Dynamic Surface Tension of UV-Curable Inkjet Inks

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Abstract

Properties like adhesion of inkjet prints on unporous media are strongly determined by wetting characteristics of ink on media. In contrast to solvent based inks for UV-curable inkjet-systems the ink is not allowed to equilibrate on surfaces because the film is cured within a very short timeframe after jetting. Therefore the static surface tension is not able to characterise the ink-media interaction before the ink curing process is initiated. In a time-scale of milliseconds the dynamic surface tension measured with the maximum pressure bubble method can be used to describe the dynamic processes of ink on unporous media. In this paper we present a study of dynamic surface tension of mono-, di-, and trifunctional acrylates in order to evaluate the effect of molecular weight, structure and the behavior of mixtures on the resulting dynamic surface tension in UV-curable inkjet inks.

Introduction

In the last 5 years the importance of UV-curable inkjet inks for industrial application steadily increased. Due to environmental reasons UV-curable inks are preferred compared to solvent based inks preventing evaporation of VOC (volatile organic compounds). Further, printhead handling is much easier compared to solvent based inks because the risk of nozzle drying and clogging is low. Especially for printing on non-porous materials UV-curable inkjet inks are the first choice exhibiting good adhesion, light resistance and the formed ink films are resistant to water and many solvents. Because no solvent has to be evaporated the curing speed determines the printing speed which can be much higher compared to solvent based systems on unporous media. For inkjet inks different parameters have to be adjusted carefully in order to design a high quality system. Beside stability of the ink, viscosity, cure speed and others, also the surface tension γ has to fit within tight borders. Regarding the surface tension inkjet inks usually are characterized using the static measurement parameter γ_{st} which however applies only for equilibrated systems. For newly created surfaces it is of importance how long the surface active components need for migration to the newly formed interface. This process can be described using the dynamic surface tension γ_{dyn} which allows a time-dependent characterization within milliseconds (corresponding to kHz when observing the formation frequency of new surfaces). The meaning of the dynamic surface tension for ink drop formation at the nozzle plate is not clear because ink drops are ejected on a much shorter time scale compared to the measurement frequency for γ_{dyn}[1]. In inkjet printing a typical process time for the drop formation was found to be $5x10^{-5}$ s[2]. Although the time is much shorter than the dynamic surface tension measurement according to Zhmud and Tiberg[1] dynamic surface tension critically influences nozzle operation. At least the sequence of drop formation may be slower if the printhead does not operate in heavy duty cycle and surface formation may contribute stronger. Depending on the surface energy of the nozzle plate the required ink surface tension for printhead operation may be much higher than desired for adequate wetting of the printing substrate. In this case an ink would be optimal having a high surface tension at short time scale and exhibiting a strong decrease of γ_{dyn} with increasing time.

The wetting of media determines print quality and adhesion. Surface defects like orange peel and pinholing may occur if surface tension is higher than the media surface energy. Especially for UV-curable inks the dynamic surface tension is important because when UV-lamps are applied after printing, a first curing starts soon after impact of the drop on the surface. Further, drop on drop characteristics (the lay down of a second drop on the first layer) will be mainly determined by dynamic surface tension rather than static surface tension because the spreading of the first drop on the media as well as the second drop on (halfcured ink) happens within a very short timeframe of less than a second.

Whereas for aqueous systems the surface tension is usually adjusted by adding surfactants in order to reduce the high surface tension of water, in UV-curable inks each component itself has already a much lower surface tension compared to water. Until now, dynamic surface tension investigations are mainly focused on surfactant migration properties in water. In contrast to aqueous systems including surfactants for UV-curing inks the surface tension is influenced by every single component. The time the molecule needs for diffusion and orientation may depend on molecular size, chemical structure and polarity. In order to adjust the dynamic surface tension for UV-inks a detailed knowledge of γ_{dyn} of every component alone and in mixtures is therefore necessary. There are very few results dealing with dynamic surface tension of UV-curing systems, Fies et al.[3] compared the properties of some typical components used in the printing industry. However, for inkjet inks a large amount of components is necessary including mono-, di-, and trifunctional monomers, oligomers and polymers. In this article we present a detailed study on dynamic surface tensions of inkjet ink acrylat components and focus on mixtures of different substances. The aim is to develop inks with low dynamic surface tension for good wetting before UV-curing takes place.

Experimental

For dynamic surface tension measurement a BP2 from Kruss with software Laboratory Desktop was used. The system works according to the method of maximum bubble pressure. Gas passes through a capillary, in this investigation a Teflon capillary with an diameter of 0.4 mm was used, continuously forming bubbles. The pressure reaches a maximum when the bubble achieves maximum radius of curvature (Fig. 1).

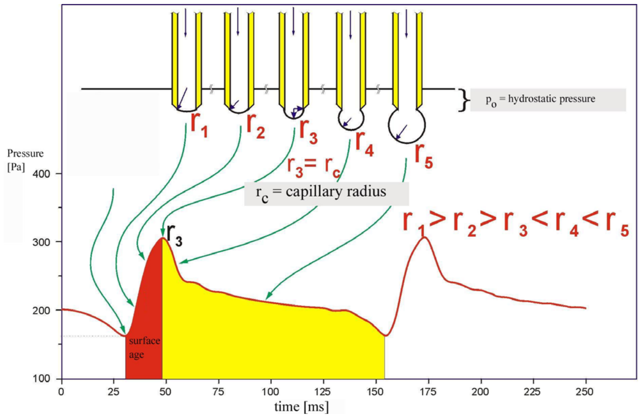

Figure 1. Principle of maximum bubble pressure method[4]

According to equation 1, the dynamic surface tension is proportional to the pressure difference of the maximum pressure and the hydrostatic pressure in the capillary:

$$\gamma = \frac{(p_{\max} - p_0) \times r}{2} \tag{1}$$

γ : surface tension
p_{max} : maximum pressure
p_0 : hydrostatic pressure in the capillary
r : capillary radius

Measurement data were obtained within a time period of 10-10000 ms, in most cases data were collected only up to 1000 ms. The temperature was adjusted to +/- 0.5°C.

The acrylates investigated are shown in Tab. 1. Acrylate components were used from Cray Valley except TBCH and AOA which were supplied by BASF.

With this setup a measurement repeatability of 0.5 mN/m is obtained for two successive measurements of one component (Fig. 2).

Table 1. List of Used Components with Abbreviations

Component	*Abbreviation*
Dipropyleneglycol diacrylate	DPGDA
Tripropyleneglycol diacrylate	TPGDA
4-Tert.-Butylcylohexyl acrylate	TBCH
Isobornyl acrylate	IBOA
Isobornyl methacrylate	IBOMA
Tetrahydrofurfuryl acrylate	THFA
Tetrahydrofurfuryl methacrylate	THFMA
2-(2-Ethoxyethoxy)ethyl acrylate	EEEA
Polyethyleneglycol-200 diacrylate	PEG200DA
Polyethyleneglycol-400 diacrylate	PEG400DA
Polyethyleneglycol-600 diacrylate	PEG600DA
Isodecyl acrylate	IDA
Lauryl acrylate	LA
Isooctyl acrylate	IOA
Propoxylated Trimethylolpropane triacrylate	TMPPOTA
Ethylenegycol dimethacrylate	EGDMA
Diethyleneglycol dimethacrylate	DGDMA
Triethyleneglycol dimethacrylate	TIEGDMA
Tetraethyleneglycol dimethacrylate	TTEGDMA
Amine-modified oligoether acrylate	AOA
Modified aliphatic urethane acrylate	AUA

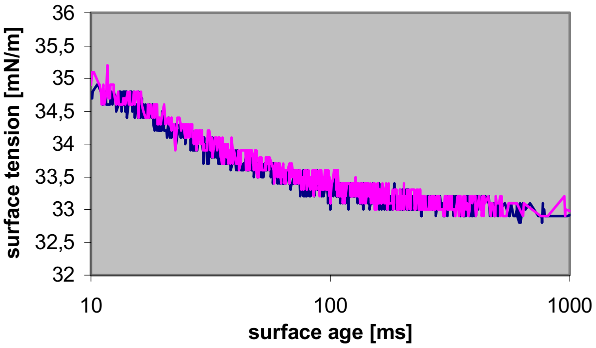

Figure 2. Repeatability of dynamic surface tension measurements using EEEA at 20°C

Results

Influence of Molecular Structure on Dynamic Surface Tension

For inkjet inks TPGDA is a common used di-functional monomer. The dynamic surface tension of TPGDA is shown in Fig. 3. A slight decrease of γ_{dyn} within the first 100 milliseconds can be observed, the equilibrium is reached after about 0.5 s. Instead of TPGDA due to environmental regulations the use of DPDGA may be preferred.

Comparing both γ_{dyn} (Fig. 3) the additional propylene group of TPGDA lowers the surface tension in the short lifetime region as well as in the equilibrated state similarly and thus facilitating the wetting of the media surface. Because of better wetting characteristics TPGDA is the better choice for fast processes compared to DPGDA.

As expected from the comparison in Figure 3 of DPGDA and TPGDA also the influence of a methacrylate-group is rather small. The methacrylic group lowers the surface tension to a similar extent as the propylene group (Fig. 4). Also, the gap between the acrylic and the methacrylic derivative is similar for smaller and higher surface ages. Even a successive increase in chain length of an ethylenegylcol backbone is not able to change the time-dependent behavior of γ_{dyn} as can be seen in Fig. 5.

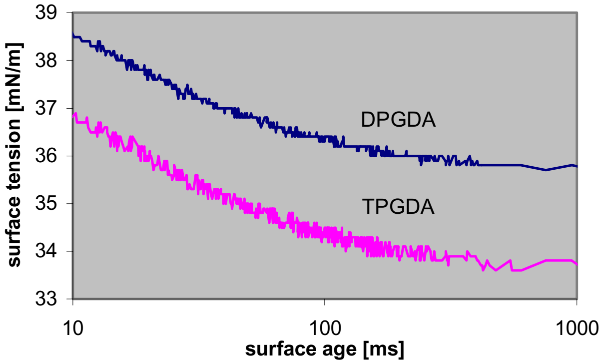

Figure 3. Comparison dynamic surface tension of DPGDA and TPGDA at 20°C

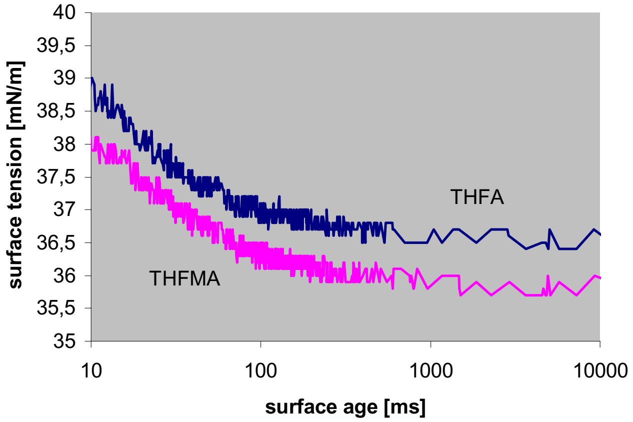

Figure 4. Comparison of dynamic surface tension of THFA and THFMA at 20°C

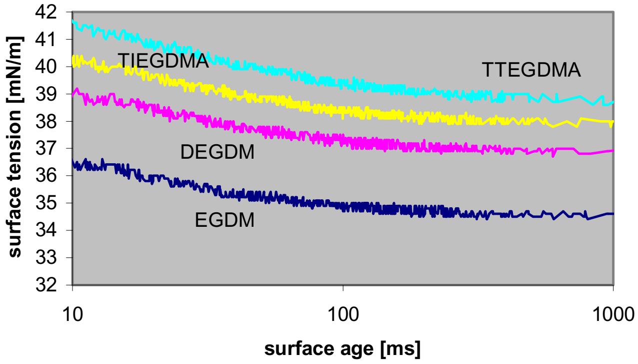

Figure 5. Dynamic surface tension of EGDMA, DEGDMA, TIEGDMA, TTEGDMA at 20°C

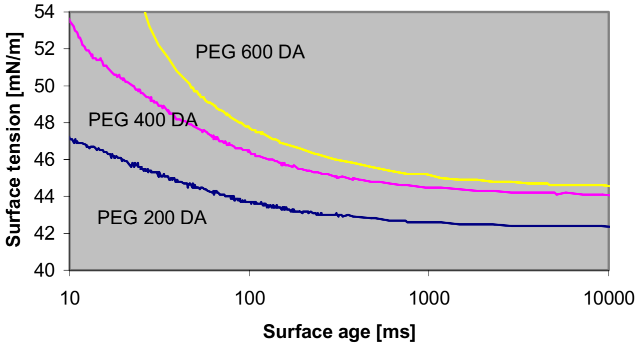

Figure 6. Dynamic surface tension of PEG 200/400/600 DA at 20°C

The comparison of acrylate and methacrylate as well as different chain length of backbone show that these structural changes do not change the dynamic behavior of the molecule. The small differences in structure does not affect the difference of γ_{dyn} at short and long surface ages, i.e. $\gamma_{dyn}^{10} - \gamma_{dyn}^{1000}$ is similar irrespectively their structure. Such a weak dependence on surface age is also observed for LA, IDA, IBOA, IBOMA and IOA.

The behavior changes more strongly if the molecular weight is increased, i.e. if γ_{dyn} is compared for different polyethylene-diacrylates. In Fig. 6 PEG 200, 400 and 600 DA are compared regarding their dynamic surface tension.

The higher the molecular weight, the higher is the difference $\gamma_{dyn}^{10} - \gamma_{dyn}^{1000}$ while the equilibrium surface tensions almost approach each other.

For fast curing processes increasing wetting problems are expected going from PEG 200 DA to PEG 600 DA because of the increasing value of γ_{dyn}^{10}. On the other hand components with high $\gamma_{dyn}^{10} - \gamma_{dyn}^{1000}$ allow to adjust a higher surface tension at the nozzle plate to prevent extensive nozzle plate wetting without the risk of substrate wetting problems. Therefore a screening was performed in order to find components with high dependence of the dynamic surface tension on surface age.

Following the idea that molecular weight has an impact on the dynamic behavior monomers with higher molecular weight and oligomers, which are necessary to improve film characteristics, on ether and urethane base were included in the investigation. One examples of such monomer is TMPPOTA having a similar weight compared to PEG600DA indicating that molecular weight is the main parameter to determine dynamic behavior. Indeed, the dependence of surface tension on surface age is similar to PEG600DA. Accordingly, oligomers also show a strong dependence of the surface tension on the surface age. In Figure 7 for comparison also THFA as a typical monomer is depicted.

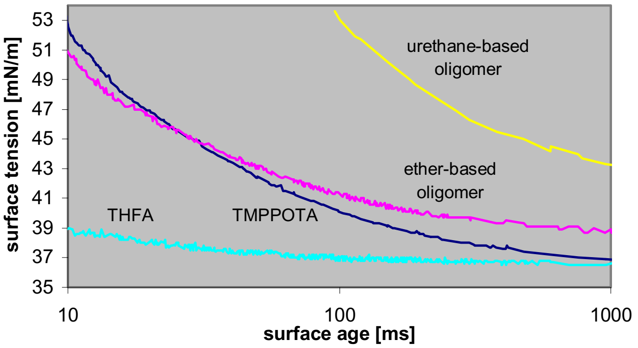

Figure 7. Dynamic surface tension of high molecular weight monomers and oligomers. For comparison also THFA is shown

If used alone wetting problems for the oligomers and TMPPOTA are expected for fast processes. For inkjet inks not the single component is important but the characteristics of the mixture of all ingredients necessary to adjust film properties, viscosity etc. Dynamic surface tension measurements of single components alone are therefore not expressive, investigation of mixtures is the next step to understand better the surface activity of UV-curable inkjet inks.

Mixtures

In order to reach the viscosity necessary for inkjet printheads high viscous components are diluted with monomers. A mixture of TMPPOTA with TPGDA is shown in Fig. 8. Although the static surface tension is the arithmetic average if mixed 50:50, for short surface ages γ_{dyn} is strongly reduced.

A similar effect is observed for a commercially available amine-modified polyether acrylate. Using 50% TPGDA the strong increase with shorter surface age is reduced to an extent typical for TPGDA (Fig. 9).

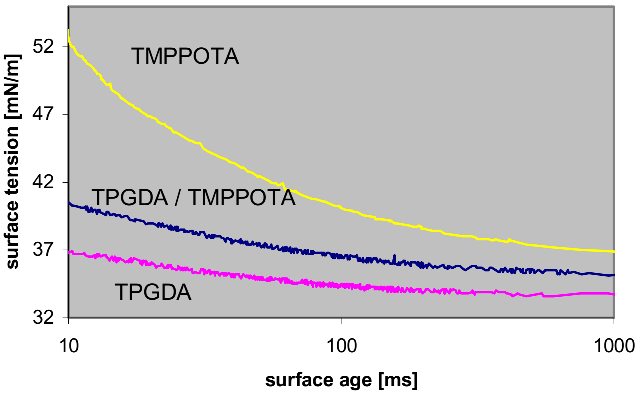

Figure 8. Comparison of dynamic surface tension of TMPPOTA, TPGDA and a 1:1 mixture of both at 20°C

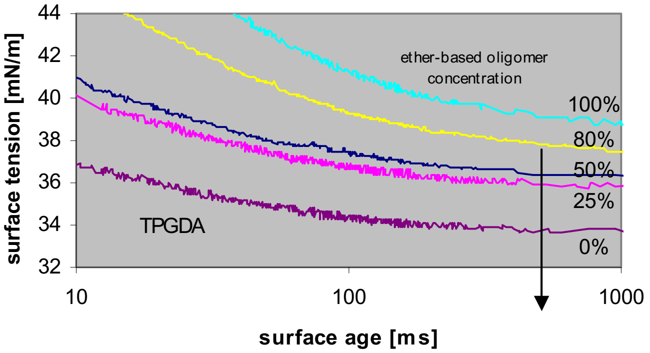

Figure 9. Influence of ether-based oligomer concentration of dynamic surface tension of TPGDA at 20°C

Comparing γ_{dyn}^{10} and γ_{dyn}^{1000} for the mixtures of oligomers and TMPPOTA the dynamic behavior of the mixture is completely determined by the monomer at concentrations of 50% or more. One possible explanation for this result may be connected with the higher mobility of the monomer compared to the oligomer. For long surface ages both molecules may migrate and orient to the surface to the same extent. If the surface ages are small, the migration of smaller molecules facilitates the orientation at the newly formed surface. As a consequence for practical work improved wetting is expected only for concentration of TPGDA above 50%, less than 30% would result in wetting problems because of high γ_{dyn}^{10} = 45 mN/m. (Fig. 10). Monomer are therefore not only diluents in order to obtain the target viscosity but also necessary to reduce the dynamic surface tension γ_{dyn}^{10}.

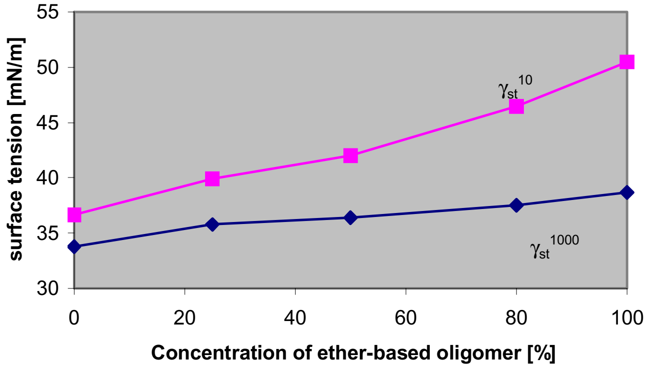

Figure 10. Comparison of γ_{dyn}^{10} *and* γ_{dyn}^{1000} *in mixtures of ether-based oligomer and TPGDA*

On base of a wide acrylate screening and investigation of mixtures an UV-ink with a strong decrease in γ_{dyn} for good printhead characteristics is designed. Because of high γ_{dyn}^{10} there is no risk of extensive wetting of the nozzle plate. To reduce wetting problems connected with high surface tensions necessary for some printheads, the ink was designed to show an extreme drop of γ_{dyn} within the first 500 ms. The dependence of γ_{dyn} on surface age is compared with an UV-ink available on the market in Fig. 11.

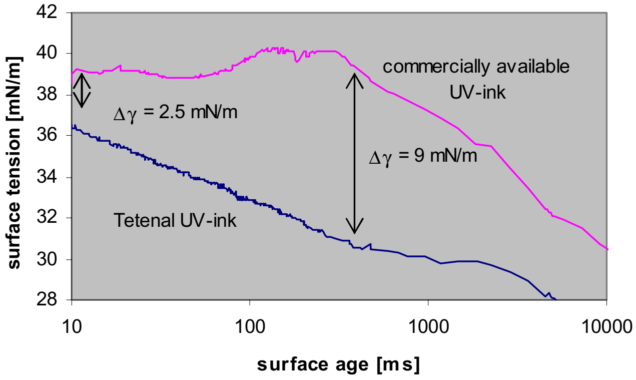

Figure 11. Comparison of dynamic surface tension of an optimized Tetenal UV-ink to an competitor ink

γ_{dyn}^{10} of both inks are comparable but the dynamic surface tension of Tetenal ink decreases strongly within the first 500 ms whereas γ_{dyn} of the other UV-ink remains almost unchanged. The gap is about 9 mN/m at a surface age of 500 ms. The gap remains for longer surfaces ages although decreases slightly.

The printing characteristics of this special designed ink are superior compared to usual UV-inks because of a much lower surface tension for substrate wetting combined with a high surface tension necessary for good printhead operation. This advantage is especially important for high speed processes, i.e. where the ink is not allowed to equilibrate for more than 500 ms.

Summary

A wide range of acrylates were investigated regarding their dynamic surface tension. The surface tensions of many molecules like TPGDA, THFA and IBOA are almost independent on surface age. Small changes in molecular structure, e.g. exchange of acrylic and methacrylic groups, addition of propylene groups and ethylene groups have only a small impact on dynamic behavior. In contrast molecules with higher molecular weight exhibit a much steeper drop of the dynamic surface tension within the first 500 ms which is attributed to the mobility of the molecules. From experiments with mixtures of viscous components and diluents results a concentration of about 50% necessary to reduce the high surface tension at low surface ages and to match the dynamic behavior of the diluent. From the results of dynamic surface tension measurements an ink is designed showing a high surface tension at short surface ages to prevent extensive wetting of the nozzle plate but exhibiting a drop within the first 500 ms to assure good substrate wetting also for fast printing processes.

References

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Biography

Dr. Umberto De Rossi studied chemistry and recieved his Ph.D. in pysical chemistry at the Free University in Berlin in 1996. After a post-doctorate at the Max-Planck Institute of Surface and Colloid Science Dr. De Rossi joined Tetenal and worked on photographic solid and liquid chemistry. Parallely he established a research division for inkjet inks and papers and is currently head of R&D at Tetenal. Dr. De Rossi holds several scientific publications.