Invisible set-off of photoinitiators and acrylate monomers from UV-printing inks onto polyolefins

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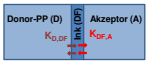
Introduction

The transfer of printing ink components from packaging into the food need to be considered for food regulatory compliance. At outside printing two mechanism of transfer can occur principally: Permeation through the packaging layers and (invisible) set-off from the printed side to the food contact layer at storage of the packaging material on a roll or in a stack with subsequent migration into food.
Aim of the study was to investigate set-off processes at UV-printing ink layers kinetically and derive parameters for theoretically predicting set-off and migration as well as for experimentally simulating set-off.

Method

For the study a OPP film (30 µm) was printed with 3 ink systems. Each colour was full area printed, wet in wet (worse case printing). Two coverages were investigated: 200 % (black, cyan) and 400 % (black cyan, magenta, yellow). A part of the printed film was lacquered with a dispersion lacquer (non-UV). These printed OPP films were used as donor materials (D). The printed side was brought into contact with various acceptor materials (A) which represent the food contact layers. Here the data of polyolefin films are presented: PE film (40 µm) and PP film (30 µm). Set-off experiments were conducted under defined conditions: the donor/acceptor pairs were stored under pressure (0.46 kg/dm²) at 40 °C and 60 °C. Samples taken after 1, 3, 6, 8, 10, 15, 20, 40 days (40 °C) or 1, 2, 4, 6, 8, 10, 15 and 20 days (60 °C). Donor and acceptor films were separately extracted and photoinitiators and acrylates quantitatively determined by LC-MS or GC-MS.
Ink system 1: conventional UV ink (non-food grade), 6 photoinitiators (200 – 400 Da), 6 acrylate monomers (250 – 500 Da)
Ink system 2: low migration UV ink (food grade), 2 polymeric photoinitators, 2 polymeric acrylate monomers
Ink system 3: low migration UV ink (food grade), 3 photointiators (300 – 400 Da), 2 acrylate monomers (250 Da, polymer), 400 % printing contained conventional magenta ink: 3 photoinitators (200 – 300 Da), 2 acrylate monomers (300 – 450 Da).
Partition coefficients K between donor PP and printing ink and acceptor films and ink were calculated using a thermodynamic approach from a 3-layer system as the concentration in the ink is not directly accessible. $K_{D,Ink}$ was derived from the experiment with PP as acceptor .



$$K_{D,DF} = \frac{c_D}{c_{DF}} = \frac{m_D \cdot V_{DF}}{V_D \cdot m_{DF}}$$

$$K_{A,DF} = \frac{c_A}{c_{Fs}} = \frac{m_A \cdot V_{DF}}{V_A \cdot m_{DF}}$$

$$m_{D+DF} = m_D + m_{DF}$$

$$K_{A,DF} = \frac{m_A \cdot (V_D \cdot K_{D,DF} + V_{DF})}{V_A \cdot m_{D+DF}}$$

Equilibrium concentrations calculated in three ways from masses m in 1 dm²:
$m_{Donor+Ink}$ (eq) and $m_{Acceptor}$ (eq)
$m_{Donor+Ink}$ (eq) and $m_{Acceptor}$ (eq)=$m_{Donor+Ink}$(t=0) - $m_{Donor+Ink}$(eq)
$m_{Donor+Ink}$ (eq) = $m_{Donor+Ink}$(t=0) - $m_{Acceptor}$ (eq) and $m_{Acceptor}$ (eq)

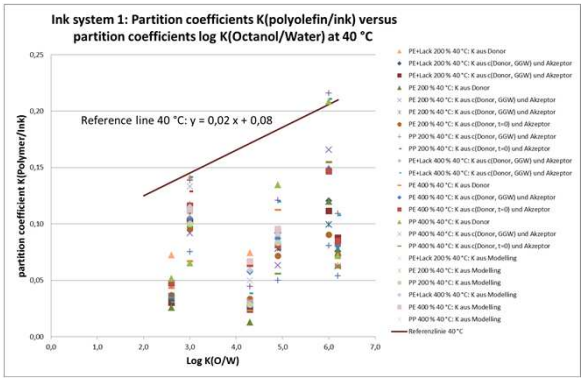


Figure 1: Partition coefficients $K_{(Polyolefin/Ink)}$ from ink system 1 and reference line for estimation of partition coefficients of other ink components and ink systems.

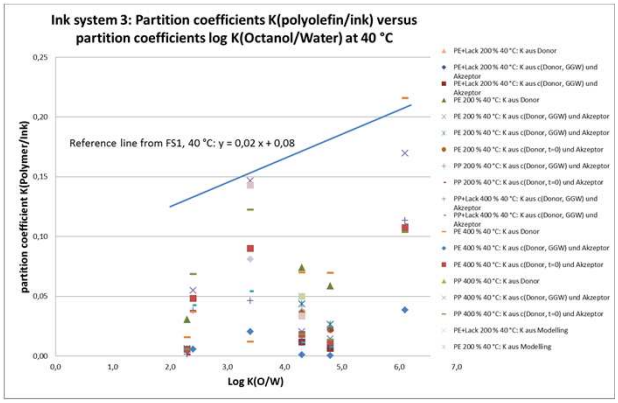


Figure 2: Partition coefficients $K_{(Polyolefin/Ink)}$ from ink system 3 and verification of reference line from ink system 1 for estimation of partition coefficients of other ink components and ink systems.

Results and Conclusions

Partitioning equilibrium with thin polyolefin films (PE 40 µm, PP 30 µm) was reached within short term for "monomeric" photoinitiators and acrylates (Ink systems 1 and 3) whereas "polymeric" photoinitiators (ink system 2) were diffusion controlled since only low or not detectable migration was found. Equilibrium of the polymeric PI was largely from being reached after 40 days / 40 °C or 20 days / 60 °C. The lacquer layers did not act as barriers for low and medium molecular weight photoinitiators and acrylates but for high molecular weight components only .
The partition equilibrium of photoinitiators and acrylates between polyolefins and UV inks was always on the side of the ink ($K_{Polyolefin/Ink} < 1$).
The values of $K_{(Polyolefin/Ink)}$ of photoinitiators and acrylates were in a relatively narrow range: 40 °C: 0.01 – 0.22; 60 °C: 0.01 - 0.4 (log K(O/W) 1.7 – 6.2). The thermodynamic approach enabled to calculate the partition coefficients of many experiments within short term using Microsoft Excel.
A mathematical relation between $K_{(Polyolefin/Ink)}$ and polarity described by log $K_{(O/W)}$ could not be established. But for rough estimate of partition coefficients $K_{(Polyolefin/Ink)}$ of other PI or acrylates, an upperbound reference line was established in ink system 1 (**Figure 1**). For verification, this upperbound line was applied to the measured partition coefficients $K_{(Polyolefin/Ink)}$ of ink system 3 (**Figure 2**). Also in this system, taking K values from the line slightly overestimates the measured values or fits them.
The partition coefficients may be used to predict set-off and migration (permeation) from the UV ink layer during storage of the packaging materials and migration into food after filling. The data were established for flat films with intimate contact. The prediction may also be used for containers (e.g. yoghurt cups) under (worse case) assumption of intimate contact in the stack.
In order to simulate set-off in the inner part of roll, it is not necessary to apply high pressures as they occur in the roll. It is sufficient to assure intimate test contact of printed layer and food contact side.

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