The Influence of Surfactants on the Interfacial Tension and Droplet Formation in UV Curable Jet Inks

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Abstract

Is the droplet formation predictable by physical measurements? How strong does the interfacial tension influence the droplet formation? In this paper commercial surfactants of the different classes made of organic, fluorocarbon and silicone chemistry were investigated. To verify their performance and ability of adjusting the interfacial tension, different methods of surface tension measurement such as static surface tension, dynamic surface tension and dynamic contact angle were utilized. Interesting results and analogies could be observed. The influence on the droplet formation of the used surfactants was evaluated on an actual piezo drop-on-demand printhead and compared with the results gained by the physical measurement. To keep the possible interactions and dimensions as small as possible, very simple model formulations based on PONPGDA and TMPEOTA were used. In this paper the authors search for correlations in order to give guidance for the best choice of surfactant.

Introduction

How strong does the surface tension influence the droplet formation? What values measured by physical data give a good indication of the final printing results?

Surfactants are commonly used in inkjet inks to reduce surface tension and by this improve the droplet formation and the wetting behavior. But little is known about the correlation of the chemical structure of the surfactant, its effect on surface tension and finally the impact on droplet formation. A study was performed with regards to radiation-curing jet inks to get a deeper knowledge between the possible link of the performance of the different surfactants in the different physical measurements and droplet formation.

The term surfactant commonly stands for surface active agents, which lower the surface tension of (commonly aqueous) liquid media. A traditional surfactant consists of a hydrophilic part (stretching into the aqueous phase) and one hydrophobic part (stretching into the air).

In this paper the working of surfactants in radiation-curing formulation respectively UV jet inks are discussed. But a powerful surfactant in water is not necessarily a strong surface tension reducer in acrylate monomers. The different physical and chemical properties like surface tension, viscosity and polarity of acrylate monomers and oligomers compared to water does result in different behavior of the surfactants [1].

To judge on the jetting performance of jet inks on a lab scale many different tests can be used.

While droplet ejection piezo-acoustic printhead is mainly controlled by the acoustic parameters as well as the viscosity of the fluid, surface tension controls mainly the meniscus formation, reliability as a result of air ingestion and especially the formation of satellites.

This paper combines classical measurement methods for physical properties of UV curing systems with a stroboscopic analysis of the droplet ejection, its reliability and satellite formation.

Does one of the “classical” methods used to measure the surface tension and wetting behavior correlate with the jet ability?

Surfactant classes

The different classes which are very familiar and discussed and measured in this paper are [2]:

- alkoxylated surfactants
- silicone surfactants
- fluorocarbon surfactants

Alkoxylated surfactants are non-ionic surfactants built of ethylene oxide, propylene oxide with long chained primary (fatty) alcohols. Those structures have a medium surface tension reduction in aqueous media. Their low molecular weight and medium hydrophobic level deliver very mobile surfactants.

Silicone-based surfactants are highly surface active. The combination of a very low surface energy siloxane chain with organic modifications, such as polyether groups, enables to design tailored surfactants with excellent surface tension reduction.

Silicone-acrylated surfactants are designed for radiation curable formulations. Those structures can also be organomodified by polyethers, but carry additional acrylate groups that make the products crosslinkable in free radical curing.

Silicone-based gemini surfactants are novel structures within the industry. Classical T-structured surfactants have the tendency to stabilize foam. Gemini surfactants have pair-wise modifications, which can also be polyether groups. This change of structure leads to a higher surface activity and keeps the foam volumes neutral to providing defoaming properties [3].

Silicone chemistry can be utilized to build structures with different properties. In general short siloxane backbones with < 10 Siloxane units are used as substrate wetting products. Longer backbones with siloxane units > 15 create surface control products with some slip effect. All of them work as a surfactant.

Fluorocarbon surfactants have an even lower surface energy - due to the fluoric molecule - than silicone-based structures. These surfactants are already active at very low dosages, but the strong tendency of foaming and the worldwide SHE (Safety, Health and Environment) regulations may have a negative influence on the future of fluorocarbon products.

Experimental

Formulations used

For the high performance demanded of the jet inks, a low viscosity and fast curing for UV inkjet inks are of high importance. Therefore certain acrylate monomers are in the main focus of the industry. For the evaluation two of those monomers were used to formulate simple model formulations.

The two monomers were Trimethylol Propane Ethoxy Triacrylate (TMPEOTA) and Propoxylated Neopentyl Glycol Diacrylate (PONPGDA). Both products are widely used within the industry. Especially PONPGDA has gained higher importance due to the lower viscosity level of around 17 mPas at 22 °C and very good curing properties. It also gives good adhesion on paper and plastic foils and exhibits resistance to chemicals [4]. TMPEOTA as triacrylated monomer is much higher in its natural viscosity with around 70 m at 22 °C.

Those monomers were used as a basis for the formulations. To evaluate the different surface tension modifiers in their chemical classes the products were used at a dosage of 0.3 % incorporated by a VMA Getzmann dissolver into the acrylate monomers. No further ingredients such as photoinitiators or pigments where used, which could influence the surface tension and so the droplet formation.

Measurement methods

To judge the surface tension modification and wetting properties of printing inks and varnishes, the following instruments and methods are often used:

Static surface tension is often measured by the DuNuoy platinum ring or Wilhelmy plate method. A liquid sample is measured by pulling out a platinum ring or platinum-iridium plate. By withdrawing a lamella is formed. The maximum force required to pull the lamella is directly proportional to the static surface tension [5]. For our study we used the Wilhelmy plate method, using a Krüss Tensiometer K100.

Dynamic surface tension measurement is also very common within the printing ink industry. Air bubbles are blown with different frequencies and lifetimes into the formulation. The force to create those bubbles in a formulation is measured and is directly proportional to the dynamic surface tension at this respective bubble speed. This technique gives an indication for the mobility of surfactants in a formulation [5]. The apparatus used in the study is a Sita science line t60.

The dynamic contact angle was also used in this study. The dynamic contact angle allows judging the wetting as well as spreading behavior of a liquid on a surface. For example it is often used to determine the water beading on façade coatings. A water droplet is placed on the dry coating and the angle between droplet and coating measured [5]. For our study a droplet of the monomer formulation, with the volume of 3 micro-liters was placed on a substrate. Directly after that the angle in which the droplet “sits” on the surface was determined. The substrate used was an Avery™ Fascal 900 PVC film. The apparatus which was used is the Dataphysics OCA 20.

The most classical way of evaluating the wetting behavior is to draw-down the formulation on a critical substrate using a bar-coater. Reliable results can only be obtained with a minimum thickness of 4 µm. The evaluation is done visually and always in a direct comparison with the blank or control sample. For the test the Avery™ Fascal 900 PVC film was used.

In order to match the viscosity of the fluid to parameter space of the printhead, viscosity was recorded as a function of temperature. The different surfactant classes as well as the base fluids were checked on influence of different temperatures by the use of a RotoVisco1 viscometer from Haake.

Jetting methods

Jetting was carried out using commercial Xaar 126/80 (cf. Figure 1), delivering a nominal droplet volume of 80 pL in binary mode. This printhead is of the piezoelectric drop-on-demand type, utilizing a shear-mode, shared-wall principle [6, 7]. The 126 nozzles of the printhead are positioned in a straight line with a pitch of 137.14 µm providing a physical resolution 185 dpi when mounted perfectly perpendicular to the machine direction. However, this limitation may be overcome by rotating the printhead as reported elsewhere [8].

In order to match the viscosity of the fluid to the working range of the printhead, a Peltier heater was attached to the backplane to establish the desired 40 ºC for PONPGDA and 55 ºC for TOMPEOTA.

Droplet formation was observed using triggered stroboscopic illumination. The change of the trigger signal allows for the visualization of the evolution of droplet formation and break-up alongside with satellite formation and approximate volume distribution. The acquired images were analyzed using ImageJ [9] to give quantitative figures.

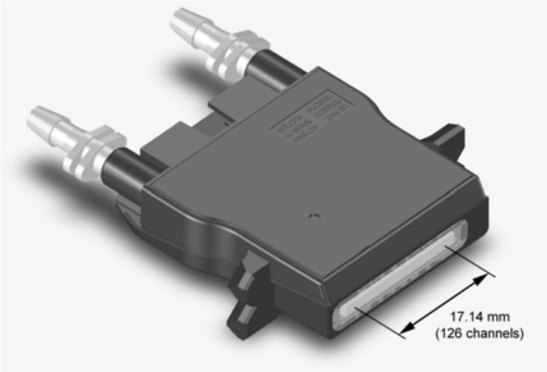

Figure 1. Xaar 126 printhead model with 126 linearly arranged nozzles

Results

Physical measurements

While working on this paper it quickly became apparent that not all described measurement methods were applicable, as reliability could not be guaranteed for our investigations. Methods and apparatus have to be reliable to judge the performance even with minor changes of the surfactant used. The two methods, static surface tension and dynamic surface tension proved to be very reliable and easy to handle for measuring the formulations. The dynamic contact angle measurement proves to be not applicable for a broad usage. For the test formulation with TMPEOTA results could be obtained. Using the method with the formulation of PONPGDA no reliable results could be observed. The method of draw-down on the substrate did not show noticeable differences between the surfactant classes.

First we want to look on the results with the formulation based on PONPGDA:

All test candidates chosen from the above described surfactant classes, with their different molecular weights, structures and hydrophobicities, were compatible in the test medium. They caused no turbidity when used at 0.3% in PONPGDA. The most powerful reduction of static surface tension was obtained with silicone and silicone-acrylated surfactants. The other classes of alkoxylated products and fluorocarbon surfactants did not show any significant effect. The key to judging the different performancees appears to be related to the molecular weight of the different classes of surfactants.

The results shown in the figure 2 show that: The higher the molecular weight of the siloxane, the lower the static surface tension.

	Static surface tension in mN/m
PONPGDA	31.2
Low Mw Siloxane	31.1
Low Mw gemini Siloxane	26.8
Medium Mw Siloxane	24.6
High Mw Siloxane	21.9
Medium Mw Siloxane acrylate	24.0
High Mw Siloxane acrylate	24.0

Figure 2: Results of the static surface tension measurement in PONPGDA

Looking at the dynamic surface tension in figure 3 the results are very different. There the higher molecular weight siloxane surfactants lowered the surface tension, but especially at a high bubble frequency and short bubble lifetime they became much weaker.

The siloxane acrylates showed here the strongest lowering of the dynamic surface tension at low and even at high frequency. The low molecular weight surfactant also gave very constant results during the measurement.

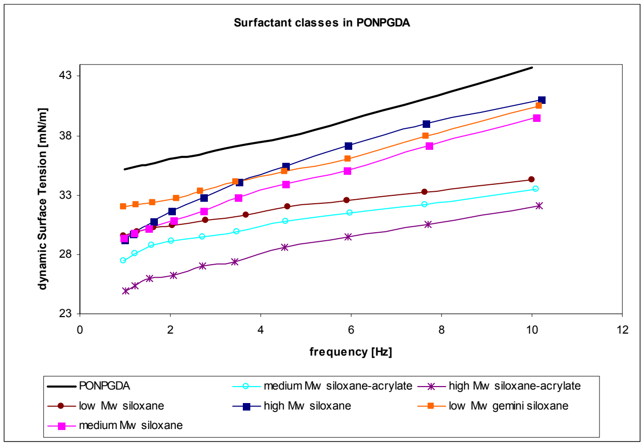

Figure 3: Results of the dynamic surface tension measurement in PONPGDA

In this section the results generated in TMPEOTA will be described:

The different test candidates showed very different trends compared to the PONPGDA. They were also used with 0.3% in the formulation. Only the low molecular weight siloxane surfactants showed no turbidity in TMPEOTA. Again it was seen that alkoxylated products showed no significant reduction of the dynamic and static surface tension. Fluorocarbon surfactants reduced the static surface tension to a minor degree, which was on a level of low molecular weight siloxane structures. The reduction of the dynamic surface tension was again close to the blank sample. Because of that reason, the alkoxylated and fluorocarbon structures were not further evaluated and discussed.

First we want to show the results of the static surface tension measurements (figure 4). It is also the case that higher molecular weight of siloxane structures leads to lower readings. The lowest readings were observed with a medium molecular weight siloxane surfactant, which showed even lower readings than all the other structures. The acrylated siloxane structures also showed strong surface tension reduction, but less than the other product classes.

	Static surface tension in mN/m
TMPEOTA	37.9
Low Mw Siloxane	28.5
Low Mw gemini Siloxane	22.5
Medium Mw Siloxane	21.1
High Mw Siloxane	22.6
Medium Mw Siloxane acrylate	21.9
High Mw Siloxane acrylate	21.7

Figure 4: Results of the static surface tension measurement in TMPEOTA

The measurement of the dynamic surface tension (figure 5) in TMPEOTA showed that the low molecular weight gemini siloxane surfactant gain by far the lowest readings. This is interesting, because the chemicals close “classical” T-structured low molecular weight siloxane surfactant showed nearly no reduction of the surface tension and was close to the blank sample. The medium molecular weight siloxane surfactant – it showed a very good static surface tension reduction – had also a low surface tension at a low bubble frequency but increased very strongly with the higher frequency and shorter bubble lifetime.

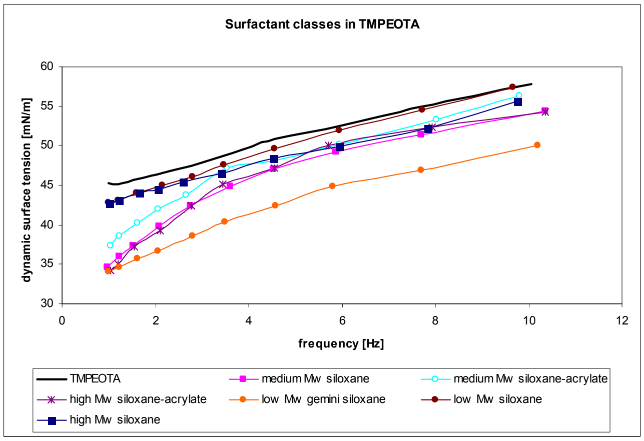

Figure 5: Results of the dynamic surface tension measurement in TMPEOTA

In TMPEOTA the dynamic contact angle could also be measured. The results obtained were quite comparable with the results and ranking found in the static surface tension measurement (figure 6). Also here the low molecular weight siloxane gemini surfactant and the medium molecular weight siloxane enable the monomer to spread rapidly on the PVC surface. The acrylated high molecular siloxane also showed very low readings of the contact angle.

It should again be pointed out that this measurement is not easy to use for this application. The number of mismeasurements is relatively high.

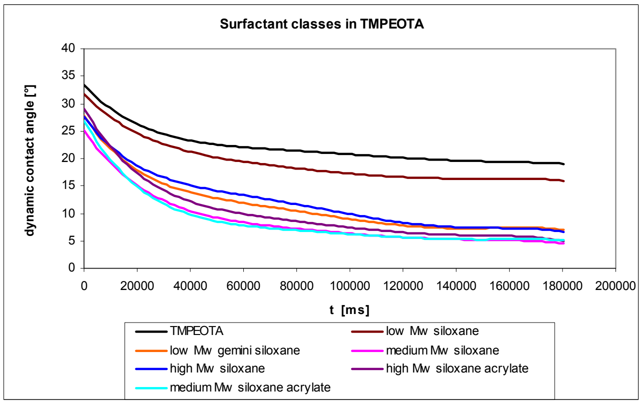

Figure 6: Results of the dynamic contact angle measurement in TMPEOTA

Jetting performance

Jetting of PONGDA was established with a common waveform at a sample clock of 1600 ns at 40°C, in order to achieve a viscosity of 10 mPa.s. The amplitude of the applied waveform was chosen to give 6 m/s for all the measured samples. The applied pressure at the nozzle plate to ensure stable meniscus formation without air ingestion was adjusted to be -8 mbar.

Stable jetting was achieved with all of the prepared PONGDA model solutions. Stability was verified on screen observing 10 adjacent channels firing at 100% duty cycle, with no losses or angle deviation for 180 s.

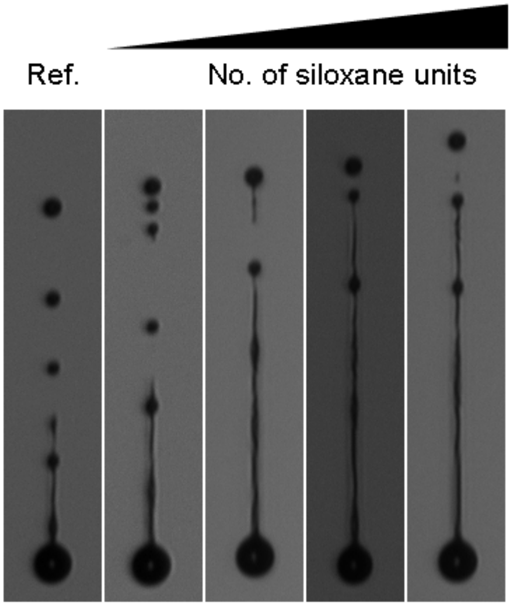

Figure 7: Influence on the number of Siloxane groups on the tail formation in PONPGDA [40 °C, 6.5 kHz, 1 mm from the nozzle plate]

Figure 7 depicts the change of tail formation at a distance of 1 mm from the nozzle, which is a typical value for the printhead-substrate distance in typical applications. From the image series the chain length contribution of the surfactant in form of satellites reduction is obvious. The longer chains potentially increase the elasticity of the model formulation and therefore allow for longer stretching of the tail with a decreased tendency for disintegration on the timescale of approx. 160 µs.

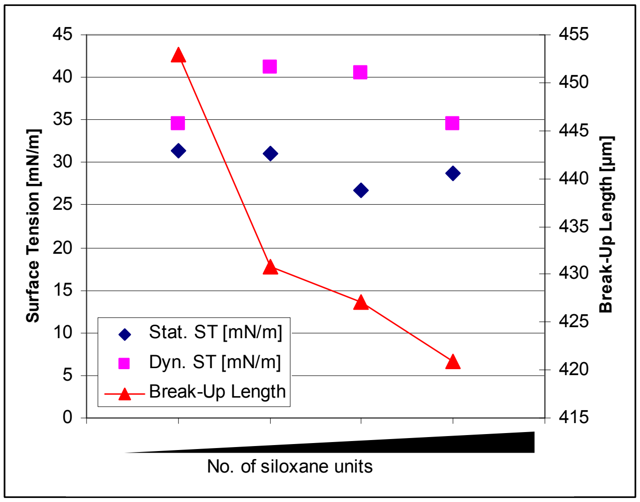

Figure 8: Influence of the number of siloxane units on the break-up length of the the jet

Figure 8 shows the behavior of the jet break-up at the nozzle as a function of siloxane units. As the dynamic surface tension increases, the break-up length, e.g. the extension of the primary jet into the air volume outside the nozzle, decreases. This suggests an increase of the force necessary for the generation of the new surface. This will accelerate the constriction of the jet and therefore and accelerated break-up. The sample with the highest number of siloxane units, however, does not fit into this trend and may be due to the deviation of the chemistry of commercial surfactant.

Discussion

In this paper two monomers and the influence of different surfactant classes were investigated. Only the additives classes of siloxane based chemistry showed significant influence on the surface tension. Alkoxilated and even fluorocarbon surfactants did not alter the surface tension to a significant degree.

Measuring the interfacial tension by the different methods of static and dynamic surface tension and using the method of dynamic contact angle indicated that different structures have different effictivity. The methods made visible the different modes of action and polarity of the evaluated surfactants. The different results obtained by the two monomers used also show the high degree of system dependency.

Printing was easily accomplished with the model formulations in a Xaar 126/80 printhead. An impact of the surfactant addition on the reliability of the printhead was not observed.

The impact of the surfactant addition was observable in the satellite formation. Especially the higher molecular weight showed less disintegration, leading to a decreased number of satellites. It was further observed that higher dynamic surface tension of the formulations enables earlier break-up.

Conclusion

The evaluation of the different chemical classes of surfactants in simple radiation curable jet ink formulation gave clearly observable results. None of used the surface tension measurement method predict the droplet formation. In order to judge the performance of the droplet formation it seems to be necessary to jet the formulations. By now there is no evident link between physical measurement of the surface tension and droplet formation.

Observed physical correlations have been disagreed in the jetting behavior and may originate from a chemical alteration. Even with simple inks the formulations, the experiments remain a multiparameter system.

However some statements can be made. The influence on the surface tension and droplet formation strongly depends on the molecular weight and chemistry of the surfactants. Siloxane chemistry proved to be excellent in adjusting the surface tension and to influence the droplet formation. Due to the polarity of the system the surfactants have to fit in the formulation used.

Outlook

Some questions were answered, some not and new ones came apparent. Further investigations are planned to gain knowledge about surfactants in UV formulations. Xaar and Evonik Tego want to further evaluate the effect on the substrate wetting abilities of the different surfactant classes and structures. Are there tailor-made surfactants possible, which combine good droplet formation and substrate wetting? The questions still remains to what extent will pigment influence the droplet formation.

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