard deviation of X

p is the selected confidence level, e.g. 95%, 99% or 99,9%.

λ is the relative confidence interval: $\lambda_{95} = 1,96$, $\lambda_{99} = 2,60$ and $\lambda_{99,9} = 3,3$

In case of a limited number of samples, the confidence interval is better expressed by means of a t-distribution, which allows for more stochastic variations in the variable:

$$X = \bar{X} + t_p s$$

where t_p is the relative confidence interval of the t-distribution at the confidence level p.

The level of significance for a t-test, depends on the number of observations, i.e. the degree of freedom in the test, as can be seen in Figure 3.5.1.

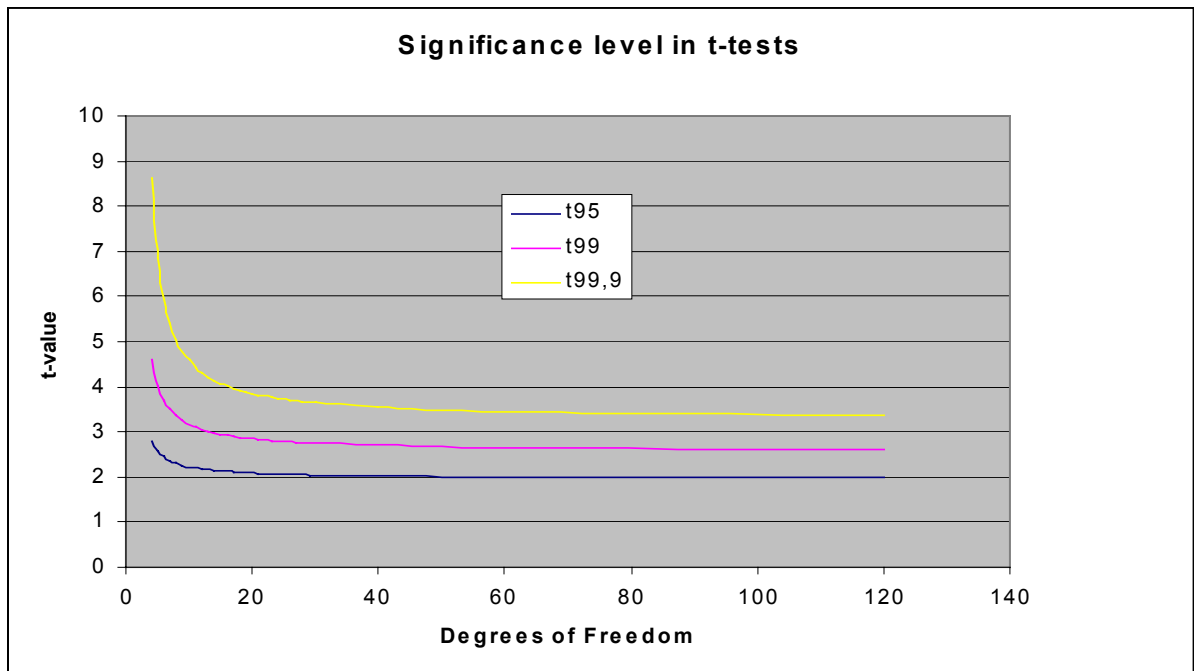


Figure 3.5.1 Significance level as a function on Degree of freedom in a t-test.

In the same way the statistical significance of the difference of the measured mean values of two test series can be estimated in the case of a normal distribution by the function

$$\lambda = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{S_1^2/n_1 + S_2^2/n_2}}$$

or in the case of a t-distribution by

$$t(n_1 + n_2 - 2) = \frac{\overline{X}_1 - \overline{X}_2}{\sqrt{n_1 s_1^2 + n_2 s_2^2}} \sqrt{\frac{n_1 + n_2 - 2}{1/n_1 + 1/n_2}}$$

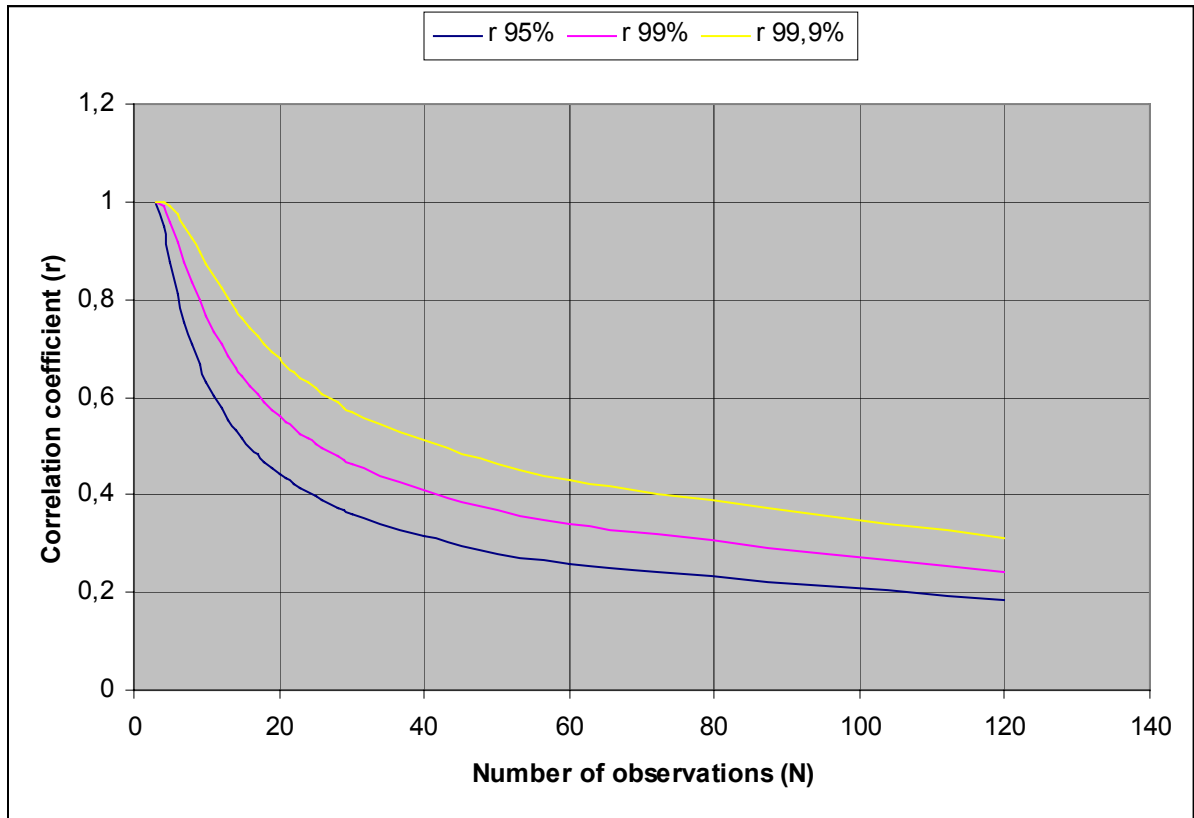
The linear correlation between two variables X and Y can be tested using the correlation coefficient r

$$r = \frac{\sum_{i=1}^N (X_i - \overline{X})(Y_i - \overline{Y})}{\sqrt{\sum_{i=1}^N (X_i - \overline{X})^2 \sum_{i=1}^N (Y_i - \overline{Y})^2}}$$

The correlation coefficient always takes values between -1 and +1, where +1 stands for a totally positive correlation, -1 for a totally negative correlation, and r = 0 for no correlation at all. The statistical significance of the correlation coefficient depends on the number of observations N, and can in turn be tested by the help of a t-test:

$$t(n-2) = \frac{r}{\sqrt{1-r^2}} \sqrt{n-2}$$

The significance level of the correlation coefficient depends on the number of observations as follows (Figure 3.5.2):



When studying a multivariable process models can sometimes be a useful tool to depict the interactions between one dependent variable and one or more independent variables. The simplest model of this kind is the linear regression model

$$y = a_0 + \sum_{j=1}^m a_j x_j + z$$

where a_j are regression coefficients

x_j are independent variables

y is the dependent variable

z is the residual term

In the linear regression analysis the residual term is minimized for the entire observation material using the "minimizing square sum" method. The linear regression analysis is an efficient tool as long as there are not too strong correlations between the independent variables or the interactions are non-linear. In these cases, where big amounts of data have to be analyzed, more sophisticated methods – such as neural networks or fuzzy logics – have to be used.

4 Results and Discussions

4.1 The Impact of Ink Properties in Ink-Jet Printing

Evaluating the data it can be seen that the variations generally are small. Still a number of inks should be chosen for testing. The inks suggested are marked in table 3.3.1. The intention is that as large a span as possible is achieved with regard to viscosity, phase angle and surface tension.

Table 4.1.1. Summary of data

Ink Code	ρ Density [g/ml]	η Viscosity [mPas]	ΔE Phase angle	γ Surface tension [mN/m]	Particle size distribution peak	Particle size range	Particle size 90%
<i>SB-M1</i>	0,9783	17,6	87,2	29,8	0,36	0,17-0,78	<0,49
SB-M2	0,9331	11,3	87,8	28,1	0,36	0,15-0,78	<0,67
SB-M3	0,9382	13,1	88,1	27,9	0,36	0,17-0,67	<0,58
<i>SB-M4</i>	0,9908	22,8	69,5	29,4	0,23	0,05-0,58	<0,42
SB-M5	0,9903	15,9	87,8	27,0	0,36	0,13-0,78	<0,58
<i>DS-SB-M6</i>	0,8721	13,4	87,9	33,4	0,07	0,05-0,49	<0,31
<i>OB-M7</i>	0,8643	11,9	87,3	28,0	?	?	?
OB-M8	0,8645	10,2	86,7	30,7	0,36?	0,11-0,8?	?
UV-M9	0,9369	13,8	84,9	28,7	0,27	0,05-0,67?	?

4.2 The Impact of Surface energetic Properties in Ink-Jet Printing

4.2.1 Dynamic wetting tests

The results of laboratory tests showing the contact angle and absorption dynamics of various ink-jet inks onto Ensocoat™ and Ensocup™ packaging boards are presented below in Figures 4.2.1 (a-h). Notice that PIJ inks (Epson) spread faster than TIJ inks (Hewlett Packard). It is interesting that PE-laminated Ensocup™ board demonstrates good wettability, and hence, printability, with respect to both inks.

4.2.2 Surface energy decomposition

To evaluate different components of the surface energy of the boards, contact angle measurements with three test liquids, including water, ethylene glycol and diiodmethane, were carried out (see Appendix I (a-f)). The contact angle is related to the adhesive energy, and the latter could be expressed through the surface energy components as

$$g^{(i)}(1 + \cos q^{(i)}) = 2[\sqrt{g_d g_d^{(i)}} + \sqrt{g_p g_p^{(i)}}]$$

$$(i = 1, 2, 3)$$

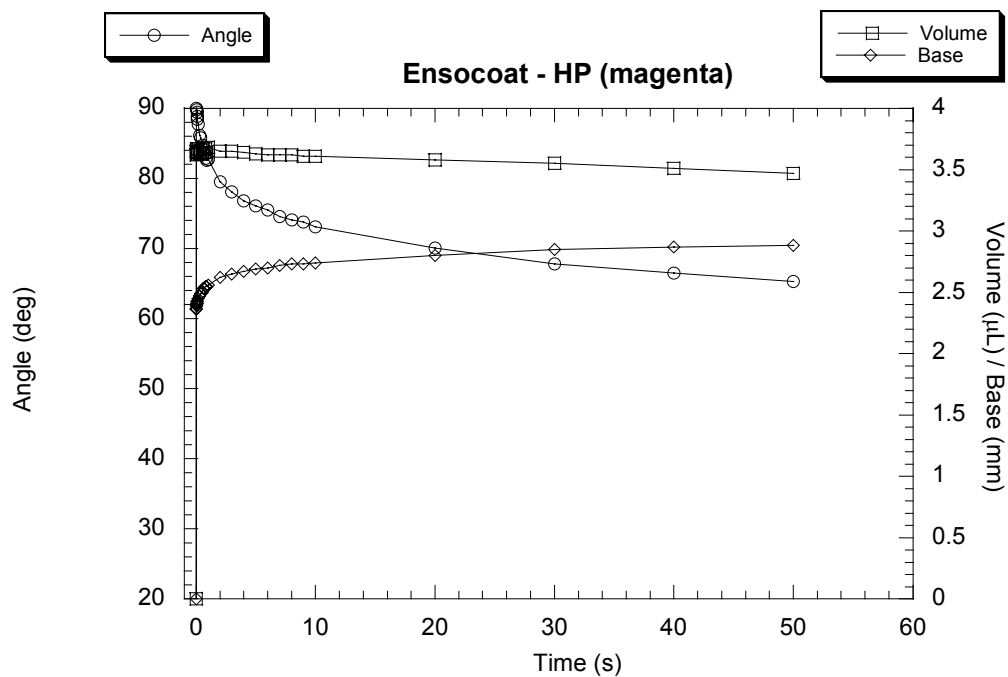
where subscripts d and p refer to the disperse and polar components of the adhesive energy, while the superscript i refers to the test liquids. The values of $\gamma^{(i)}$, $\gamma_d^{(i)}$, and $\gamma_p^{(i)}$ for the test liquids are known from literature (see Table 4.2.1), while the values of the contact angle are directly measured. This allows one to find unknown γ_d and γ_p parameters which are characteristics of the solid surface. The results are summarized in Table 4.2.2.

TABLE 4.2.1 Surface energy components for the test liquids

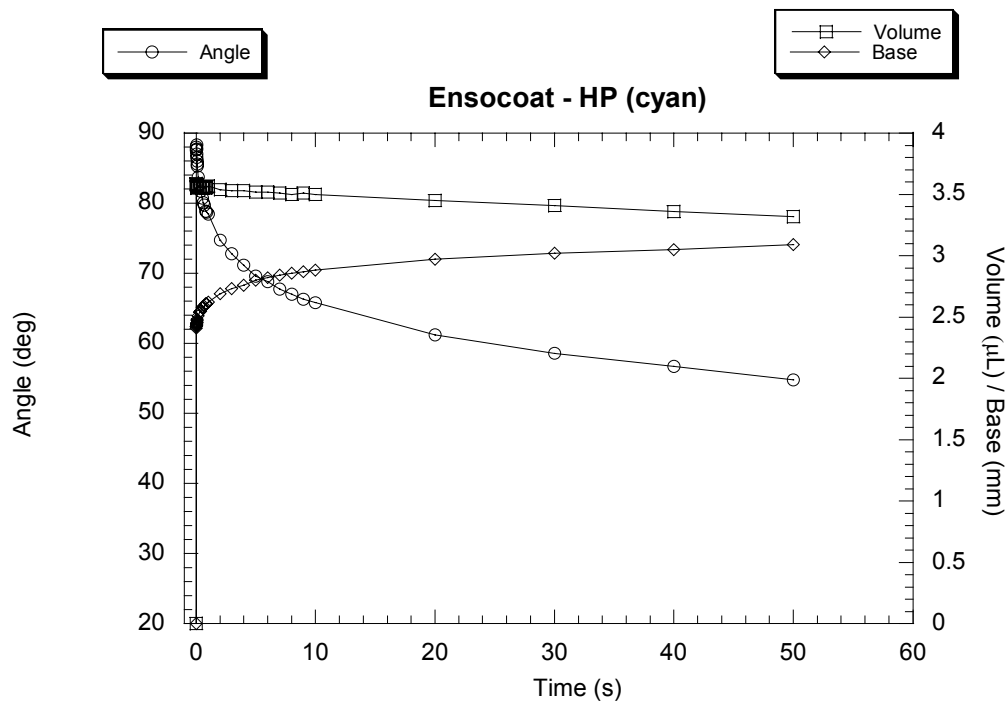
Liquid	$\gamma^{(i)}$, mJ m ⁻²	$\gamma_d^{(i)}$, mJ m ⁻²	$\gamma_p^{(i)}$, mJ m ⁻²
Water	72.8	21.8	51.0
Ethylene glycol	48.0	29.0	19.0
Diiodmethane	50.8	50.8	0.0

TABLE 4.2.2 Surface energy components for the paper substrates

Paper	Surface energy components [mJ m ⁻²]	
	Dispersive	Acid-Base
Ensocoat	28.4	0.05
Ensocup	36.6	2.5

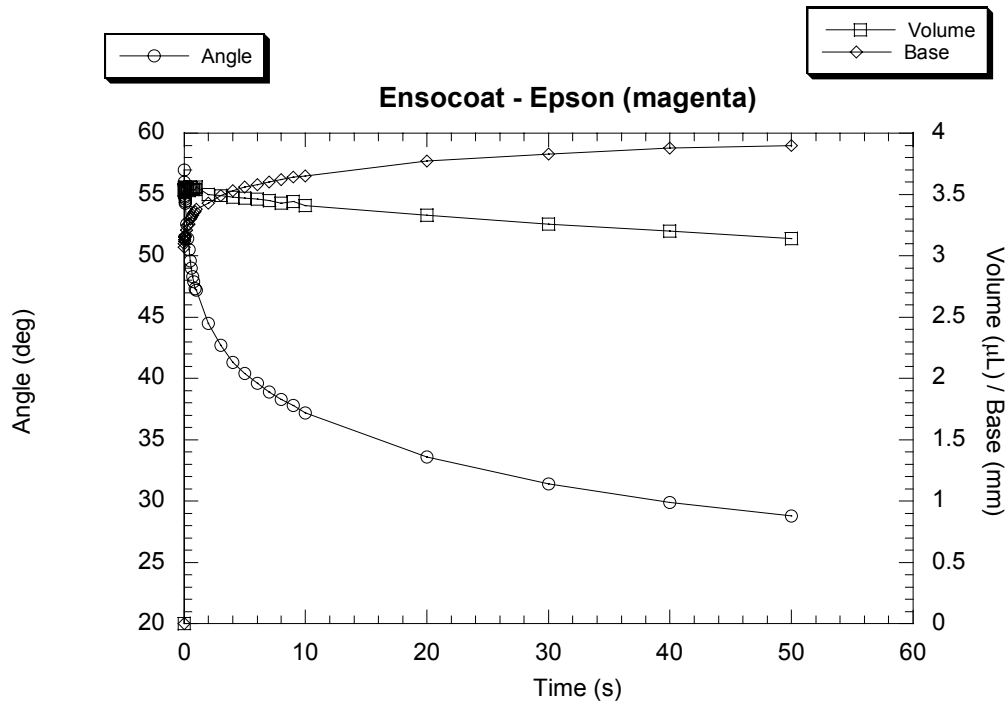


(a)

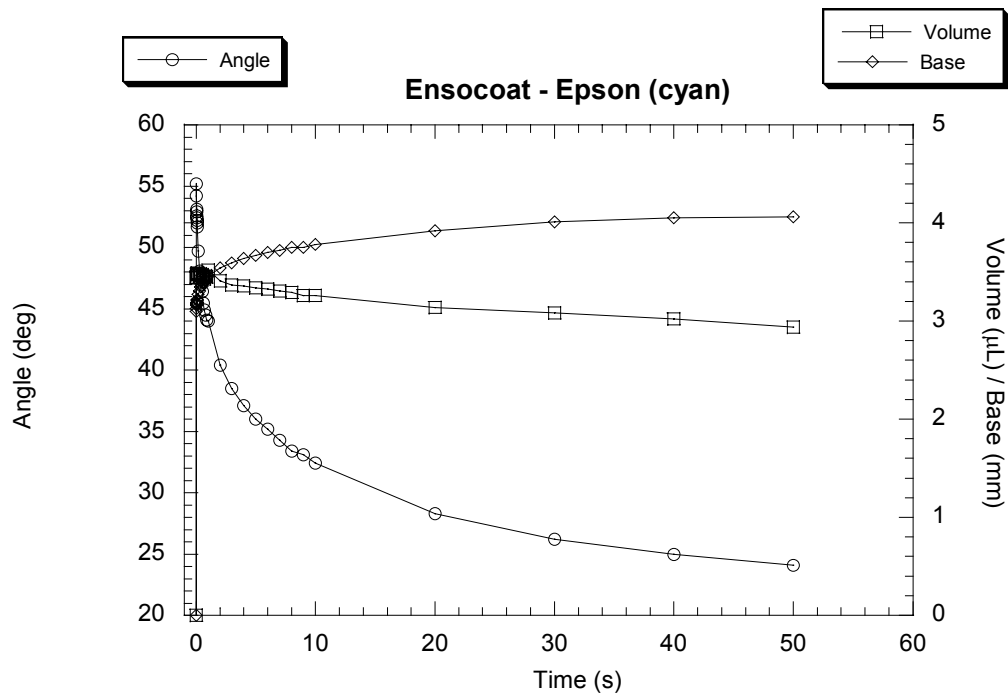


(b)

FIGURE 4.2.1 Absorption, contact angle, and spreading dynamics for drops HP and Epson ink-jet inks deposited onto the surface of Ensocoat™ and Ensocup™ packaging boards.

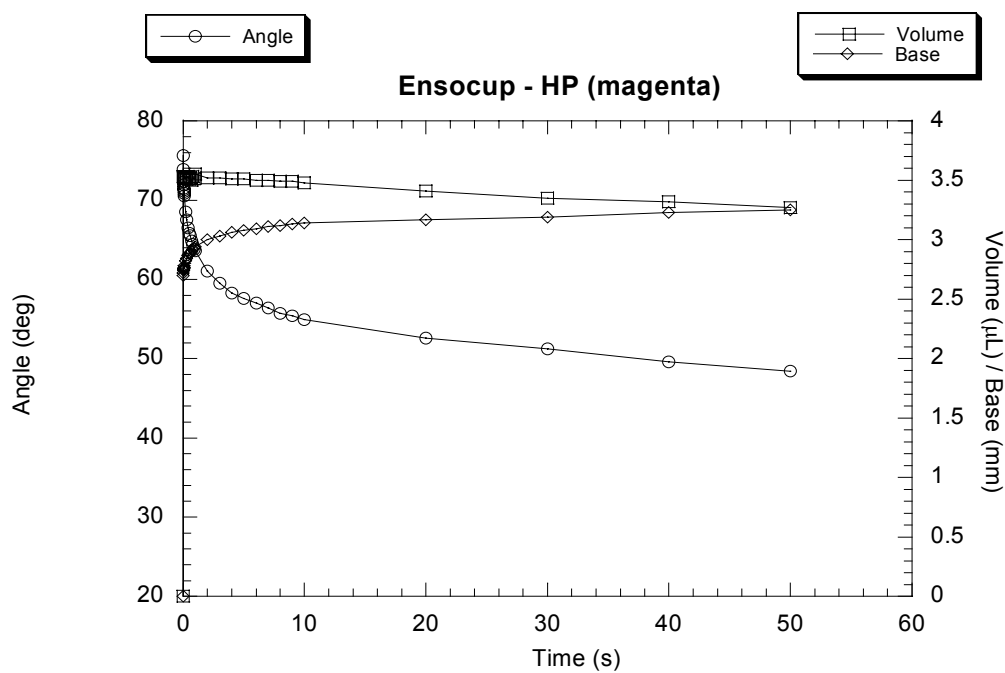


(c)

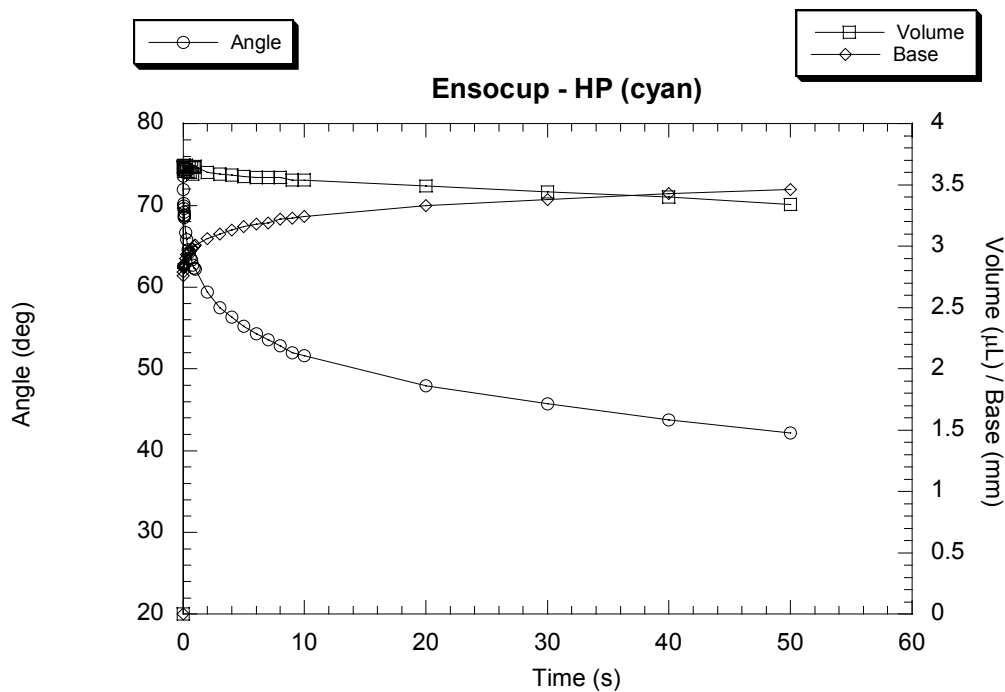


(d)

FIGURE 4.2.1 Absorption, contact angle, and spreading dynamics for drops HP and Epson ink-jet inks deposited onto the surface of Ensocoat™ and Ensocup™ packaging boards.

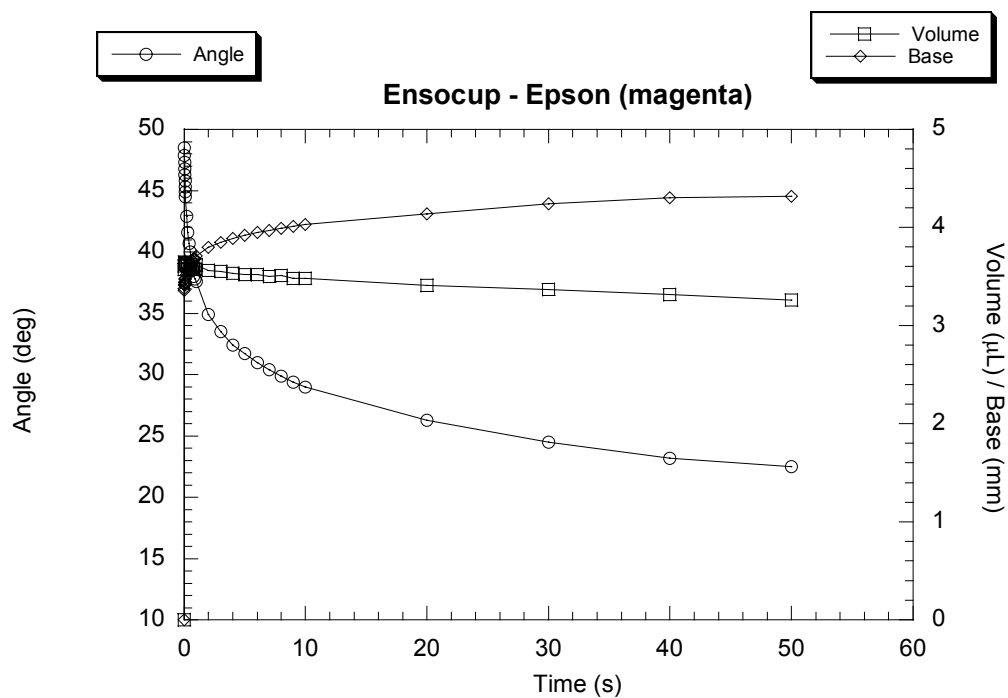


(e)

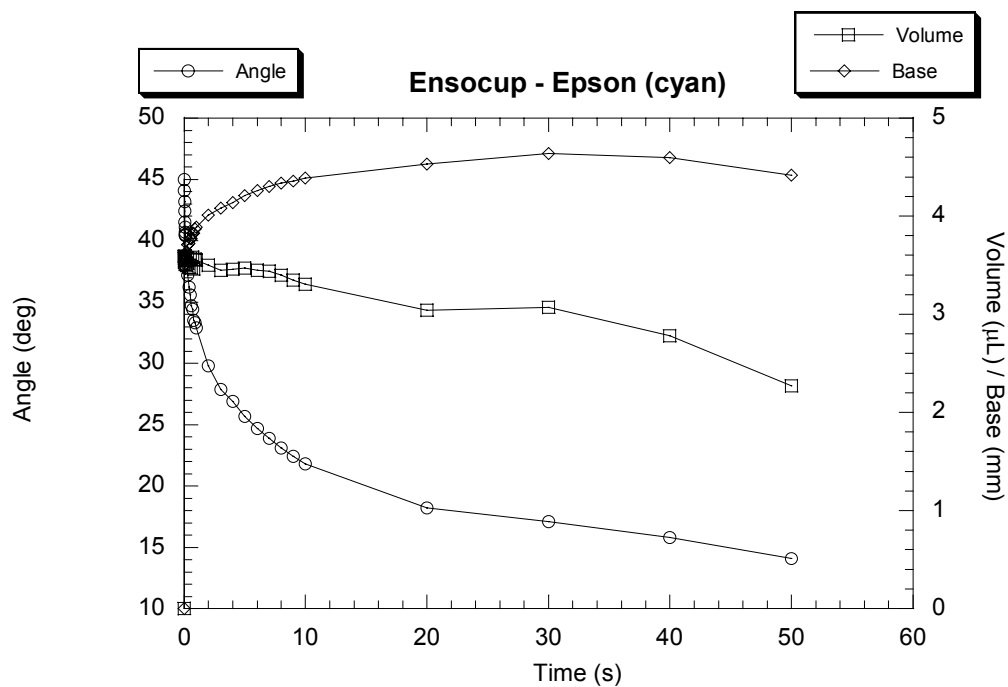


(f)

FIGURE 4.2.1 (cont'd) Absorption, contact angle, and spreading dynamics for drops HP and Epson ink-jet inks deposited onto the surface of Ensocoat and Ensocup packaging boards.



(g)



(h)

FIGURE 4.2.1 (cont'd) Absorption, contact angle, and spreading dynamics for drops HP and Epson ink-jet inks deposited onto the surface of Ensocoat and Ensocup packaging boards.

4.2.3 Profilometry

The results concerning the surface topography of analysed substrates are summarised in Figures 4.2.2-4.2.6. The data are self-explanatory. The only comment to be made is that the surface of PE-laminated board (Ensocup™) seems to contain a significant amount of small holes.

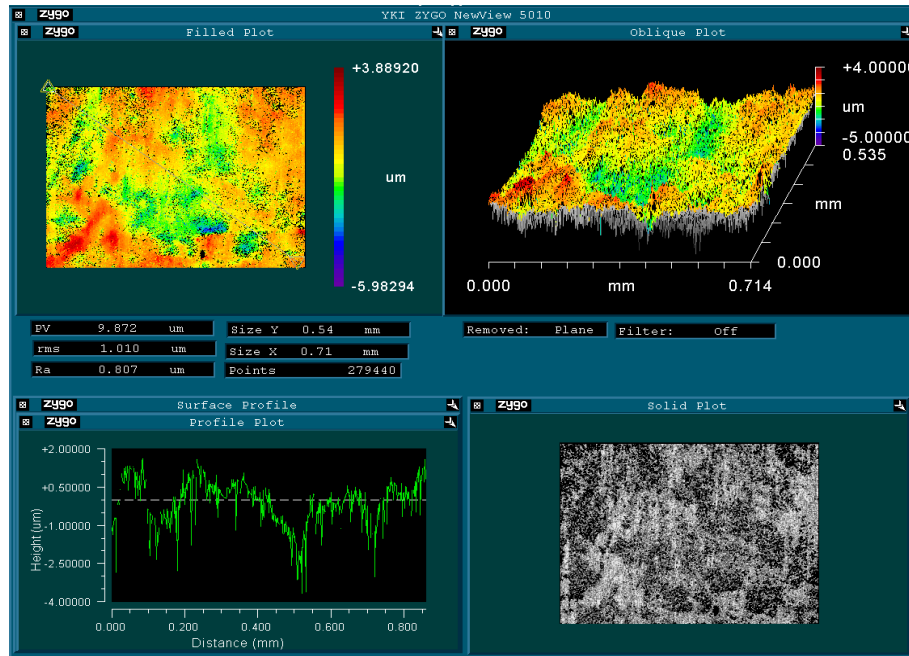


FIGURE 4.2.2 Surface profile of Ensocoat™ paperboard on the coated side.

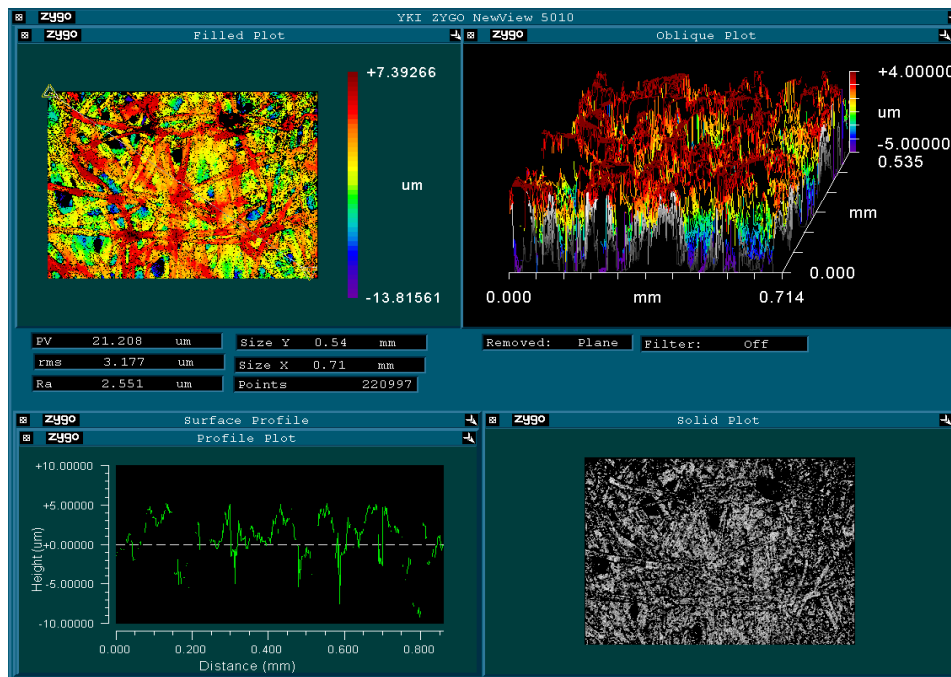


FIGURE 4.2.3 Surface profile of Ensocoat™ paperboard on the uncoated side.

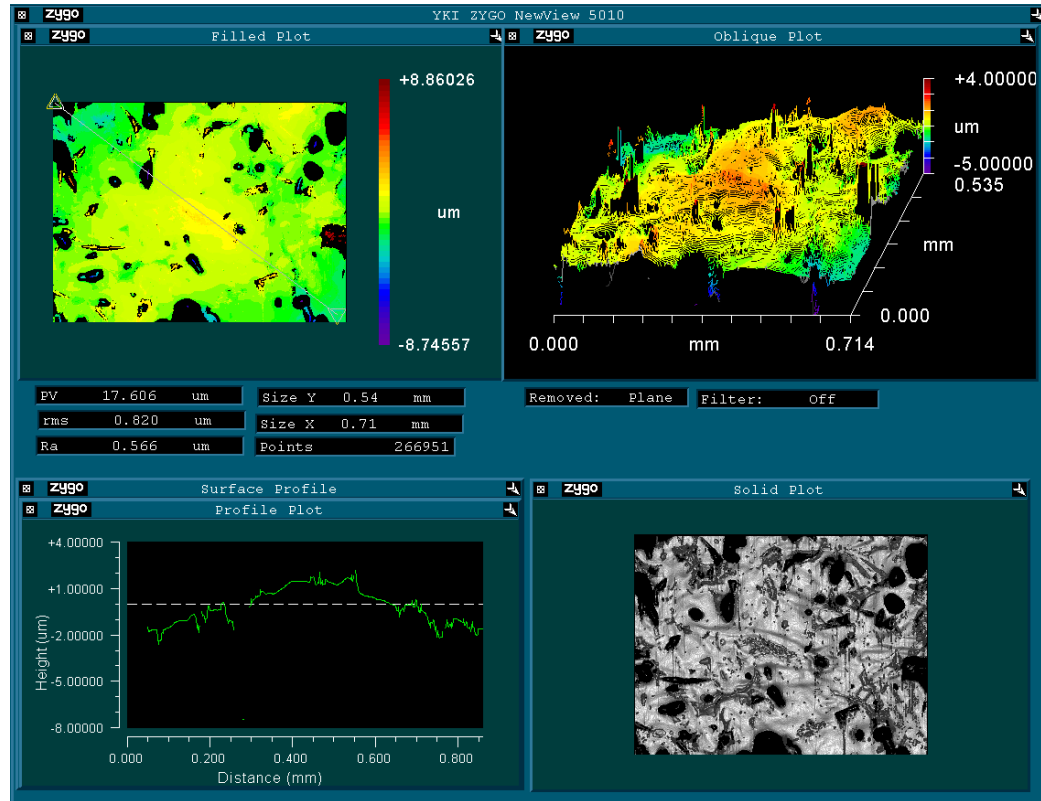


FIGURE 4.2.4 Surface profile of Ensucup™ paperboard on the glossy (PE-laminated) side.

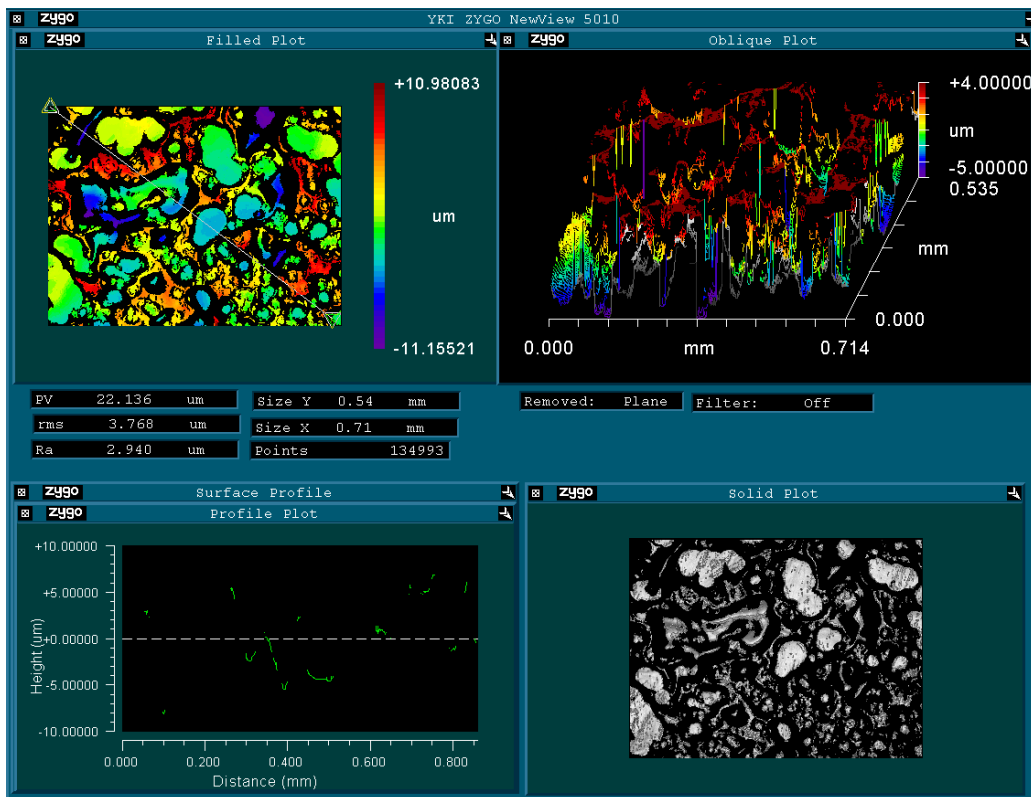


FIGURE 4.2.5 Surface profile of Ensucup™ paperboard on the matt side.

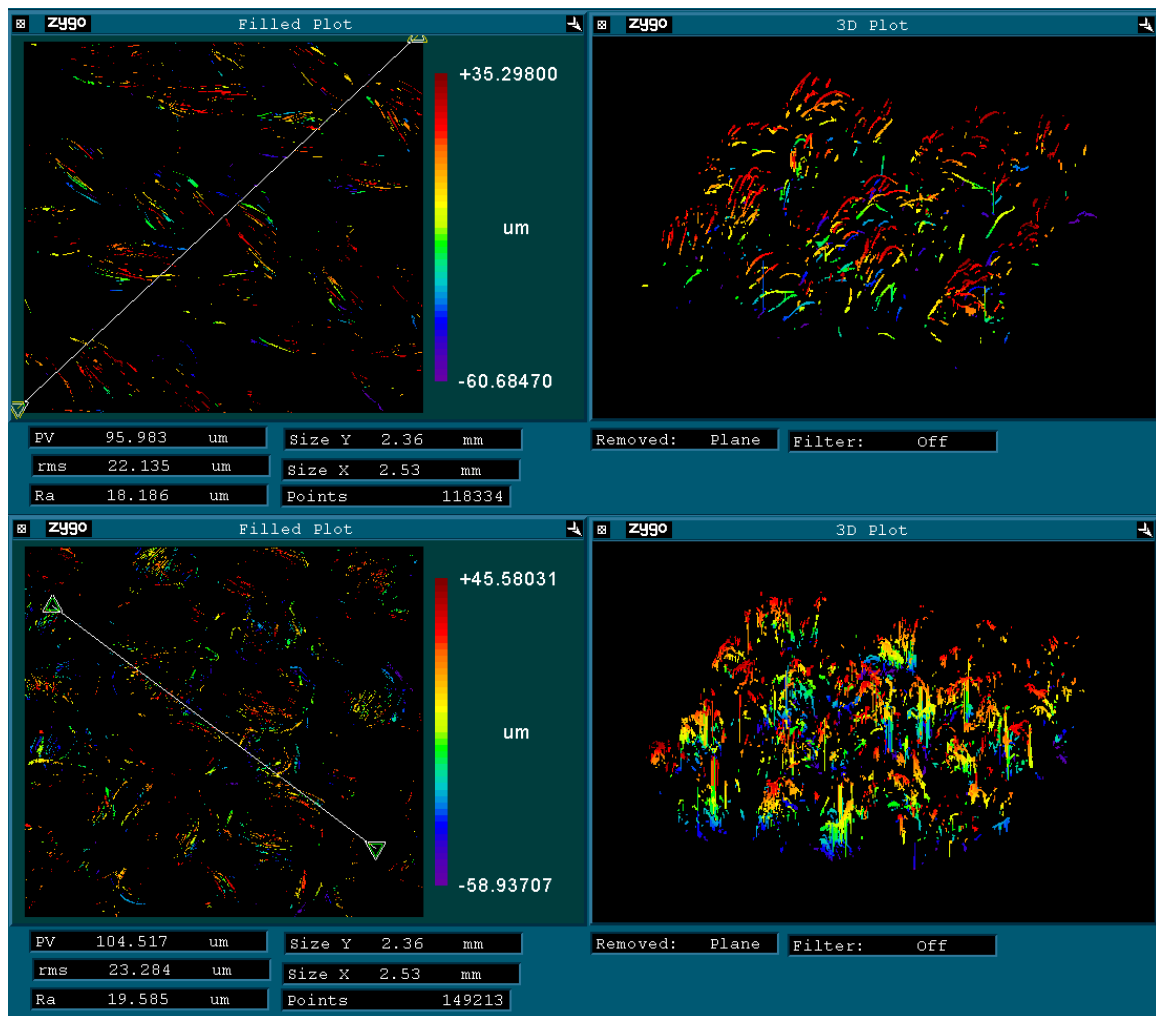
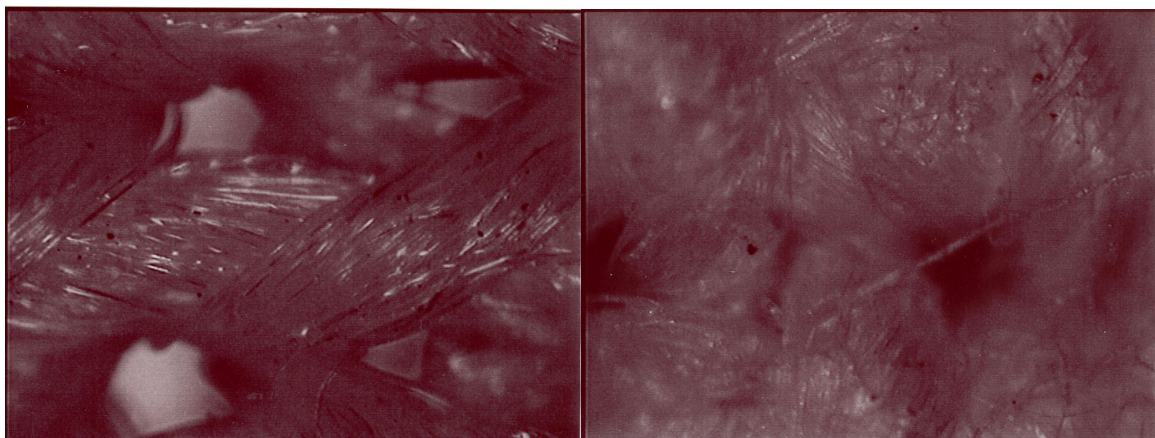


FIGURE 4.2.6 Surface profile of printing substrates provided by Big Image Systems: top - substrate 1, bottom - substrate 2. These substrates represent fibrous sheets with a thickness of about 1 mm. The material is plied from synthetic yarn (fibre diameter $\sim 10 \mu\text{m}$) and has a fuzzy surface (see the microscopic images below).



Fabric Substrate 1

Fabric Substrate 2

An example of the spreading dynamics observed for solvent-based inks provided by Xaar-Jet look is shown below:

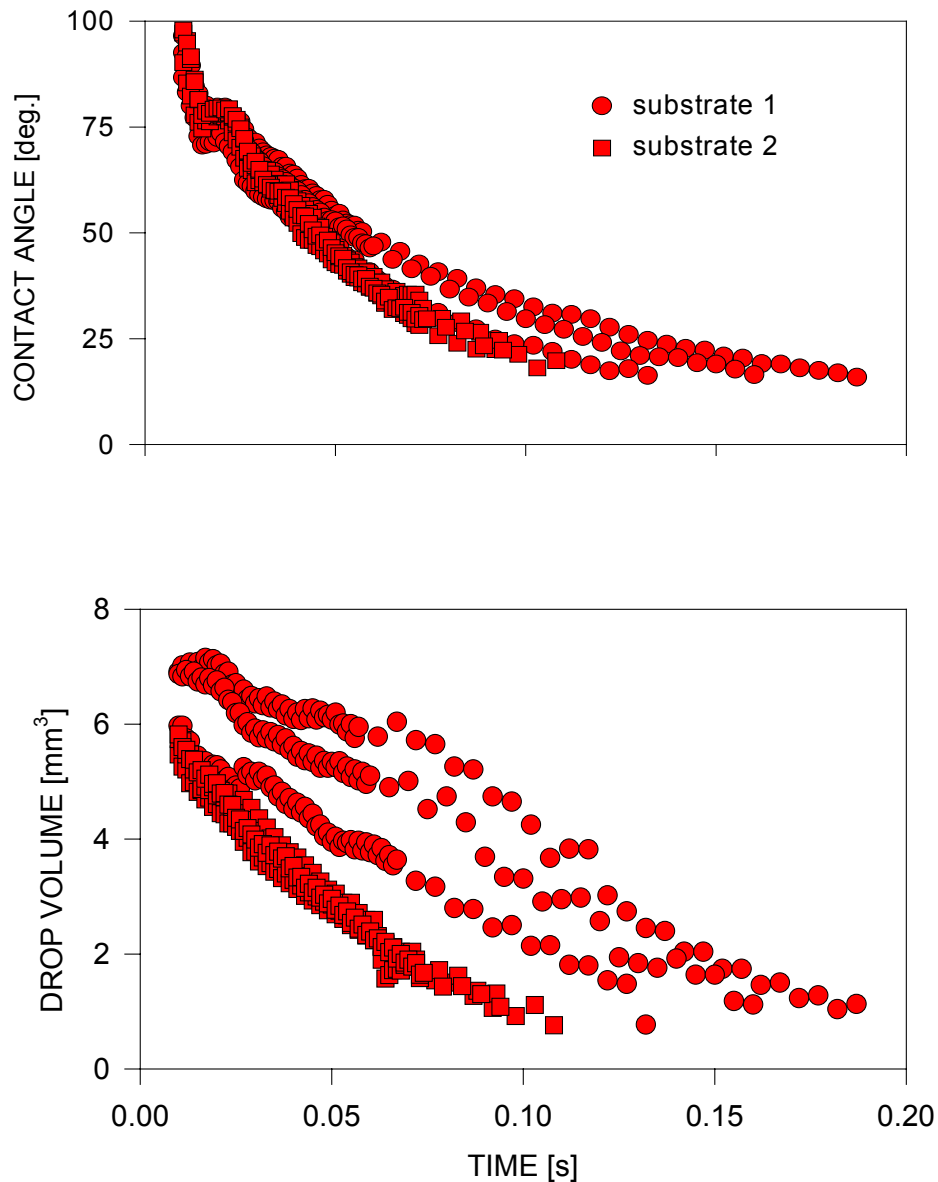


FIGURE 4.2.7 Contact angle and ink imbibition dynamics for solvent-based magenta ink (Xaar-Jet) over the synthetic woven material provided by Big Image Systems.

Wettability of the substrates with respect to the ink is similar. Since the surface is utterly rough, a significant scattering of the results is observed. Once absorbed, the ink is rather quickly set by drying and the print demonstrates outstanding water-resistance.

The whole experimental matrix contained 4 water-based ink (Epson Cyan, Epson Magenta, HP Cyan, HP magenta), 8 solvent-based pigmented inks (SB M1 - SB M8)

matched with 4 substrates (2 sorts of paper board (Ensocup and Ensocoat) and two fabric substrates). All the combinations analyzed as shown below (Table 4.2.3):

Ink	Printing Substrate			
	Ensocoat	Ensocup	Textile 1	Textile 2
HP Cyan	✓	✓	✓	✓
HP Magenta	✓	✓	✓	✓
Epson Cyan	✓	✓	✓	✓
Epson Magenta	✓	✓	✓	✓
SB M1	✓	✓	✓	✓
SB M2	✓	✓	✓	✓
SB M3	✓	✓	✓	✓
SB M4	-	-	✓	✓
SB M5	✓	✓	✓	✓
SB M6	✓	✓	✓	✓
SB M7	✓	✓	✓	✓
SB M8	✓	✓	✓	✓

✓ done; - missing

Relevant experimental data can be found in Figure 4.2.1 and in Appendix II.

4.3 Dynamic Interactions in Ink-Jet Printing

The results of the dynamic interaction tests are presented in Figure 4.3.1 for the solvent based ink and in Table 4.3.2 for the oil based ink for the five substrates (the coated samples were tested on both sides).

Proper statistical analysis was impossible to do in these test series, because the deviation between different test points were enormous. So what we did was a visual examination of the time series of the selected test points. The judgement based analysis is based on our long-time experience of the behaviour of liquids on various surfaces.

The reason for the high deviation was usually the very rough and sometimes very orientated surface structure of the samples in comparison of the size of the drop. For example, if an ink droplet hits to a loose fiber of cotton fabric it behaves totally differently than when it hits between the fibres. Also the very strong spreading tendency of the inks, depending viscosity of inks and surface energetic factors, made dots very uneven and large, even on relatively flat surfaces.

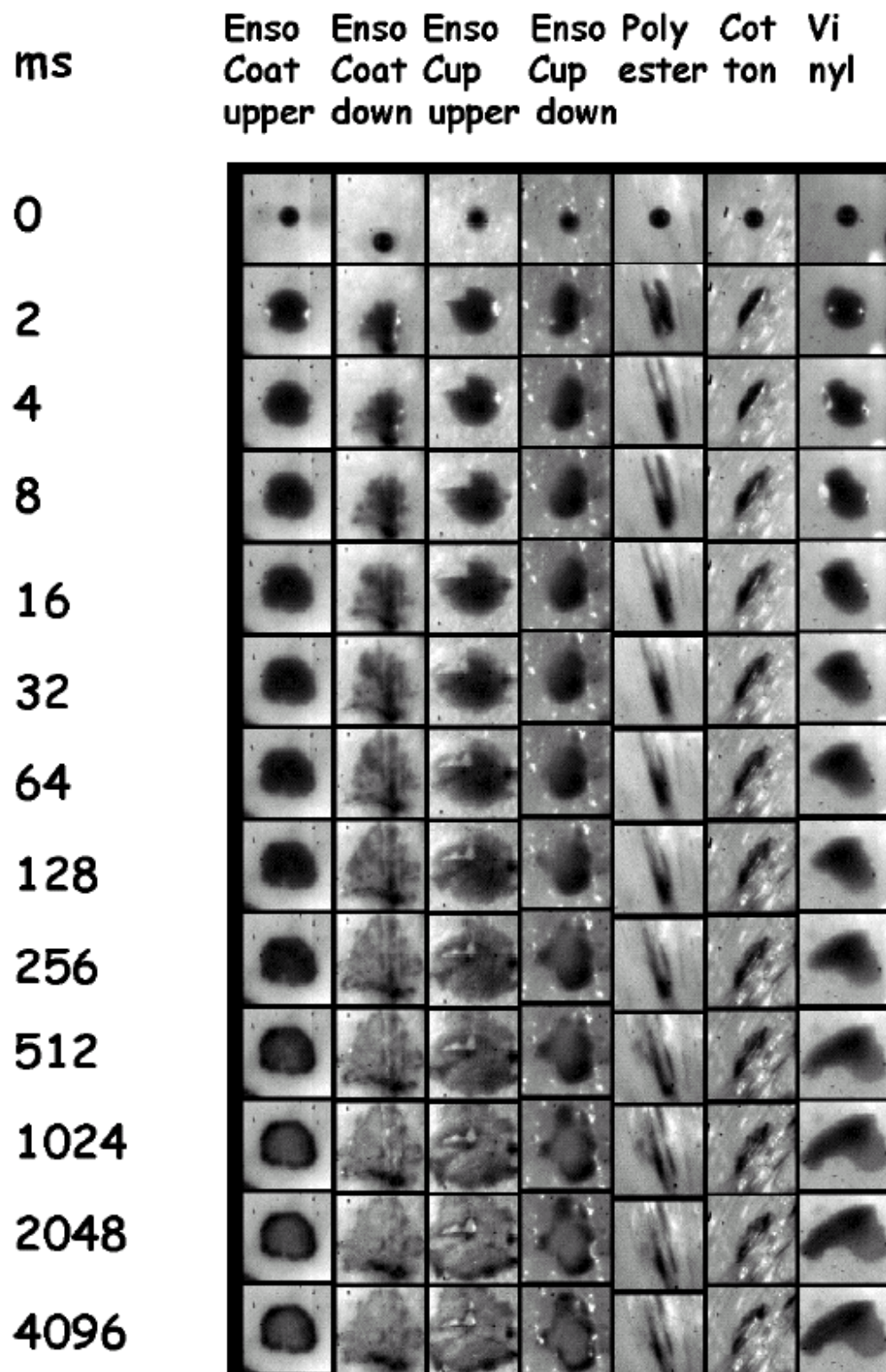


Figure 4.3.1. Ink droplet behaviour on different substrates for the solvent ink under a time span of 0...4096 ms after the contact.

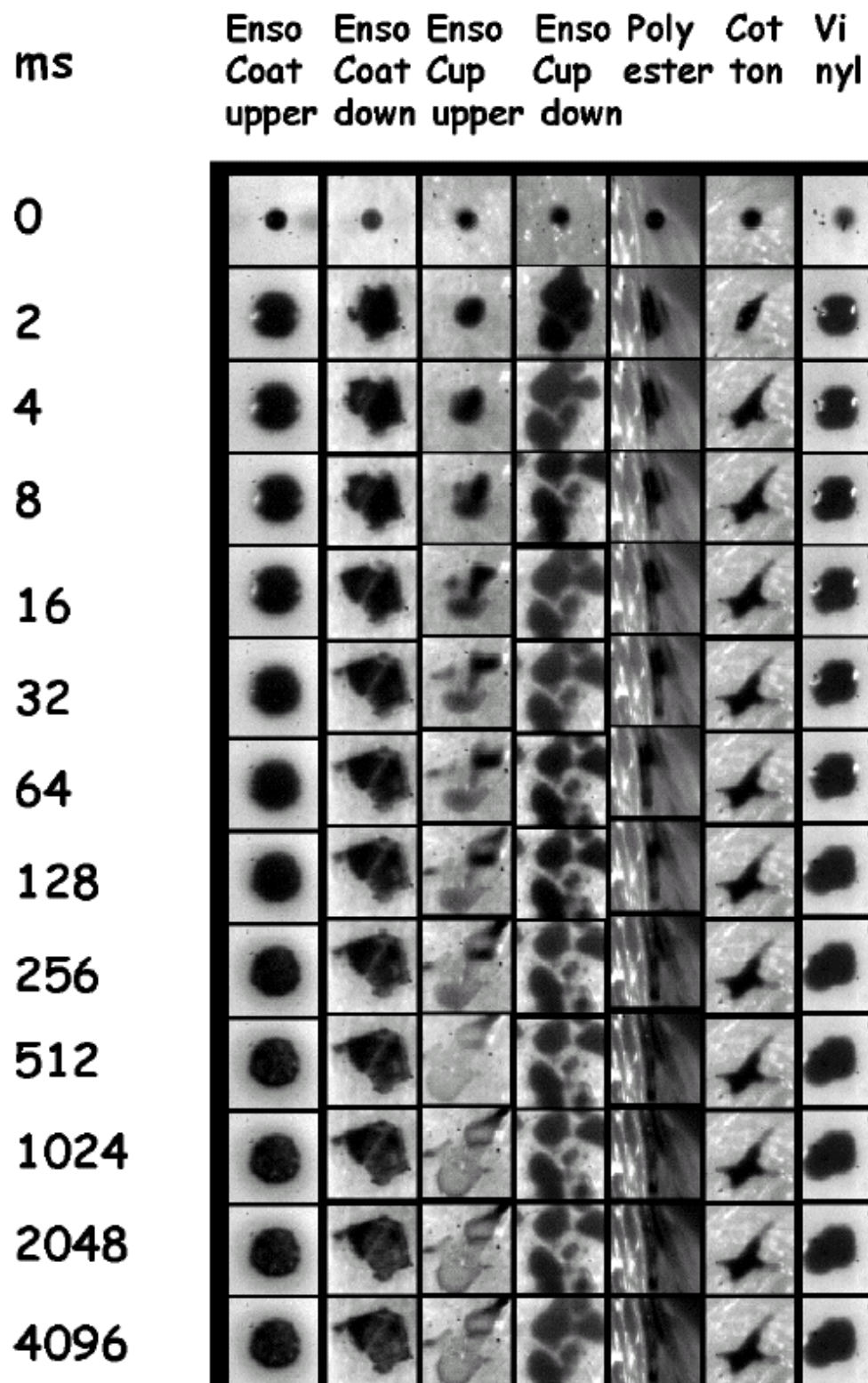


Figure 4.3.2. Ink droplet behaviour on different substrates for the oil based ink under a time span of 0...4096 ms after the contact.

These factors destroy the print quality completely, as confirmed in our visual tests, especially when we talk about high-resolution printing. But if resolution is low, which is often the case in billboard printing, the strong spreading doesn't necessarily impede as much – as long as sufficient amount of ink is added to a surface to reach the desired tone value. Of course, this approach can also lead to a bigger bleeding problem.

Only solvent based and oil based inks on different materials were analysed. The reason for this was, that the high absorption and spreading tendency made impossible to detect magenta dye sublimation ink by optical means on these very uneven materials. When graphical ink jet papers are used it is usually quite easy to analyse also magenta or even yellow dyes.

A comparison of the test samples give the following conclusions

4.3.1 EnsoCoat

When printed EnsoCoat samples are visually compared, it can easily be noticed that each paper ink combination has its distinctive finger print, even different sides of paper can be easily be identified. Usually also statistical data of negligible differences of high-quality printing papers can easily be collected by automated computer analysis. The most important part of this analysis, which cannot be visually quantified, is to obtain information of slight differences in the rate of change of these phenomena. This time, because of very unsuitable substrate and ink combinations, these analysis was neglected.

Also different inks can be distinguished, in this case the spreading is more controlled with oil based inks. Other notable information is the solvent frontier of oil based colour, which spreads to a wider area than the colour itself.

4.3.2 EnsoCupboard

Differences in the surface structure of different sides of cupboard can easily been seen. Due to this, the spreading behaviour of different inks is also different. So, by using different reference inks and other liquids – which is quite possible in our system – also differences in surface's chemimechanical structure can efficiently be determined.

4.3.3 Polyester

The behaviour of polyester is very characteristic – the long fibre network of polyester absorbs liquid very rapidly and very long and narrow dots are created. Differences between liquids are hard to see, because this very dominant mechanism.

4.3.4 Cotton

Another interesting material is cotton. Cotton repels liquid, but the furry surface structure dominates the hitting and spreading phases. This way polymorphous dots are created.

4.3.5 Vinyl

Vinyl behaves like a common, smooth plastic. If the hitting speed of a drop is high, the dot spreads during the mechanical hitting phase strongly. If the speed is low, dot spreads

by means of surface energetic powers little by little during the spreading phase. Adhesion is always a problem with smooth and dense materials.

4.4 The Formation of Ink-Jet Print Quality

The results of the quality evaluation of the full scale test prints are given in Tables 4.4.1. and 4.4.2. below.

Table 4.4.1. The visual quality of the cloth, polyester and vinyl

Material	Ink	Visual comparison ranking	Optical density	Other notes
Cloth	Solvent based	3	0.64	Dirty colours
Cloth	Oil based	5	0.56	Faded colours, banded
Polyester	Solvent based	1	1.30	Dark
Polyester	Oil based	4	0.63	Faded colours, banded
Vinyl	Solvent based	2	1.71	Surface texture visible, banded, bright colours

Solvent based inks produce darker colours than oil based inks. The overall visual quality of the solvent based samples is also estimated to be better than in oil based samples that look faded and banded. Vinyl produces the darkest colours and cloth the lightest. The surface texture of the vinyl is quite visible under the printed picture, but the colours, however, look very bright. The colours on cloth look dirty. Based on visual assessment vinyl has the best contrast and cloth the worst.

Table 4.4.2. The visual quality of the cartons. Enso1 is the top side of a two-sided PE-coated paper and Enso 2 is the bottom side. Enso 3 is the top side of a one-sided coated carton

Material	Ink	Visual comparison ranking	Optical density	Other notes
Enso1	Solvent based	4	1.68	Spread colours, no outlines
Enso2	Solvent based	3	1.49	Spread colours except yellow
Enso3	Solvent based	1	2.02	Spread colours, banded
Enso3	Oil based	2	1.07	Banded, light colours

Also on carton solvent based inks produce darker colours than oil based inks. Solvent based inks tend to spread on cartons especially on Enso1 and Enso2. Samples printed on Enso3 are banded especially when using oil based inks.

In conclusion, carton samples have lower print quality than other samples. The best material is polyester. Solvent based inks produce better image quality than oil based inks.

5 Conclusions and recommendations

It has been clearly seen, that ink jet printing sets strict demands on the printing material, because the image is created directly onto the surface of paper, usually using solvent-based inks. The print quality will decrease dramatically, if ink flows on the surface of coated paper or spreads in the capillary network of uncoated paper.

The solvent-based inks tested had some differences in flash point, which indicate that the evaporation profile was differing. The oil-based inks evaporated even more slowly. All the inks were pigmented except for one, which was a dye-sublimation ink. The printing inks have been characterised in terms of density, viscosity, phase angle, surface tension, particle size distribution, and thermo-gravimetry properties. In general the variations between the different ink-jet inks were very small. However, the thermo-gravimetric data indicated that there are some composition differences also in the solvent-based products. The oil-based products had a dry matter of about 80 wt-%, while the solvent-based have about 10 wt-% and the dye-sublimation ink has 50 wt-%.

By using high-resolution measuring equipment, the spreading and penetration of inkjet drops have been monitored for a number of common printing media including paper board and textile. The printing substrates, in their turn, have been characterized with respect to the surface energy and roughness, the two major factors determining the observed ink setting profile, ink adhesion, as well as the scuff- and rub-resistance of print.

The impact, spreading, absorption and drying of the ink droplets on the samples were observed and analysed in a testing environment on a time scale of milliseconds up to several minutes. Differences in spreading dynamics between paper grades could be noticed immediately after drop impact. However, a proper statistical analysis was impossible to do in these test series, because the deviation between different test points were too big. Instead a visual examination was performed.

The reason for the high deviation was usually the very rough and sometimes very orientated surface structure of the samples in comparison of the size of the drop. Also the very strong spreading tendency of the inks made dots very uneven and large even on relatively flat surfaces. These factors may destroy the print quality completely, especially in high-resolution printing. But if resolution is low, which is often the case in billboard printing, the strong spreading doesn't necessarily impede as much – as long as a sufficient amount of ink is added to a surface to reach the desired tone value. Of course, this approach can also lead to a bigger bleeding problem.

Solvent based inks produce darker colours than oil based inks. The overall visual quality of the solvent based samples is also estimated to be better than in oil based samples that look faded and banded. Vinyl produces the darkest colours and cloth the lightest. The surface texture of the vinyl is quite visible under the printed picture, but the colours, however, look very bright. The colours on cloth look dirty. Based on visual assessment vinyl has the best contrast and cloth the worst.

In conclusion, carton samples have lower print quality than other samples. The best material is polyester. Solvent based inks produce better image quality than oil based inks.

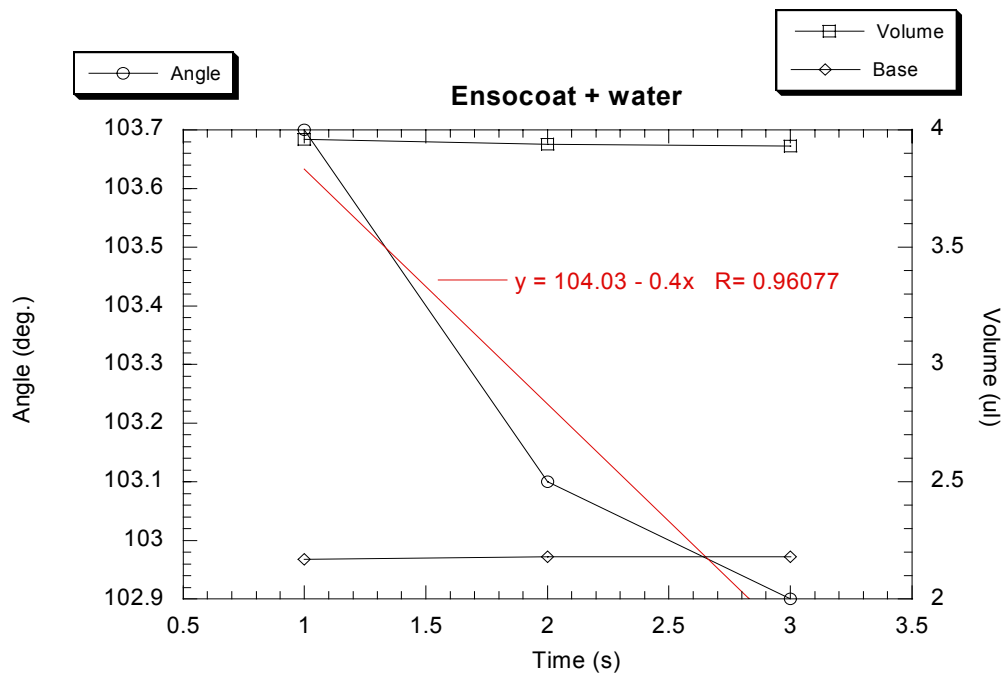
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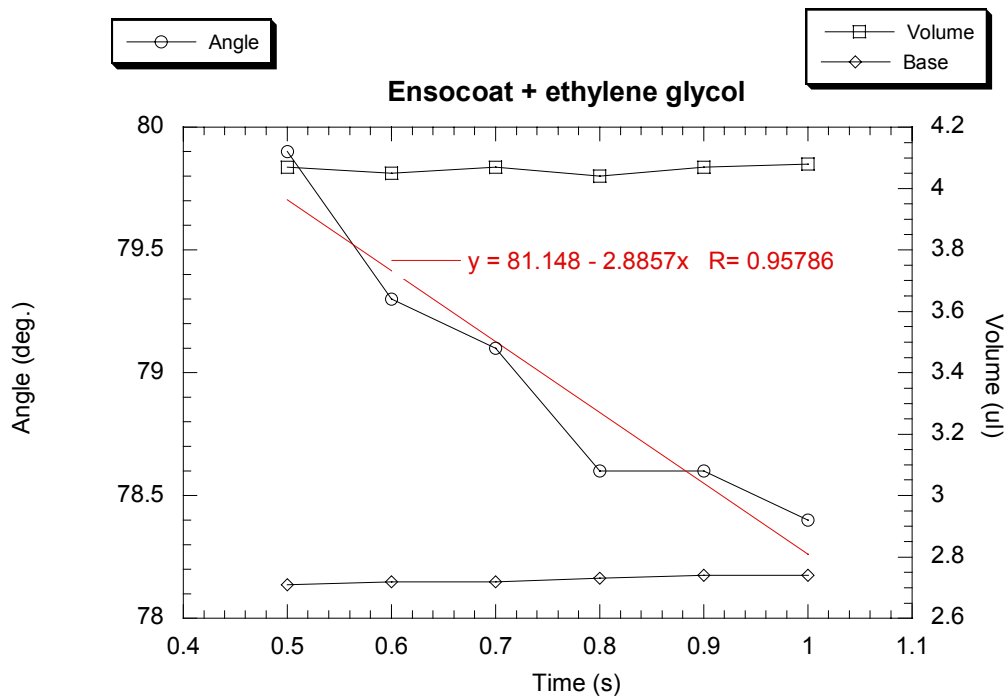
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Appendix 1: Contact angle measurements

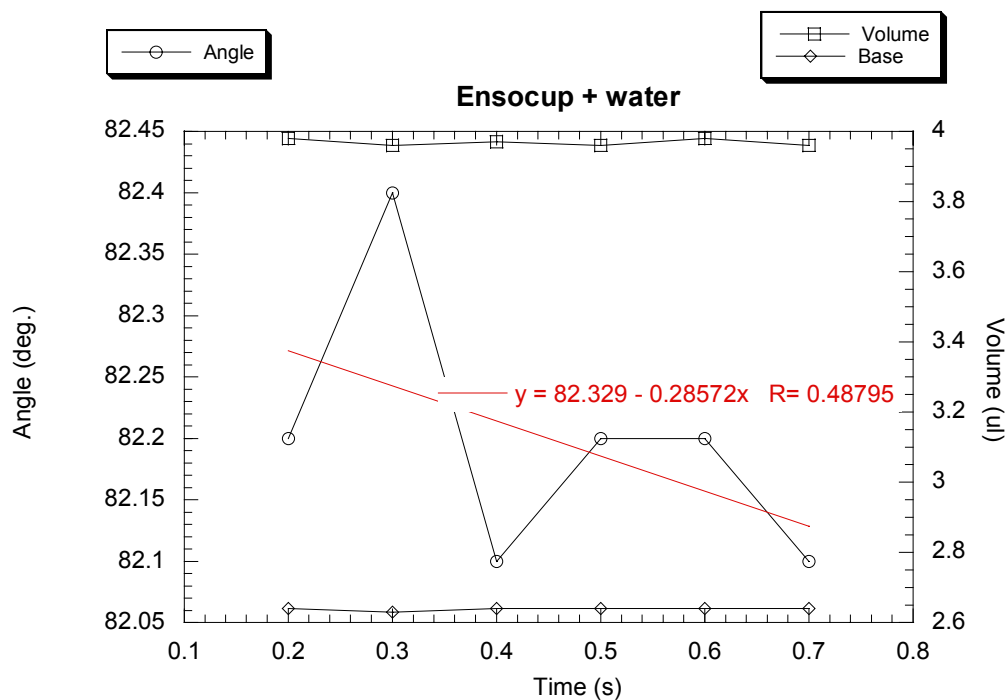
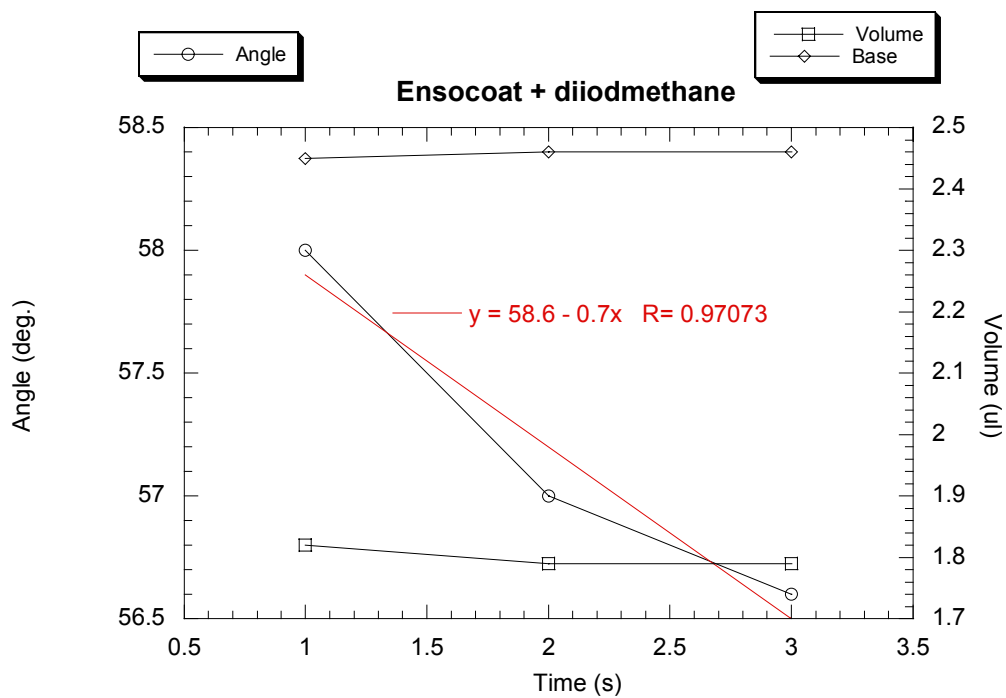


(a)

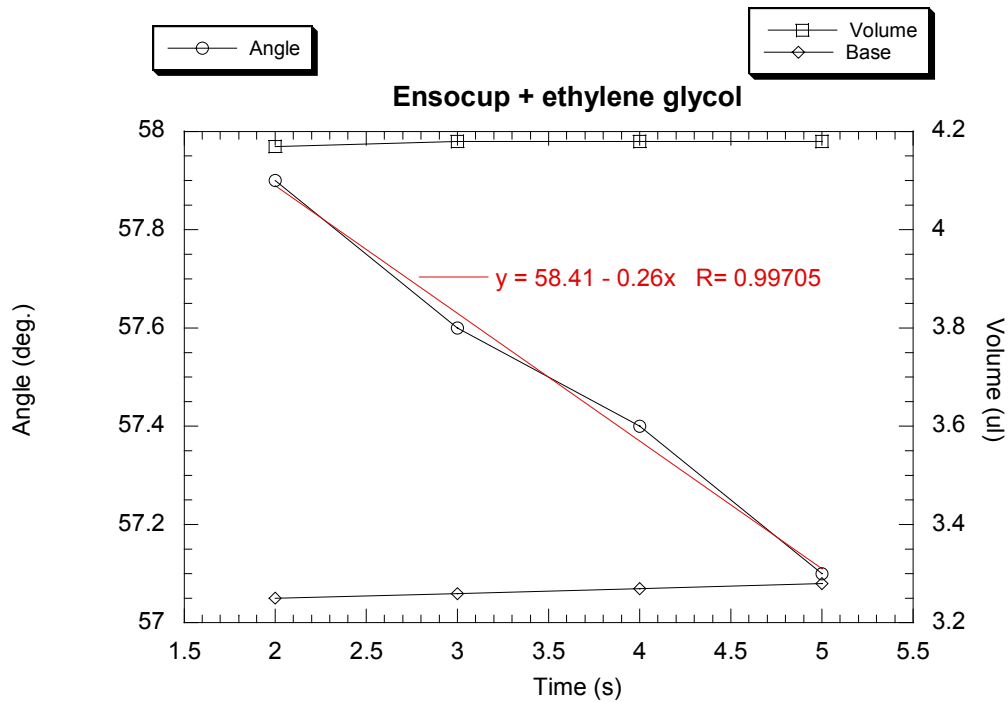


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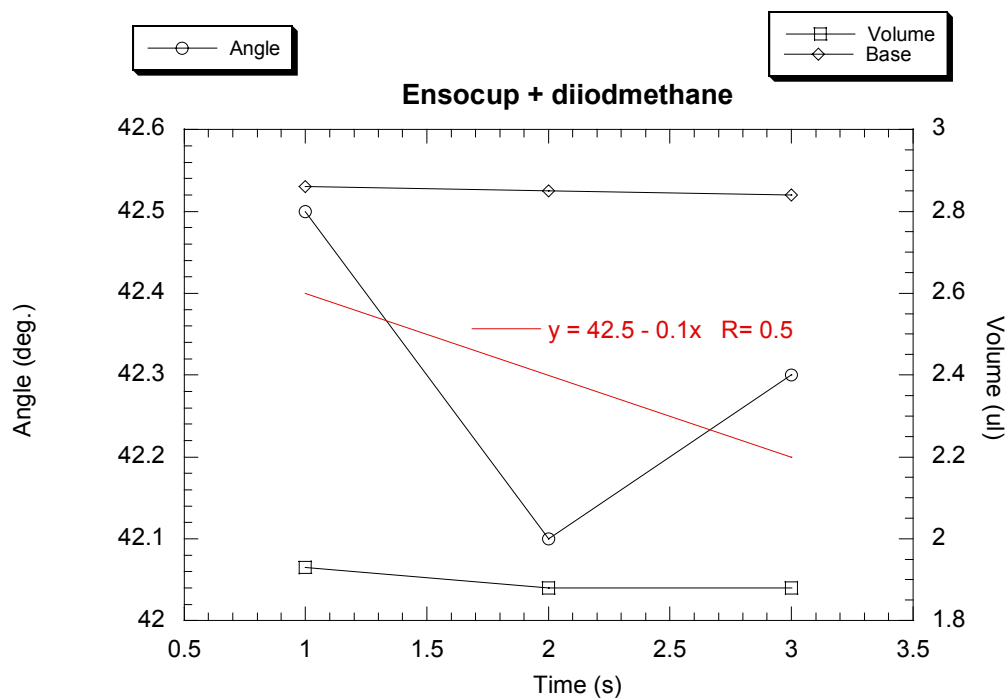
Contact angles measured for drops of various tests liquids deposited onto the surface of Ensocoat™ and Ensocup™ packaging boards.



Contact angles measured for drops of various tests liquids deposited onto the surface of Ensocoat™ and Ensocup™ packaging boards.



(e)

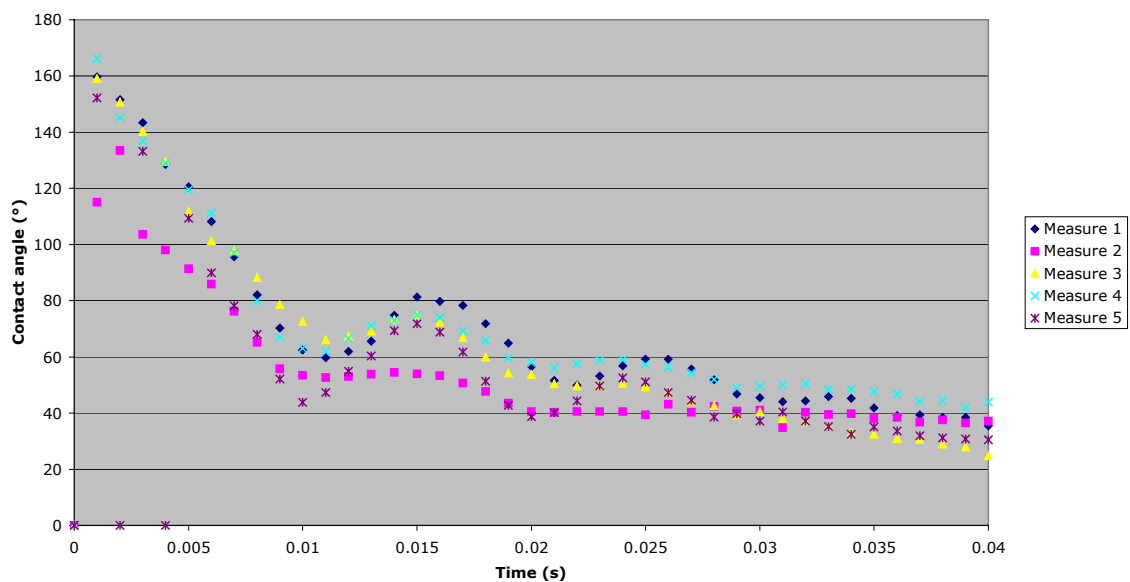


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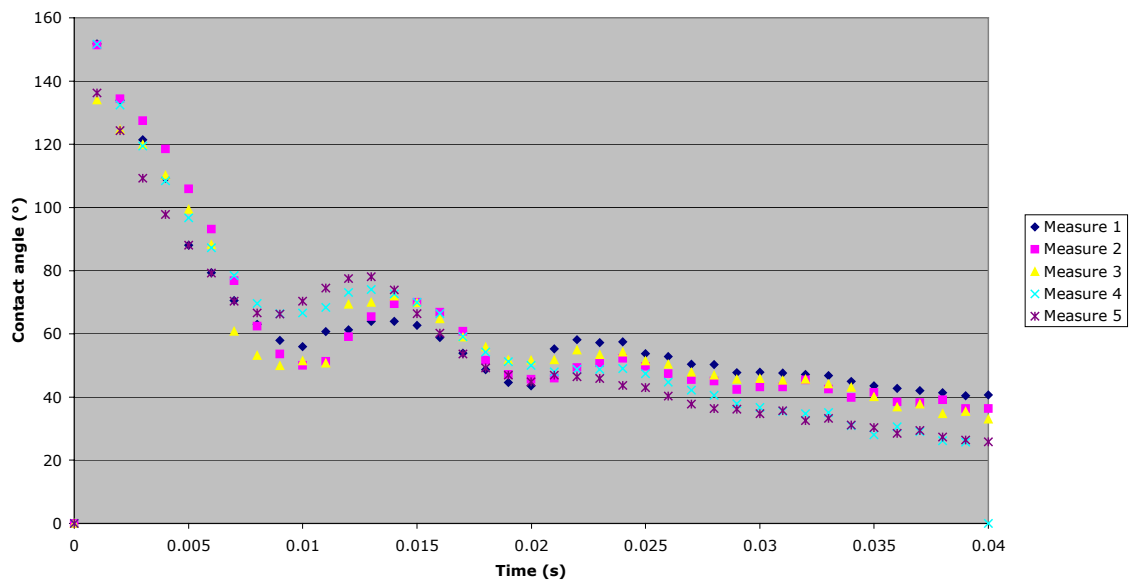
Contact angles measured for drops of various tests liquids deposited onto the surface of Ensocoat™ and Ensocup™ packaging boards.

Appendix 2: Contact angle as a function of time

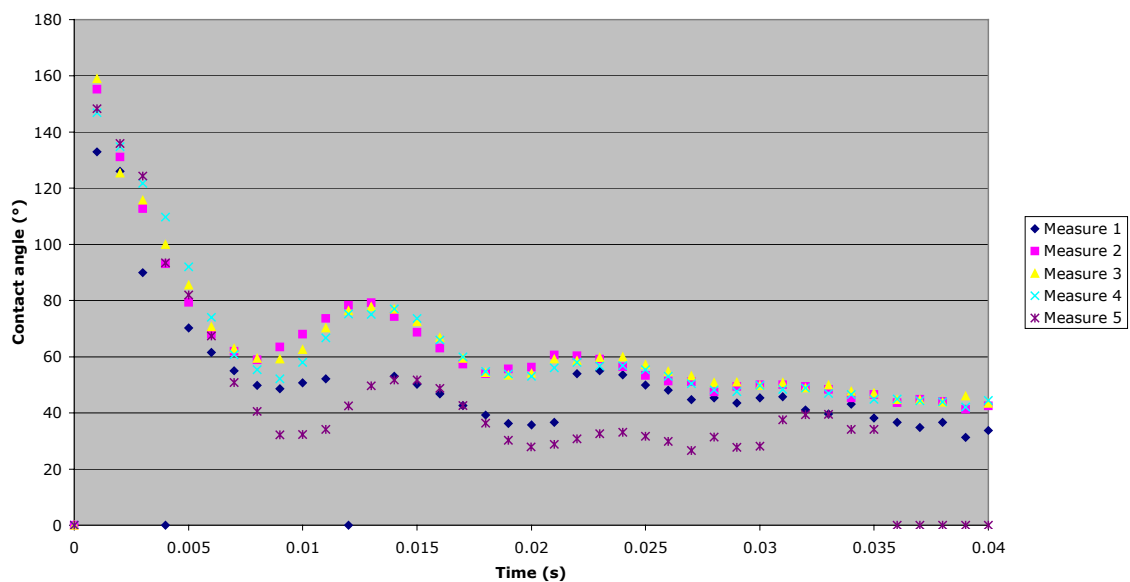
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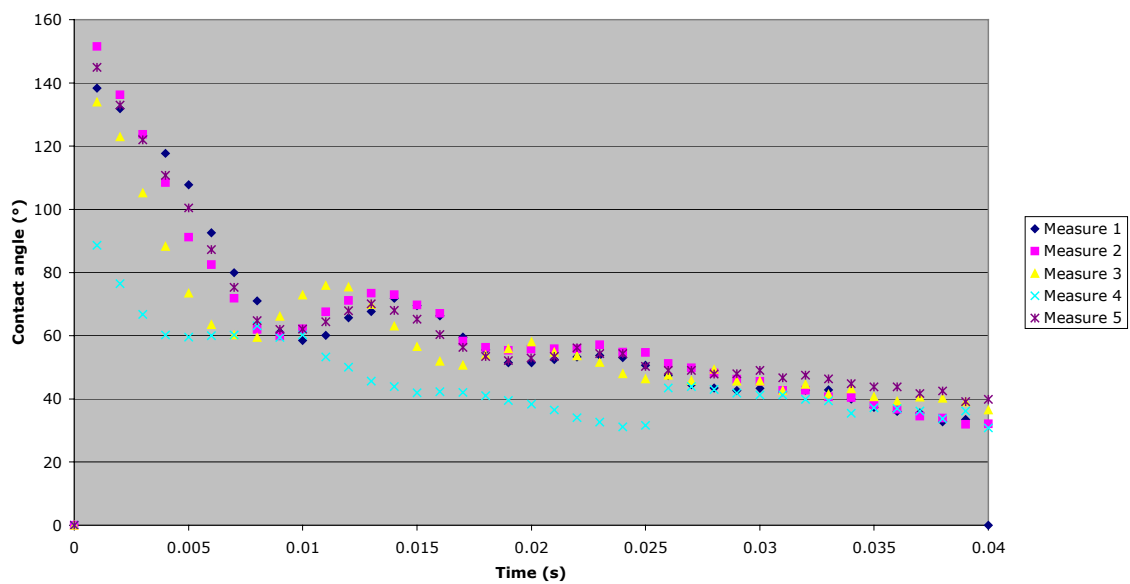
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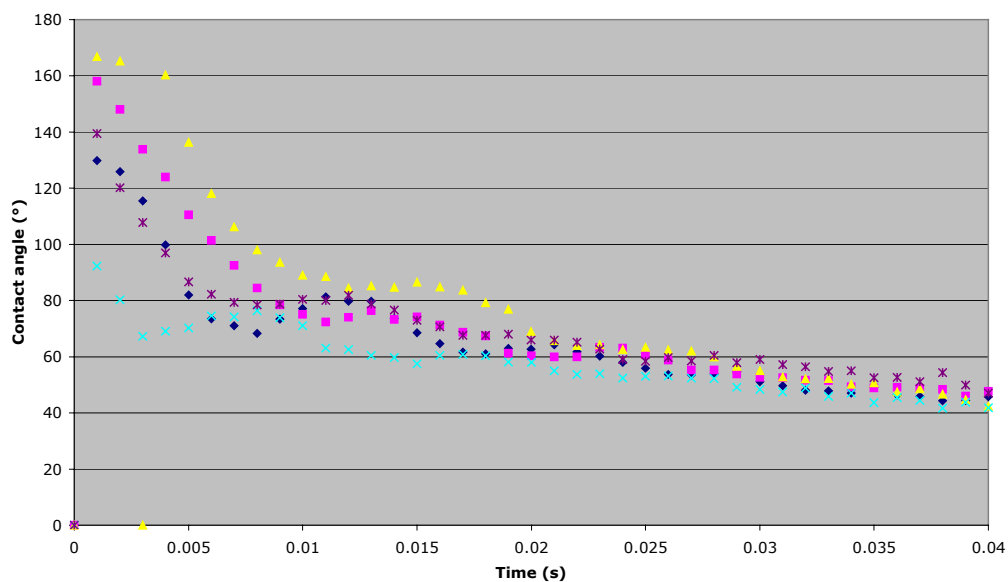
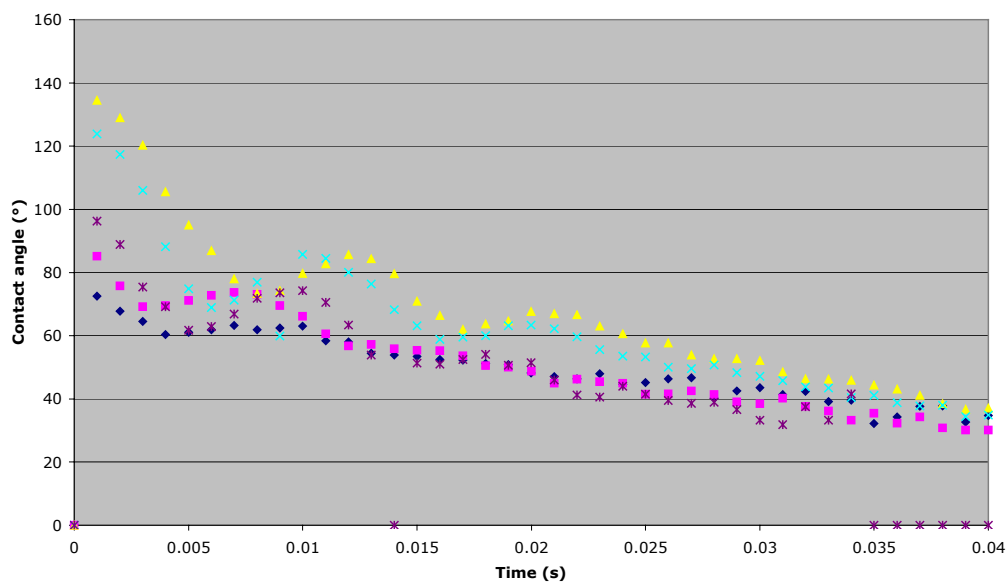


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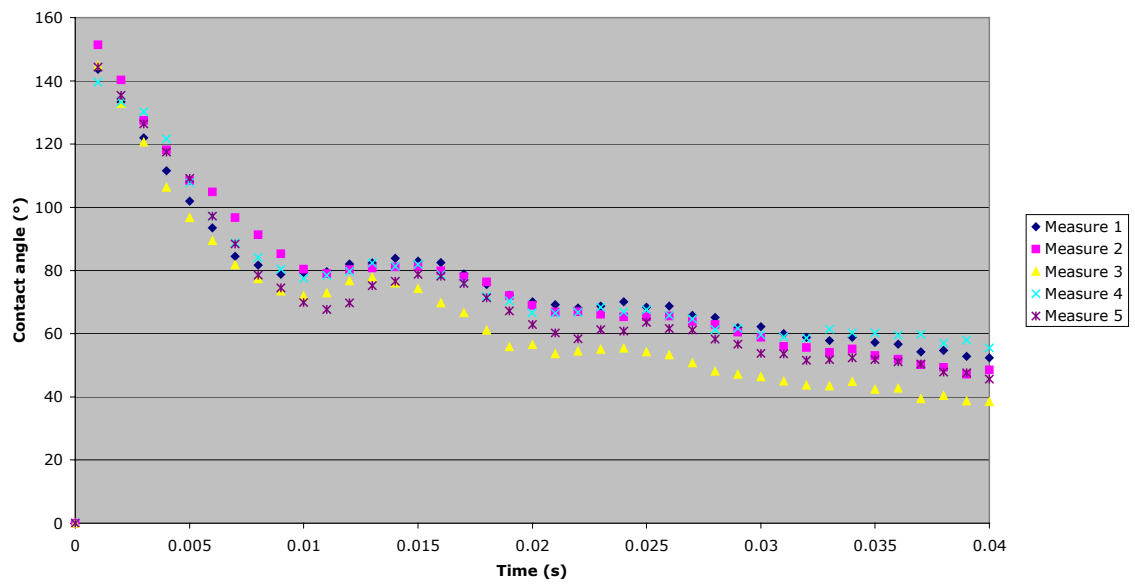


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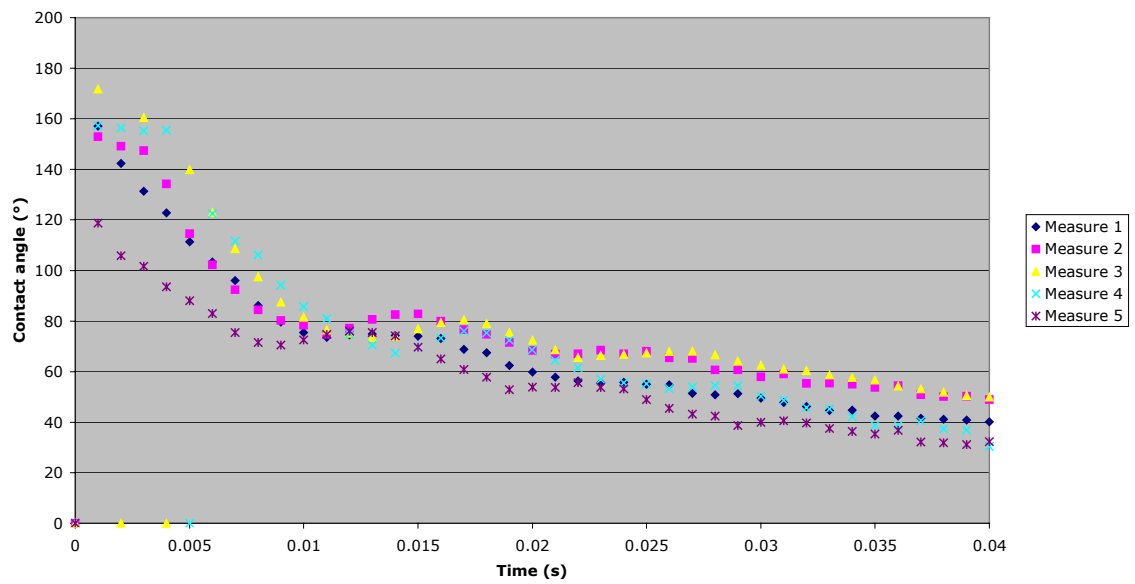


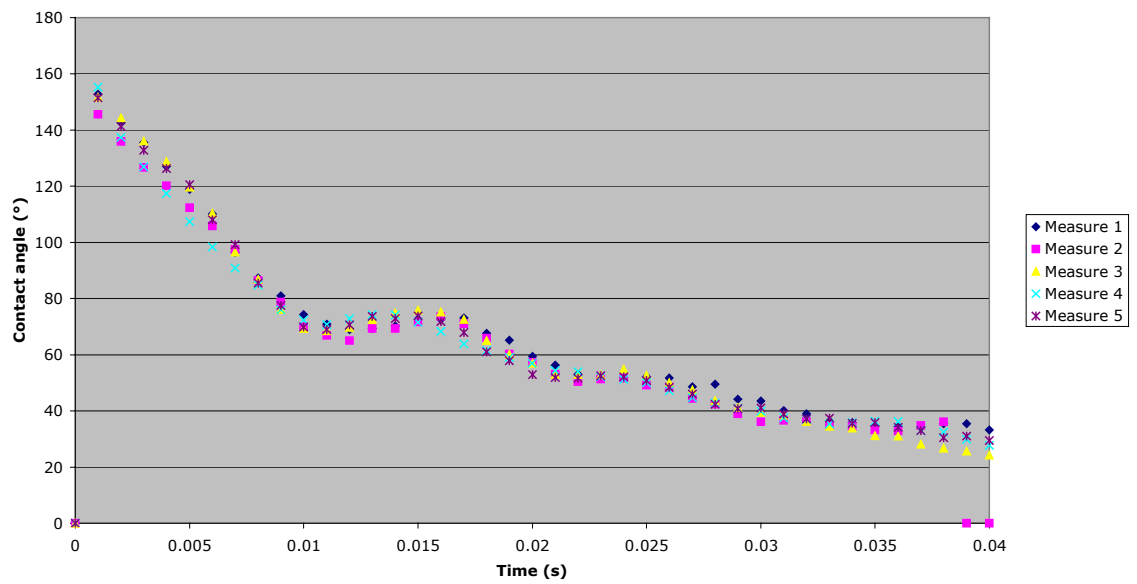
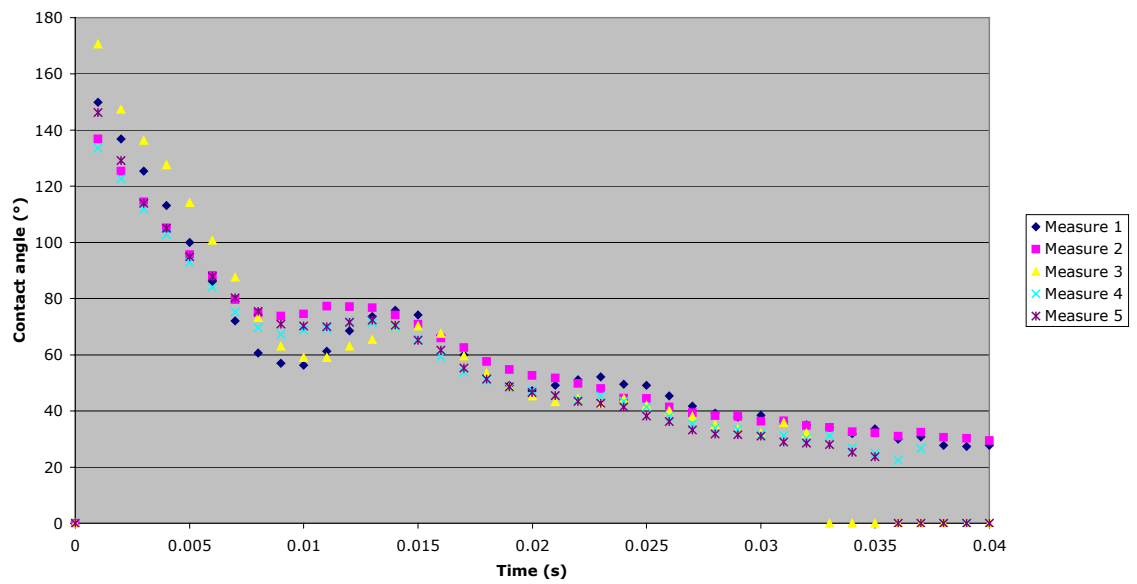
SB M5 / Textile 1**SB M6 / Textile 1**

SB M7 / Textile 1

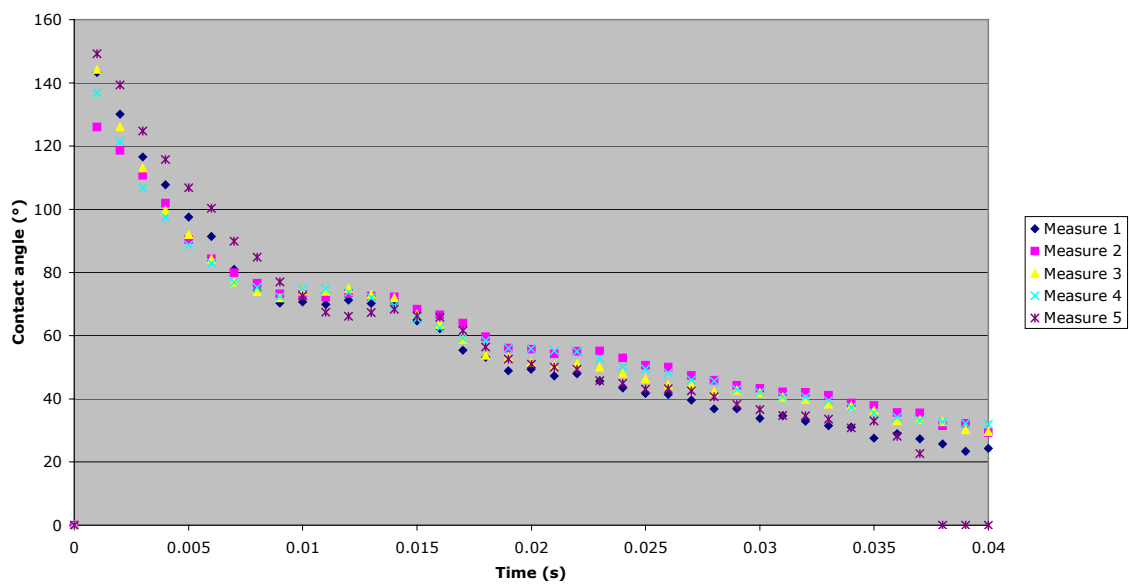


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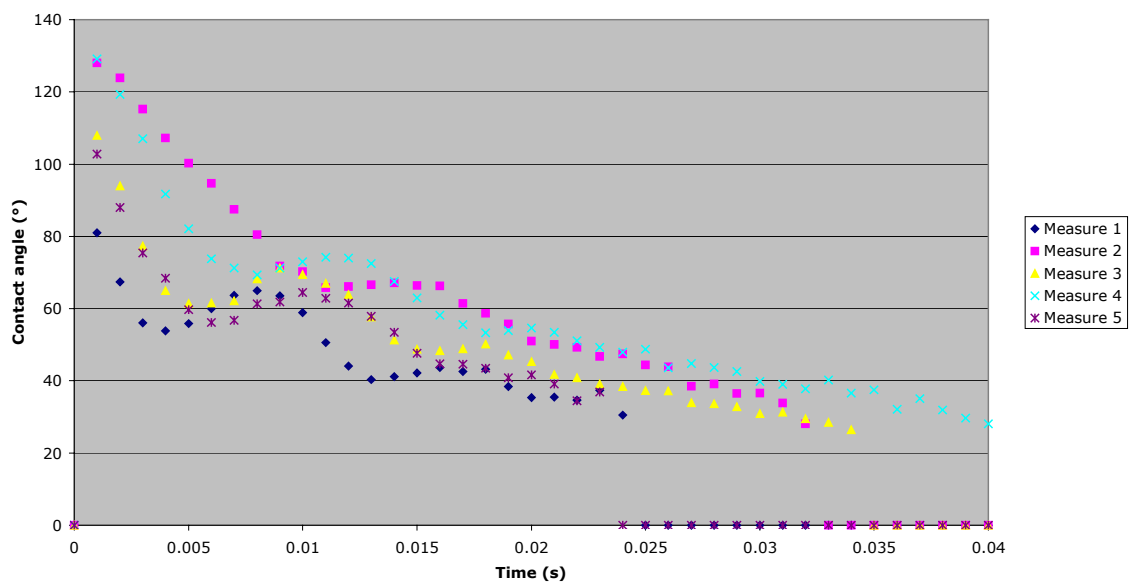


SB M1 / Textile 2**SB M2 / Textile 2**

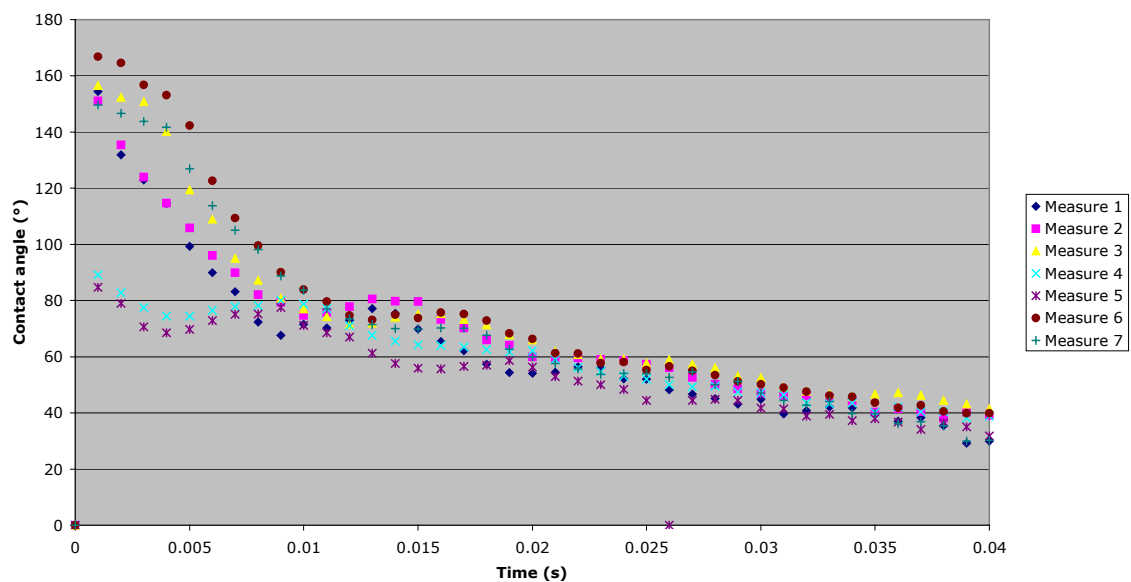
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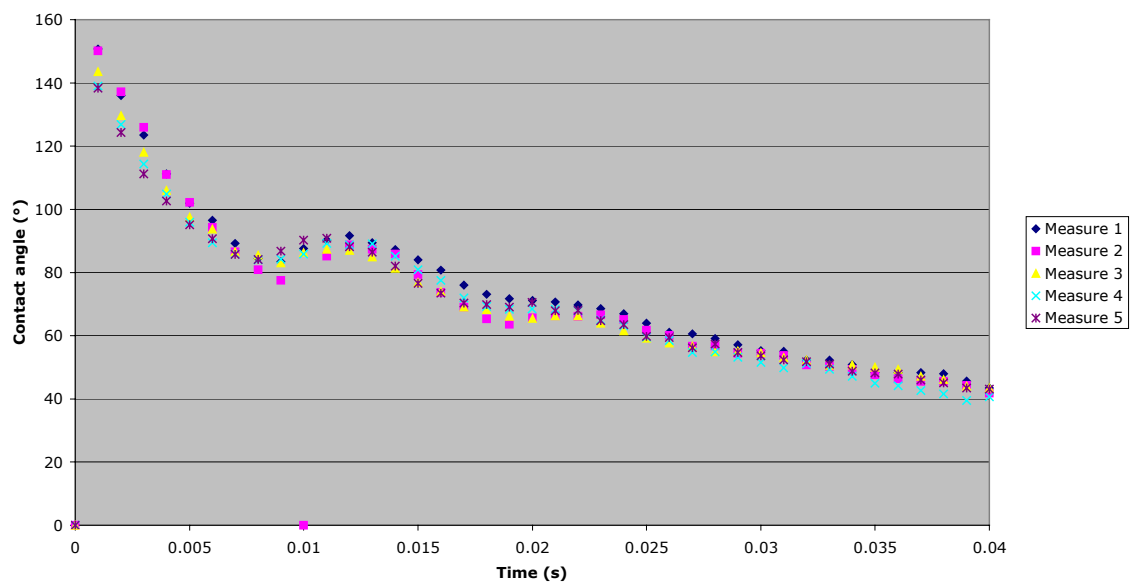
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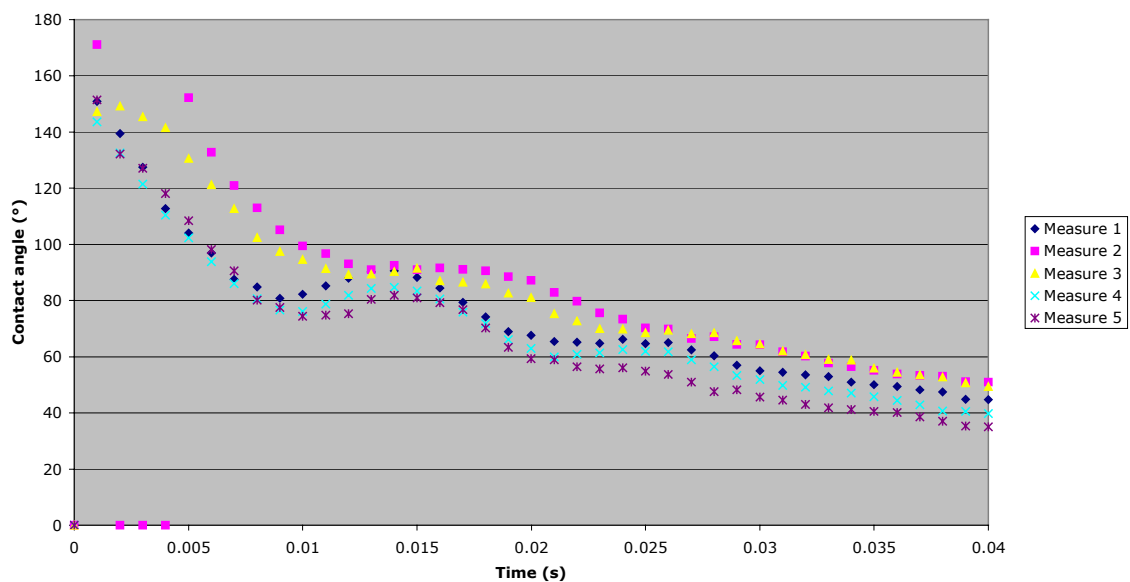
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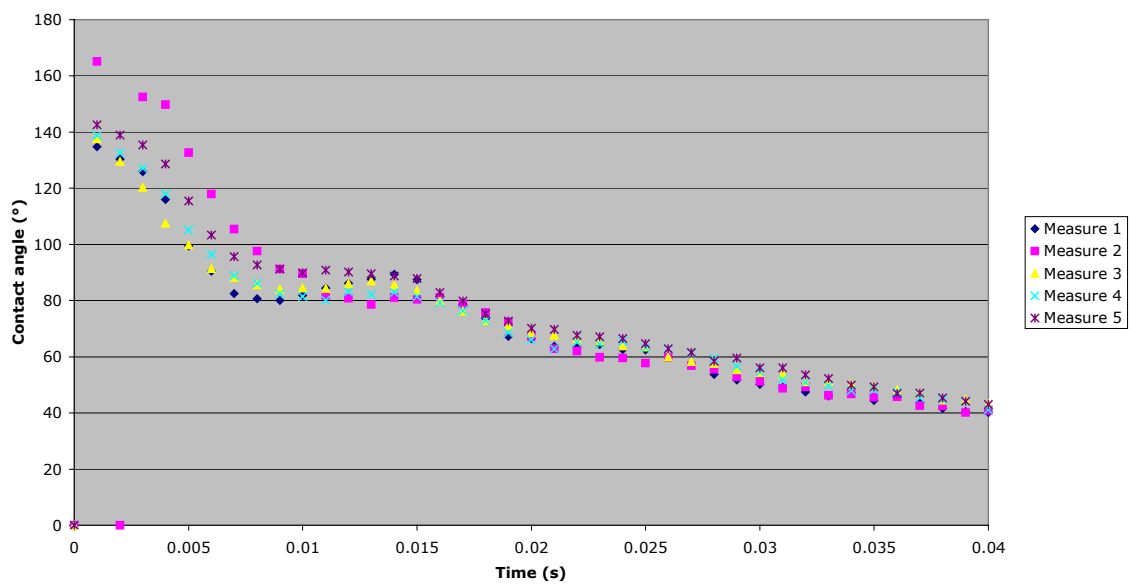
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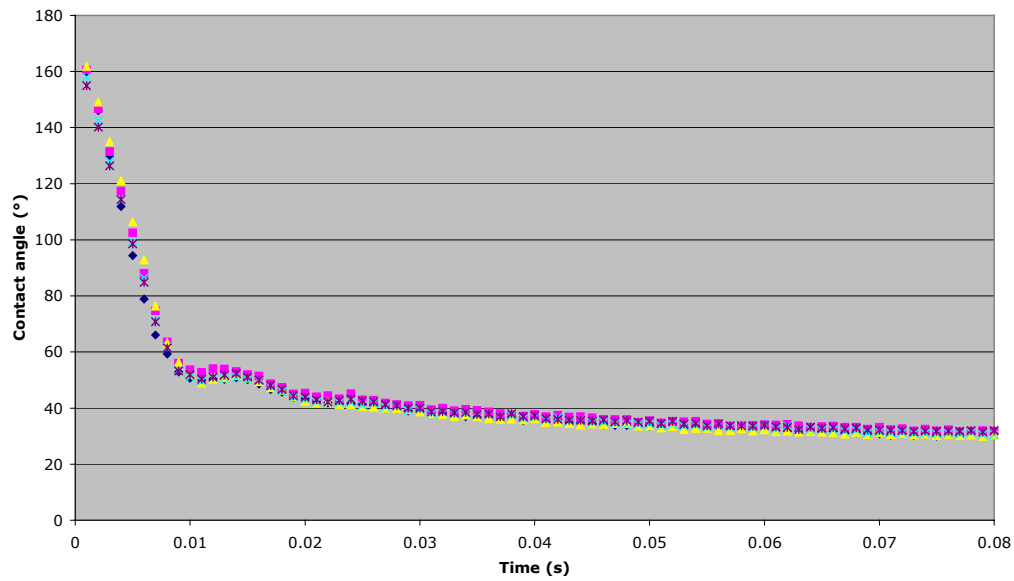
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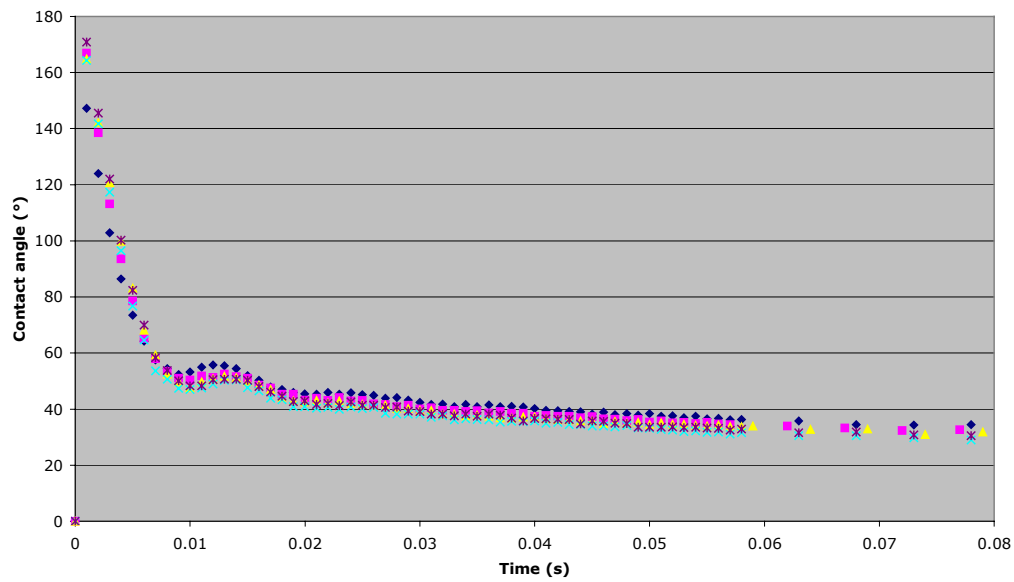
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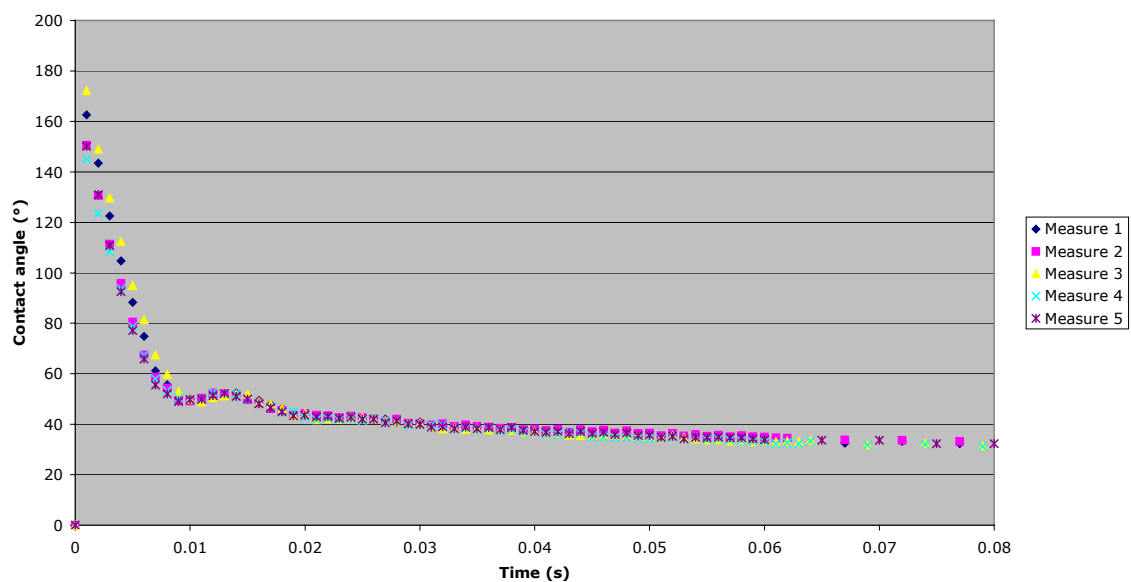
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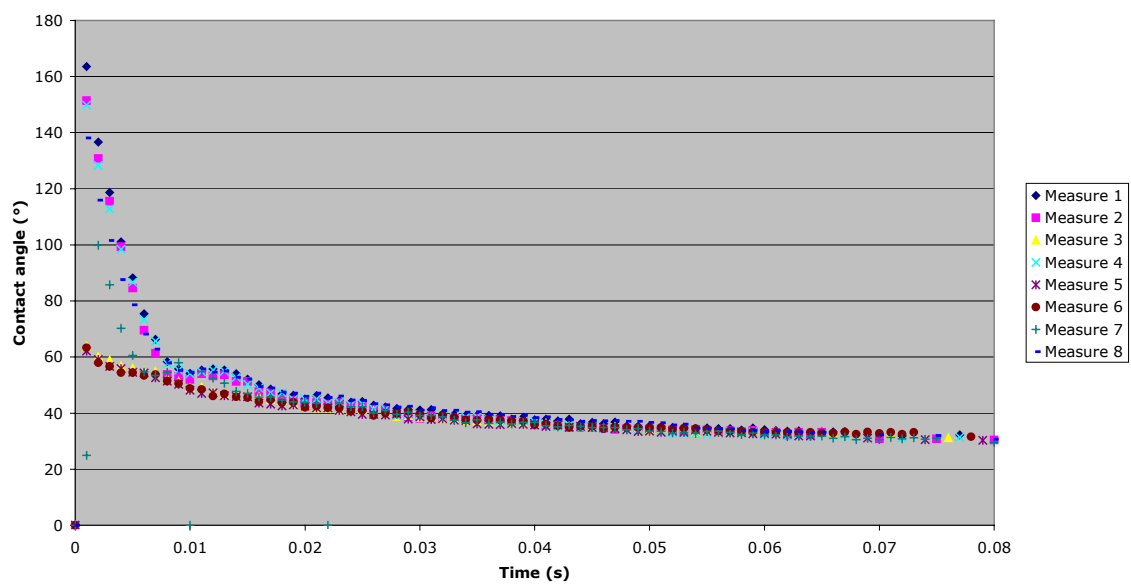
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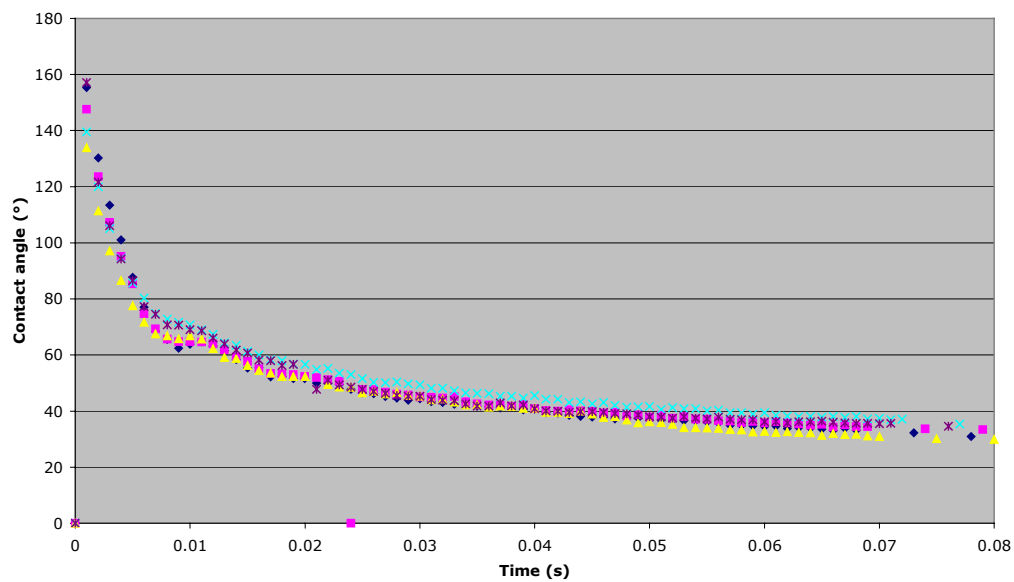
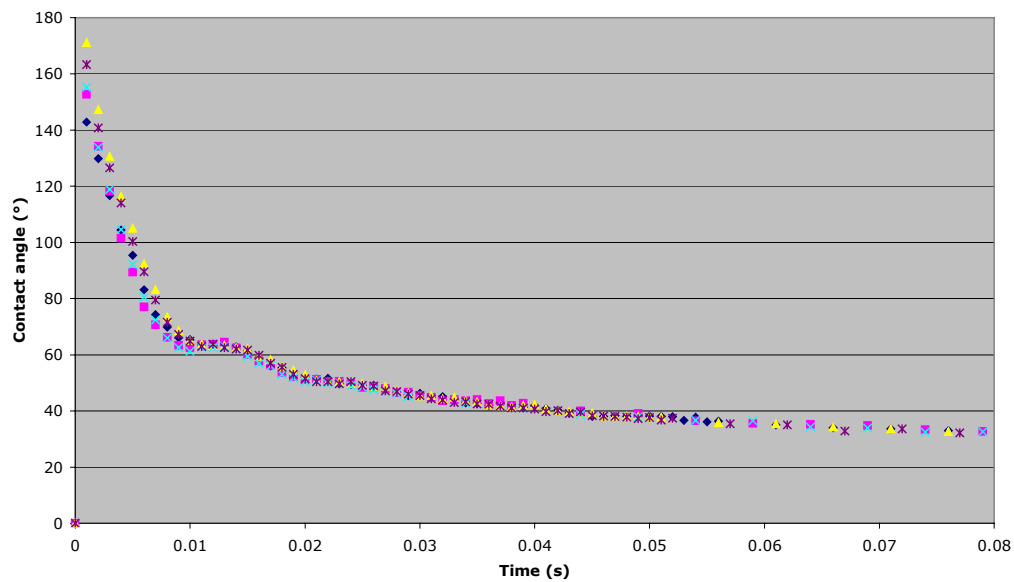


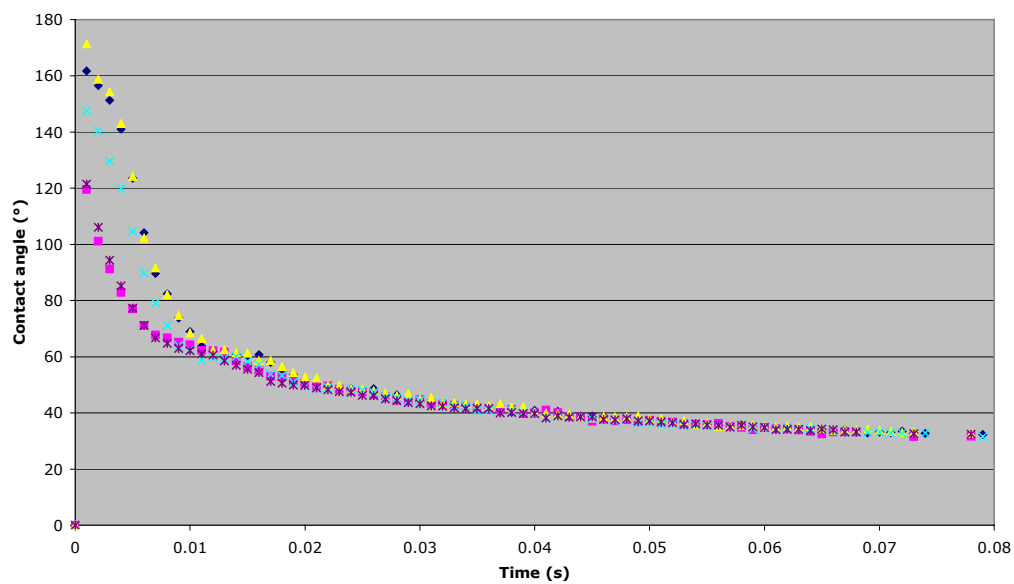
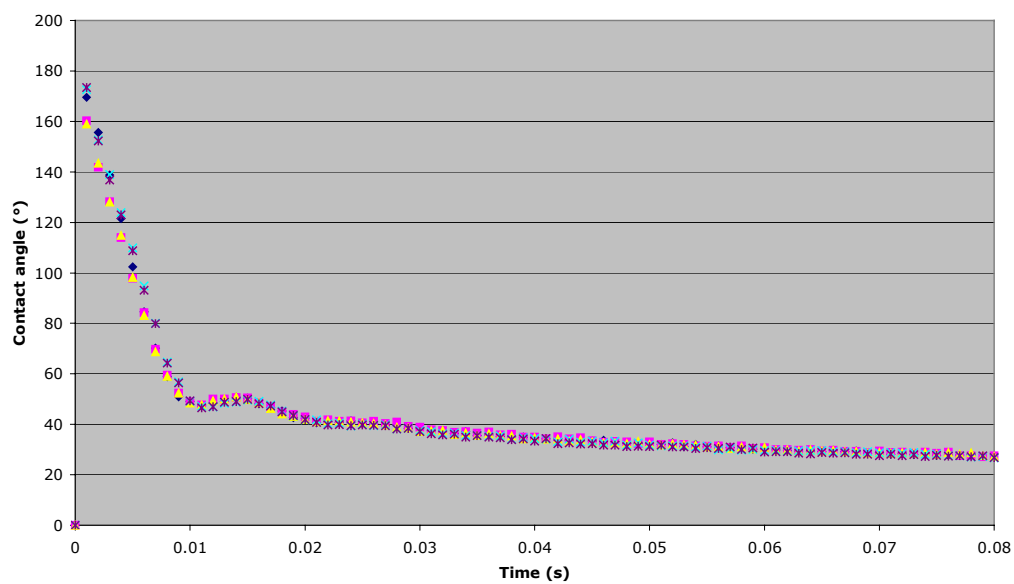
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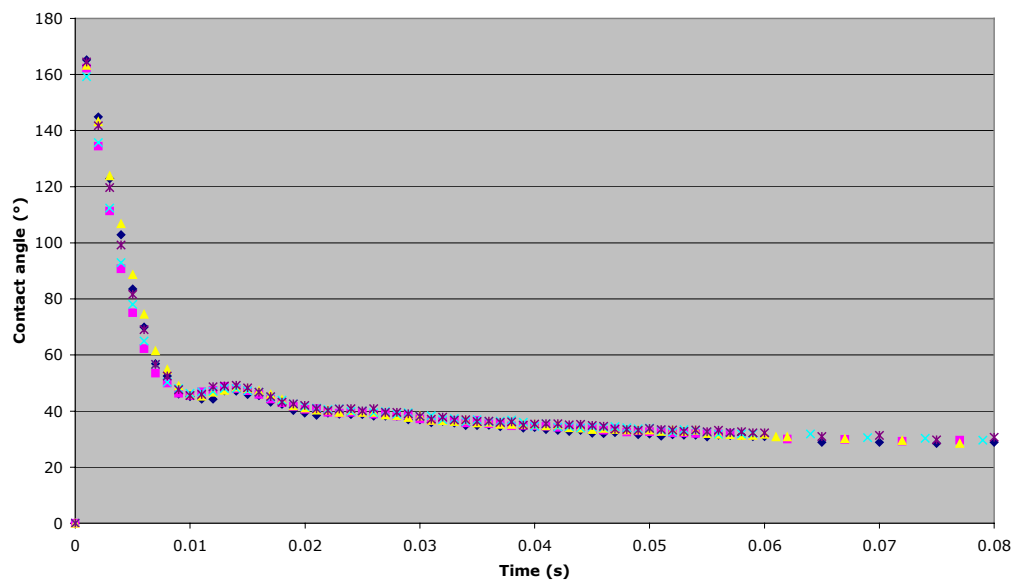
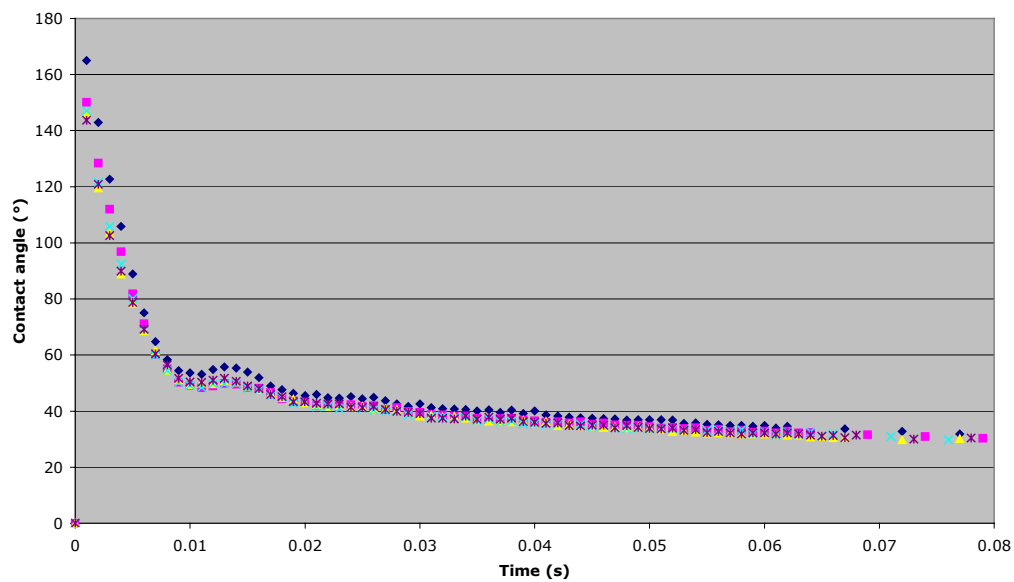


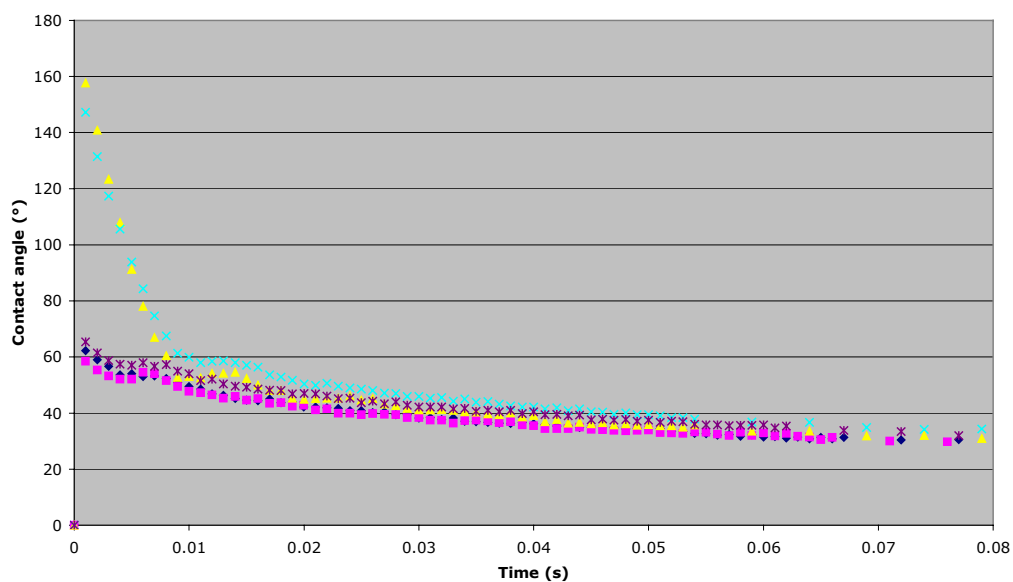
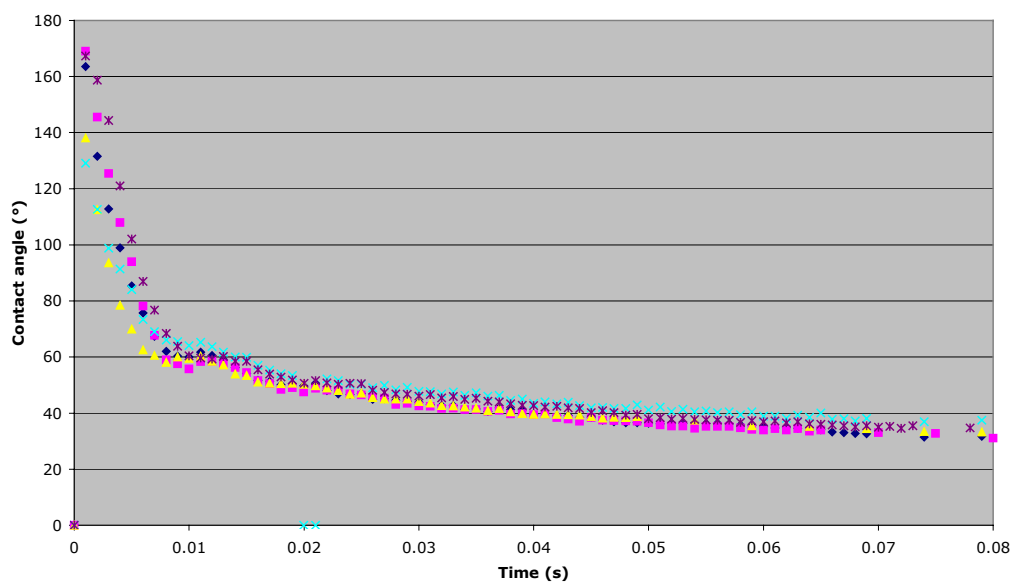
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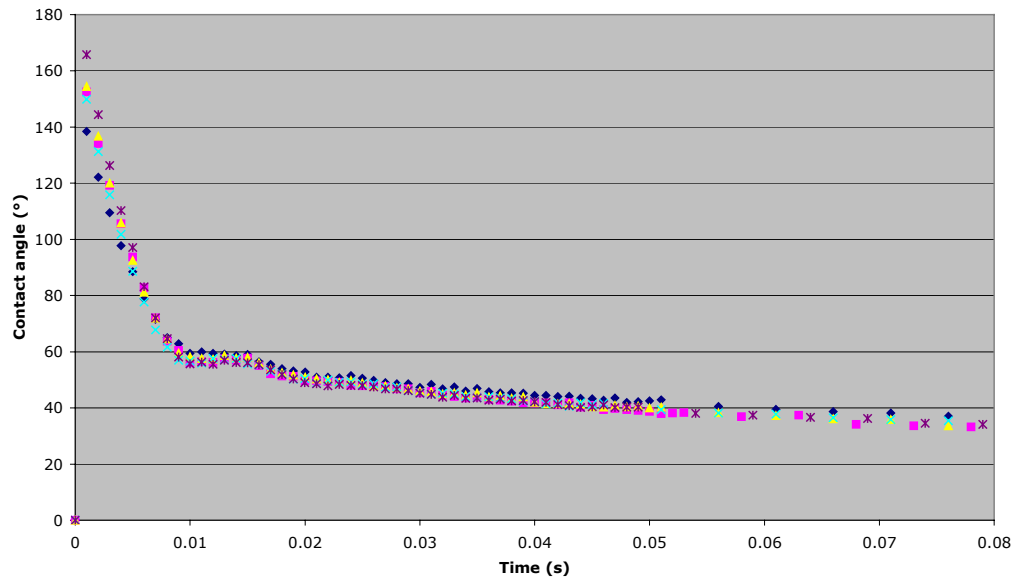
SB M6 Ensocoat**SB M7 Ensocoat**

SB M8 Ensocoat**SB M1 Ensocup**

SB M2 Ensocup**SB M3 Ensocup**

SB M5 Ensocup**SB M6 Ensocup**

SB M7 Ensocup



SB M8 Ensocup

