

Degradation products of photoinitiators used in UV-curable inks

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Introduction

UV-curable inks are more and more important for printing food packaging. UV curing has several advantages compared with the conventional thermal curing. The possible absence of solvents reduces the release of volatile organic compounds (VOC). Additionally the use of UV radiators at ambient temperatures reduces the energy consumption significantly. Hence, due to the lack of photoactive moieties of most of the useable monomers photoinitiators need to be used. These substances easily undergo homolytical and heterolytical cleavage reaction when exposed to UV light. Some of the products act as polymerization initiators and are incorporated into the polymer chain. Other products have a high migration potential even after complete curing of the ink layer. To assess the food safety of printed packaging the cleavage products need to be considered.

Experimental

Several frequently used photoinitiators were dissolved in ethanol and irradiated for 1 hour with UV light (750 W). After treatment the degradation products in the ethanolic solution were characterized using LC-MS/MS. As chromatographic system a Surveyor separation module from Thermo Finnigan equipped with a low-pressure gradient pump, autosampler and column heater was used. The different degradation products of each photoinitiator were separated on a Spherclone ODS(2) column (150 x 3 mm, 5µm, Phenomenex). A LCQ Deca iontrap massspectrometer (Thermo Finnigan) was used for data acquisition and processing. Ionization of the analytes was achieved using an atmospheric pressure chemical ionization interface in the positive (APCI⁺) and the negative ion mode (APCI⁻).

Results

As examples the degradation of the following photoinitiators Irgacure 379, TPO and Methyl-2-benzoylbenzoate were illustrated. After UV irradiation of the Irgacure solution some new substances could be detected in the APCI⁺-mode (Figure 1). Beside 4-Morpholinobenzoic acid (retention time RT = 1.0 min), 4-Morpholinoacetophenone (RT = 4.3 min) and Ethyl-4-morpholin-4-ylbenzoate (RT = 7.3 min) further two not identified species were determined. However no Irgacure 379 (RT = 12.3 min) could be analyzed in this solution. Ethyl 4-morpholin-4-ylbenzoate was formed by esterification of 4-Morpholinobenzoic acid with the ethanolic solvent. This reaction was not expected under UV curing conditions.

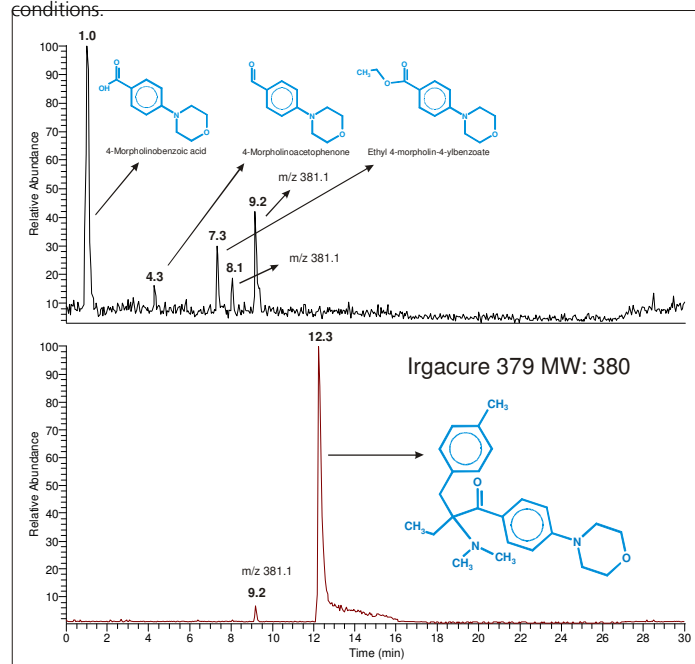


Figure 1: Chromatograms of an UV irradiated (on top) and a not UV irradiated solution (below) of Irgacure 379 and the corresponding degradation products of this photoinitiator (APCI⁺-mode)

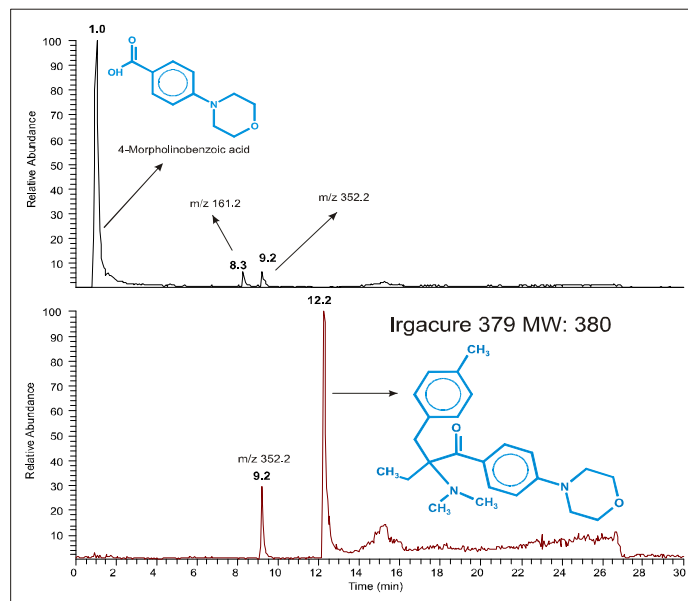


Figure 2: Chromatograms of the same solutions shown in Figure 1 measured in APCI⁻-mode

In the corresponding APCI⁻-mode (Figure 2) a similar view was obtained. 4-Morpholinobenzoic acid (RT = 1.0 min) as well as two unknown substances at a retention time of 8.3 min (m/z 161.2) and 9.2 min (m/z 352.2) were found. And also no lead compound could be detected. Similar results as already mentioned in detail for Irgacure 379 were observed for TPO and Methyl-2-benzoylbenzoate (Table 1). After irradiation with UV light a couple of new substances could be determined in the ethanolic solutions of the two photoinitiators. The corresponding peak for the lead compound was significantly reduced or totally disappeared.

Table 1: UV degradation products of TPO and Methyl-2-benzoylbenzoate after UV irradiation in an ethanolic solution in comparison to a non irradiated solution

Ionization method	TPO				Methyl-2-benzoylbenzoate			
	UV irradiated solution		not UV irradiated solution		UV irradiated solution		not UV irradiated solution	
	RT [min]	m/z	RT [min]	m/z	RT [min]	m/z	RT [min]	m/z
APCI ⁺	5.8	209.3	7.2	241.0	7.5	247.0	10.4	348.9
	6.1	209.3			14.4	425.1		
	7.2	241.0						
	7.8	255.0						
	9.2	464.5						
	9.7	464.5						
	9.7	464.5						
APCI ⁻	5.1	253.2	7.2	225.1	1.3	163.1	1.1	163.1
	5.9	209.3			10.2	217.3	10.4	348.0
	6.1	209.3			13.3	163.1		
	6.9	209.3			13.9	441.3		
	9.2	209.3						
	9.7	209.3						
	9.7	209.3						

Conclusions

The results show, that several new substances were formed during initiation process. These substances mostly have lower molar weight and should not be incorporated into the polymer chain. Thus are supposed that the degradation products have a higher migration potential than the photoinitiator. Nearly all of these substances are not toxicological assessed until now. However, the toxicity could be higher in contrast to the corresponding photoinitiator resulting in a potential elevated risk for human health. All the represented results were obtained for the degradation in ethanolic solutions. In additional studies the photoreactions will be investigated under printing conditions. To avoid underestimation of the potential hazard for human health further migration tests should be focused on the photoinitiators and their possible degradation products as well.



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