Study of the photo-products obtained from the UV curing of Benzophenone and Ethyl-4-(dimethylamino) benzoate

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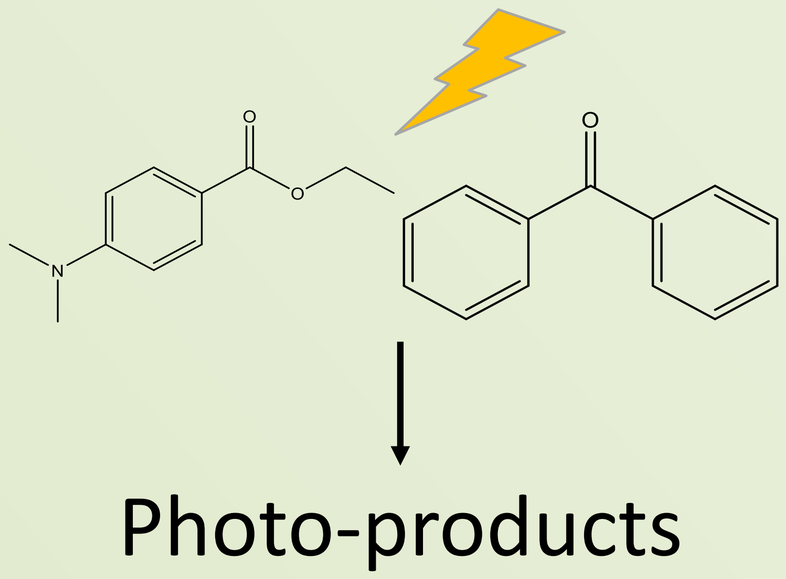
INTRODUCTION

Potential food safety issues concerning printing inks used in food contact materials, are not only related to the migration of photoinitiators into foodstuffs. Also many other components of the curing inks formulation and neo-formed products during the UV curing process, should be considered. This process have been widely studied in the photochemistry area; however, from a Food Safety point of view, the attention given by the authorities have only been focused on photoinitiators.



OBJECTIVES

In this study, the photocuring process of two common components of a type II photoinitiation system, benzophenone (BP) and ethyl-4-(dimethylamino) benzoate (EDB), was reproduced at laboratory scale in order to investigate the possible photo-products generated during the curing process.

For that purpose, different mixtures of BP and EDB were exposed to a UV curing lamp to replicate the UV curing process. Different exposure times and distances to the UV source have been tested. Finally, in order to identify the possible photoproducts generated, the exposed solutions were analyzed by HPLC-DAD and GC-MS.

METHODOLOGY & RESULTS

Different mixtures of BP and EDB have been under a Hg UV lamp. Different variables have been studied: photoinitiator and coinitiator proportions (1:1, 2:1 and 3:1), distances to the UV lamp (50 – 150 mm) and time of exposition to the UV source (0 to 10 min). The solutions have been analyzed by HPLC-DAD and GC-MS. The chromatographic conditions of each technique are on the tables 1 and 2:

1. HPLC-DAD

The HPLC-DAD chromatograms showed that, regarding the photo-products, the proportions of photoinitiator and amine synergist and the distance to the UV-light only are not critical factors in the photopolymerization process, observing only quantitative differences in the photo-products created. Nevertheless, the time of exposure to the UV light has been found as a important factor in the generation of different photo-products as it can be seen in figure 1. More time of exposure achieve a higher number of photo-products and increase (or decrease due to other side-reactions) the concentrations of them.

Model	HP 1100 (Hewlett-Packard)		
Column	Kromasil C18 (250 x 3.2 mm I.D., 5 µm particle size)		
Column temperature	30 ºC		
Flow rate	0.5 ml min^{-1}	**Injection Vol**	20 µl
Wavelenght (nm)	246, 256, 308 and 374		
Gradient	**Time (min)**	**Water (%)**	**AcN (%)**
	0	40	60
	2	40	60
	23	0	100
	30	0	100

Table 1: Chromatographic conditions of the HPLC-DAD analysis.

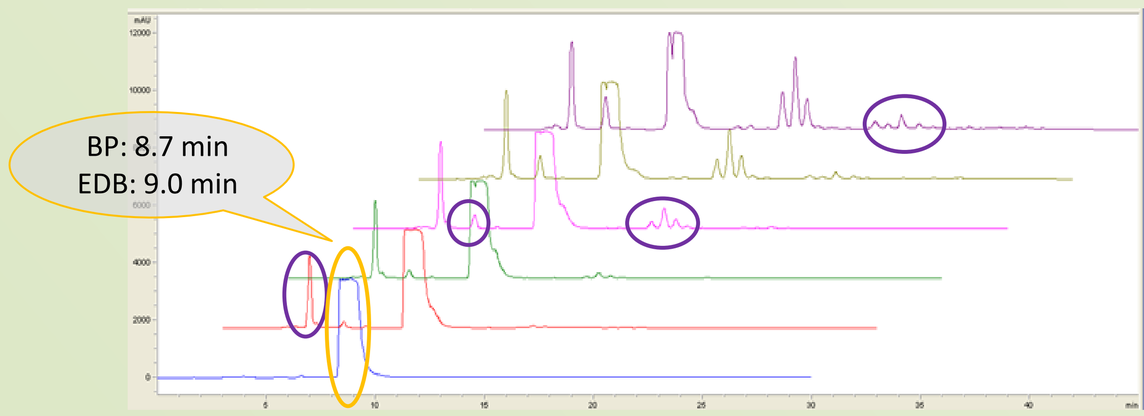


Figure 1: Chromatograms of the solution BP:EDB (1:1) that have been exposed to the light 0 (blue), 0.5 (red), 1 (green), 2 (pink), 5 (brown) and 10 min (purple). In the yellow circle it can be observed the broad peak corresponding to the photoinitiator and the amine synergists. In the purple circles, the new created photo-products.

2. GC-MS

The GC-MS analysis have provided a good match of a total of 23 compounds. 5 of these compounds have been already reported (1) as set-off contaminants in food packages: benzocaine, 4-hydroxybenzoic acid; benzenemethanol; benzaldehyde and 1,1-diphenylethylene. Also, the presence of the dimer of benzophenone (Benzopainacol) is in agreement with other works (2). Finally, to confirm the presence of these tentatively identified photo-products, the 13 available standards of these compounds have been injected confirming the presence of 4 of them: benzaldehyde, benzocaine, benzene, 1,1'-ethenylidenebis- and benzoic acid ethyl ester. All these molecules are presented in the figure 2.

Model	Trace 1300 GC- ISQ LT S MS detector (Thermo Scientific)		
Columns	ZB-5MS (30 m x 0.25 mm i.d. x 0.25 µm film)		
Flow rate	1.0 ml min^{-1}	**Injection Vol**	1 µl Split (1:100)
Voltage	70eV	**Mode**	Full Scan (40-450 Da)
Tª ramp	**Time (min)**	**Temperature**	
	0.00	50	
	5.00	50	
	30.00	300	
	35.00	300	
Transfer line Tª	280 ºC	**MS Tª**	310 ºC

Table 2: GC-MS chromatographic conditions.

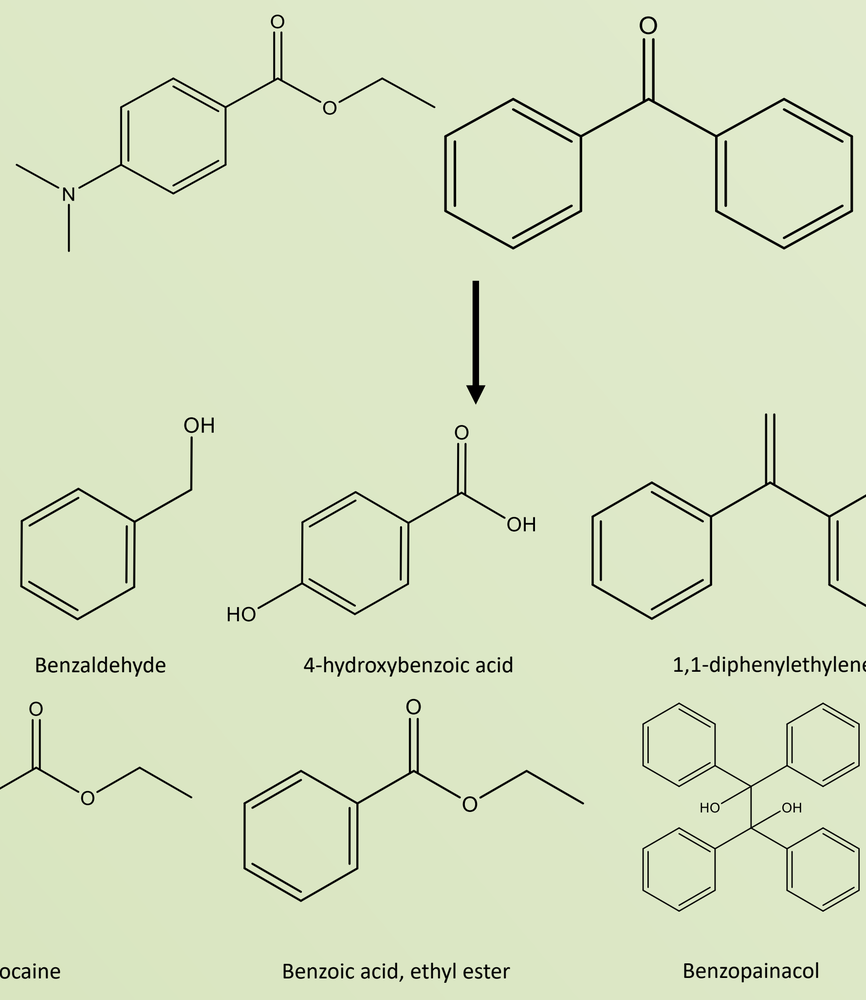


Figure 2: Main photo-products obtained from the UV curing process of the BP:EDB solutions.

CONCLUSIONS

- The photopolymerization process of a BP-EDB mixture has been studied at lab scale in order to determine the photo-products created. Different variables of the photopolymerization process have been tested, being determined that only the time of exposure to the UV source have influence in the photo-products created.
- **23 photo-products have been tentatively identified**. 5 of them have been already reported as photo-products or print-related contaminants. Also, to confirm the presence of these compounds, the 13 available standards have been injected and 4 photo-products have been confirmed: **benzaldehyde**, **benzocaine**, **benzene, 1,1'-ethenylidenebis-** and **benzoic acid ethyl ester**.
- Only **benzaldehyde** and **benzoic acid, ethyl ester** are in the European list of *authorized substances for plastic materials and articles intended to come into contact with food.* Nevertheless **benzaldehyde can provoke organoleptic changes in the food**. On the contrary, if we use the Cramer rules to evaluate the toxicological profile of the confirmed compounds, it results in **two molecules that may have significant toxicity** as **benzocaine** and **1,1' ethenylidenebis benzene** (Class III in the Cramer classification).

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2. Green WA. 2010. Industrial photoinitiators: a technical guide. Boca Ratón (FL): Taylor & Francis.