Analysis of acrylate esters from UV-printing inks in food packaging materials and their migration into food

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Background

Liquid UV-printing inks are cross-linked by radiation with UV-light within a few seconds. Reactive diluters (monofunctional acrylic acid esters) belong to the printing ink formulation for viscosity adjustment. Cross-linkers are added to the printing ink formulation to realize a fast polymerization process. However, this process is not complete. Some of the cross-linkers and reactive diluters remain unbound in the polymer and can migrate into food, because of their low molecular weight and high vapour pressure. The cross-linkers consist of di- to hexa functional acrylic acid esters with very differing structures. The free double bound of the acrylic acid is highly reactive. 50 substances, which can be used for printing inks, are listed in the EUPIA-Guideline on printing inks [1].

Summary

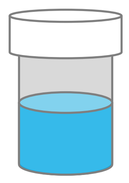
Substances like HDDA, 2-EHA, TPGDA, TMPDA, LA, DPGDA were identified in UV printed food packaging labels. TMPDA was found in amounts up to 277.9 µg/sdm in 10 of 12 labels. The sum over all these substances was between 45.4 and 460 µg/dm². To estimate a possible migration into the food, a simulated migration for 10d, 40°C with oat flakes and simulant for dry food was carried out. For HDDA and TPGDA a migration through a PE and PP film was investigated. The recovery rate for HDDA (sum of the amount in the label, PE or PP film and oak flakes) was only between 63 and 77 % (40°C), respectively. So it seems that the acrylic acid esters might react with food components.

Analytical methods

1 sdm of the label in 20 ml vial + 9 ml ethyl acetate

3 g oat flakes in 20 ml vial + 9 ml acetonitrile

1 h ultrasonic bath extraction



IS + fill up to 10 ml in a volumetric flask, filtration

GC-MS

The investigated samples were UV-printed labels (12) of food packagings. An extraction of the labels was performed with ethyl acetate by ultra sonic extraction. The oat flakes of the migration testings were extracted with acetonitrile instead of ethyl acetate. Also a GC-MS method for 19 acrylic acid esters were established.

Validation parameters:
Recovery rate of the method: 86 – 111 % over all standard substances
Limit of detection:
0.1 – 1.0 µg/sdm

Migration testing conditions:

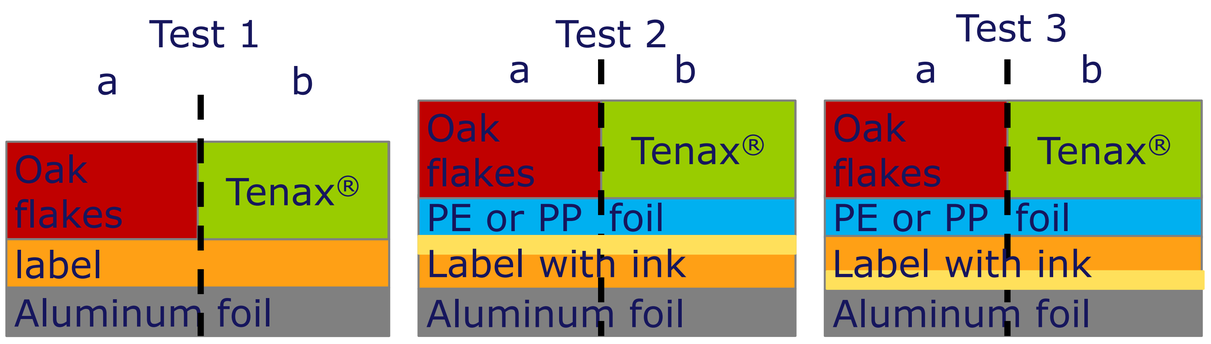


Fig. 1: Scheme of migration testing conditions, yellow: position of the ink on the label

In fig. 1 the migration testing conditions are shown. The tests were performed with a 60 µm PE or PP foil respectivly for 10 d, 40°C in a twist-off glass with oak flakes or MPPO (dry food simulant).

Test 1: The printed side of the label is in direct contact with the food or food simulant

Test 2: The label is labeled on a aluminum foil, but not in direct contact with the food, the ink is in direct contact with the PE or PP foil

Test 3: The label is labeled on a PE or PP foil, but not in direct contact with the food

Results

Screening of the labels:
2-EHA, TPGDA, TMPTA, LA, HDDA and DPGDA have been detected in labels from market samples with amounts up to 277.9 µg/sdm for one substance (fig.2). TMPTA (fig.3) was used in 10 of 12 labels as cross-linking agent. The detectable total amount over all unbound acrylic acid esters was analysed ranged between 45 and 460 µg/sdm.

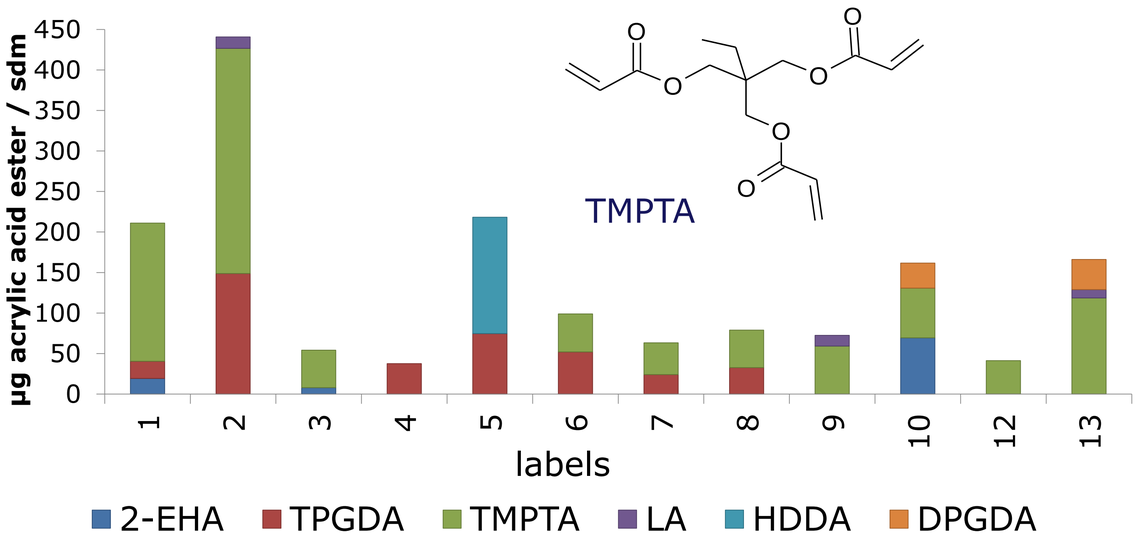


Fig. 2: Amount of acrylic acid esters detected in UV-printed labels by GC-MS; 2-EHA – 2 ethyl hexyl acrylate, TPGDA – tripropylene glycol diacrylate, TMPTA – trimethylene propyl triacrylate, LA – lauryl acrylate, HDDA – hexandiol diacrylate, DPGDA – dipropylene glycol diacrylate

Migration testing:
Test system 1: 15% of the HDDA remains in the label, but only 10 % could be detected in the oak flakes (fig.3, Test 1a). For TPGDA 100 % was recovered, but more TPGDA (68%) remains on the label (fig.4, Test 1a). The amount of HDDA on the label is higher when testing with the dry simulant (fig.3, Test 1b).
Test system 2: More HDDA and TPGDA remains in the label.
Test system 3: Again only 13 % HDDA remains on the label, but also a very low amount (12%) was detected in the oak flakes (fig.3, Test 3a), while in the dry simulant amounts up to 62% were analysed. It seems, that HDDA might react with food components.

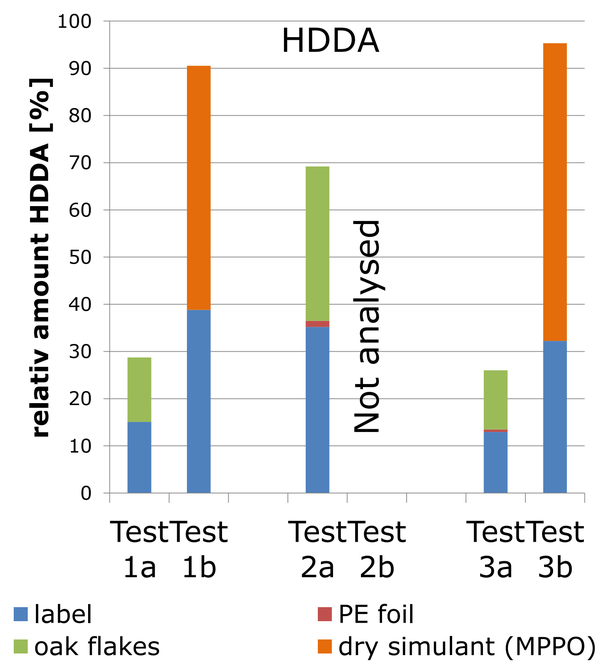


Fig. 3: Relative amounts HDDA of the different migration testings for 10d, 40°C, PE foil

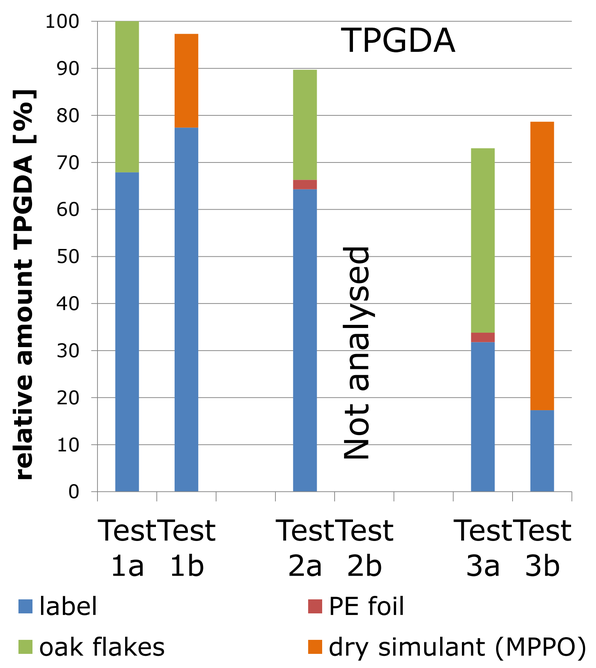


Fig. 4: Relative amounts TPGDA of the different migration testings for 10d, 40°C, PE foil

Literature

[1]: European Printing Ink Association (EuPIA). EuPIA-Guideline on Printing Inks for the non-food-contact surface of food packaging materials and articles, 2009