

Does the storage time of food packaging material  
influence the migration degree  
of 4-phenylobenzophenone photoinitiator  
from packaging materials to food?

Przemysław Nowakowski\*, Michał Dybowski and Rafał Typek

*Faculty of Chemistry, Maria Curie Skłodowska University,  
20-031 Lublin, Pl. Maria Curie Skłodowska 3, Poland*

*\*e-mail: [przemyslaw.nowakowski@poczta.umcs.lublin.pl](mailto:przemyslaw.nowakowski@poczta.umcs.lublin.pl)*

Nowadays, it is not possible to produce food packaging without the use of polygraphic varnishes. Their main task is to protect packaging from the effects of external factors, as well as to give the effect of clarity with greater exposure of the colors used. However, such varnishes contain in their composition low-molecular-weight photoinitiators that can easily migrate to a protected product. The aim of this work was to determine the migration of 4-PBZ from various types of substrates used in the printing industry, i.e. paper, aluminum foil and polyethylene foil. In addition, extensive studies on the impact of the storage conditions of a fresh reprint on the change in the migration of the photoinitiator to food were carried out.

**Keywords:** photoinitiator migration; 4-phenylbenzophenone; polygraphic varnish; UV curing; polygraphic substrates

## 1. INTRODUCTION

The increasing complexity of materials used in the production of packaging draws researchers attention to the possible consequences

of the presence of certain substances affecting human health and the environment in which they are found. This issue is of particular importance in the case of food packaging [1, 2]. Particular attention is paid to polygraphic varnishes [1], whose task is both to protect the packaging from external factors and to give clarity and depth to the colors used. According to the guidelines of the European Union (GMP-EC Regulation No. 2023/2006 of 22 December 2006 [3] regarding good manufacturing practice for materials and articles intended for contact with food and Commission Directive 2003/94/EC [4] with regard to good manufacturing practice of medicinal products for use and medicinal products for human use in the test phase) guidelines, materials in contact with food must be manufactured in the way, to prevent substances which may endanger consumers health from entaching food, and consequently contribute to the deterioration of the taste or aroma of the food being protected. This process is expertly defined as "component migration" and its degree should be monitored [1, 2, 5].

Currently, the most commonly used polygraph coatings are varnishes cured with EB (Electron beam) [5, 6] or UV (Ultraviolet) [7, 8] radiation. Due to the economics of the process usually the latter is chosen. In trade, free-radical varnishes cured with UV radiation are the most widespread [7, 8]. Such varnishes contain in their composition low molecular weight photoinitiators, which under the influence of UV radiation initiate the polymerization process of reactive liquid varnish components creating a hardened coating [9-13].

One of the more common photoinitiators used to cure varnish and the only of benzophenone derivatives not excluded from contact with food is 4-phenylbenzophenone (4-PBZ) [14]. The popularity of 4-PBZ results from its high reactivity, which implies in a high rate of curing of the varnish layers. However, it has some weaknesses. It has allergenic properties, causing irritation of the eyes and skin, it can penetrate into the bloodstream. This compound poses a hazard to the natural environment [14, 15]. Therefore, it is extremely important to monitor its migration from the varnish layer to food [16-18].

This paper presents the impact of storage of packaging protected with a UV-curing varnish coat on the degree of migration of unreacted photonitiator, which was 4-PBZ.

## 2. EXPERIMENTAL

### 2.1. *Materials and chemicals*

The analyte migration process was carried out by its extraction into the D2 model fluid, which constituted 95% ethanol which imitates fatty foods [19, 20].

The following polygraphic substrates were used: paper (Alaska Plus 280 g/m<sup>2</sup>), polyethylene foil (PE) (150 μm thickness) and aluminum foil (thickness 450 - 550 μm).

Polygraphic varnish most often used in practice was a mixture of the following ingredients:

- glyceryl [4PO] triacrylate 49.0%
- bisphenol A epoxy acrylate 35.5%
- amine synergist 9.5%
- dimethylsiloxane 1.5%
- 4-phenylbenzophenone 4.0%
- dimethylsiloxane modified by polyethers 0.5%

Ethanol (chemical purity grade) and aluminum foil (thickness 450–550 μm) were supplied by Krakchemia (Krakow, Poland). Polyethylene (PE) foil (150 μm thickness) was supplied by TART (Czech Republic) and paper (ALASKA PLUS 280 g/m<sup>2</sup>) by International Paper (Tennessee, USA). 4-phenylbenzophenone (4-PBZ) (99.9 %), benzophenone (99), glyceryl [4PO] triacrylate (99 %), bisphenol A epoxy acrylate (99 %), amine synergist (i.e. reaction products of diethylamine with [2-propenoic acid and and 1,1'-[(1-methyl-1,2-ethanediyl)bis[oxy(methyl-2,1-ethanediyl)]] ester]) (99 %) and dimethylsiloxane (99 %) dimethylsiloxane modified by polyethers (99 %) were purchased from Sigma (Poznan, Poland). Deionized water was purified on a Milli-Q system from Millipore (Millipore, Bedford, MA, USA).

### 2.2. *Formation of a surface varnish layer*

The sheets of paper, aluminum foil, and PE foil were coated by Flexiproof 100 (RK PrintCoat Instruments Ltd, Litlington, United Kingdom) with varnish composed of glycerol [4PO] triacrylate, bisphenol A epoxy acrylate, amine synergist, dimethylsiloxane, 4-PBZ and dimethylsiloxane modified by polyethers. 6 μm varnish

layers were formed on the applied support materials using rollers containing 160 cells per liner. The layers were cured employing the UV curing system from GEW (GEW (EC) Limited) applying 100 mJ/cm<sup>2</sup> UV dose. The used UV curing system allows for varnish curing in stable temperature. For statistical purposes each varnish layer was prepared three times. Before each curing procedure, the power of the UV lamp was controlled by a UV integrator (Technograph GmbH, Germany). The coated sheets were cut into squares (10 cm × 10 cm) and subjected to further experiments.

### *2.3. Examination of 4-phenylbenzophenone migration*

Estimation of 4-PBZ migration was performed accurately according to EN 1186-1, EN 1186-14 and PN-EN 13130-1 [21–23]. The pieces of individual packaging materials (10 cm × 10 cm) with layer of the varnish were extracted by 2 hrs at 60°C using 100 cm<sup>3</sup> of simulant D2 (95 % ethanol). The extraction process was carried out in the migration cell type E (ISEGA, GmbH, Germany). The obtained extracts (10 cm<sup>3</sup>) were spiked with ethanolic solution of benzophenone (internal standard) (20 mm<sup>3</sup> c=0.25 mg/cm<sup>3</sup>) and subjected to GC analysis.

### *2.4. Chromatographic analysis*

For qualification and quantification of 4-PBZ in the obtained extracts (experiments for the estimation of 4-PBZ migration degree) and for qualification of ethanolic extracts from PE foil, aluminum foil and paper (experiments for the determination of the indicative composition of additives contained in the applied packaging materials), gas chromatograph with mass spectrometer detector GC-MS (GC-MS 2010, Shimadzu, Kyoto, Japan) equipped with ZB-Semi Volatiles capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness; Phenomenex, USA) was used. Helium (grade 5.0) with flow rate 1.00 cm<sup>3</sup>/min as carrier gas was used. 1 μl samples were injected by an AOC – 6000 autosampler (Shimadzu, Kyoto, Japan). The injector temperature was 300°C. The following temperature program was applied: 4 min at 35°C and then a linear temperature increase up to 250°C at the rate of 5°C /min. The mass spectrometer was operated using electron ionization (EI) mode at 70 eV; the ion source temperature was 220°C. The chromatographic analysis was carried

out in SIM mode monitoring ions characteristic for 4PBZ ( $m/z = 152$ , 181 and 258) and benzophenone ( $m/z = 77$ , 105 and 182).

### 3. RESULTS AND DISCUSSION

Fig. 1. shows the degree of migration of 4-PBZ from various types of substrate, i.e. paper, aluminum foil and polyethylene foil. According to the obtained data, the highest level of migration of the analyte is observed when paper is used as the varnish substrate. In this case, the 4-PBZ migration is about 35% higher than for aluminum substrate and up to 55% higher than for polyethylene substrates. This result is so surprising that the varnish was applied in the same amount and cured under identical conditions. The differences in the degree of component migration are most likely the result of influence of the substrate type on the degree of cross-linking of the varnish and its adhesion to the substrate on which it was applied.

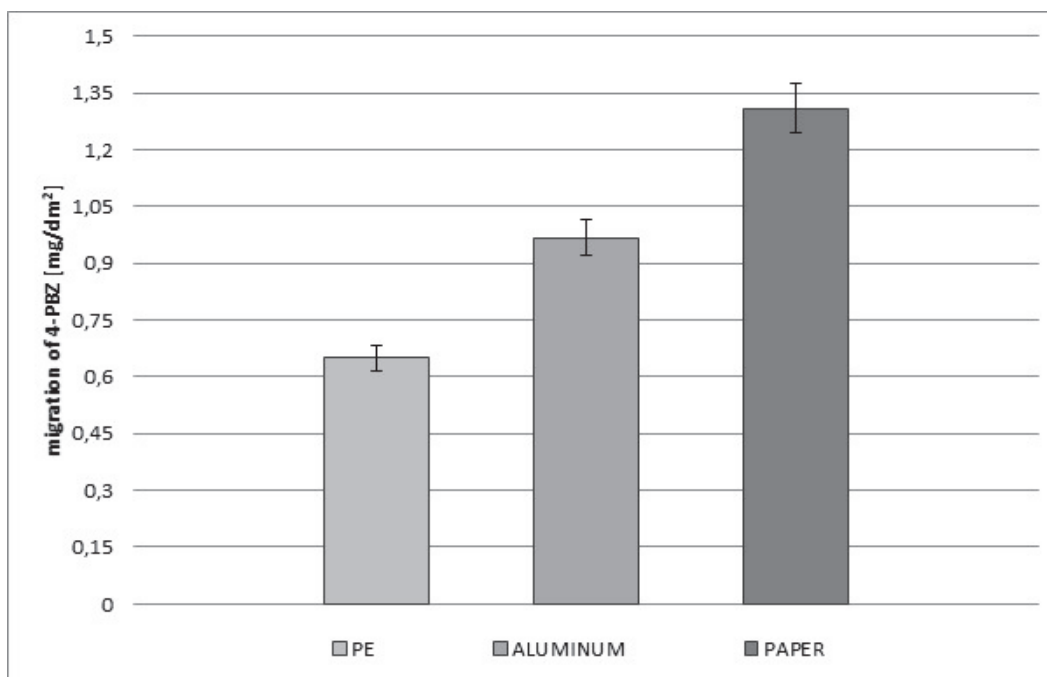


Fig. 1. Migration degree of 4-PBZ from various types of substrates, i.e. paper, aluminum foil and polyethylene foil.

With this in mind, it was decided to conduct an experiment, the purpose of which was to verify whether the conditions of storage of a

freshly prepared reprint affect the change in the degree of migration of the photoinitiator to food. For this purpose, identical varnish layers of 6  $\mu\text{m}$  were applied on substrates. Reprints were left for 24 and 48 hours in a darkened room, and at the same time (i.e. 24 and 48 hrs) were exposed to UV light. The obtained results of the migration test of the 4-PBZ photoinitiator are shown in Fig. 2. (PAPER light and dark: star and triangle; Aluminum light and dark: circle and square with plus; PE foil light and dark: square and rhombus).

There is lack of data in the literature regarding the impact of packed products storing on the photoinitiators migration degree. There are only few available articles describing the impact of storing of alloyed coatings using solvent components on the emission of low-molecular volatile organic compounds [24–27]. Nowadays varnish coatings cured by UV radiation have become very popular. These coatings are cheaper and more environmentally friendly in production [1, 2, 28]. With time, low-molecular photoinitiators included in UV varnish, can migrate to foodstuff [13, 29]. Therefore, it is important to get to know the possibility of photoinitiators migration into food products during storing.

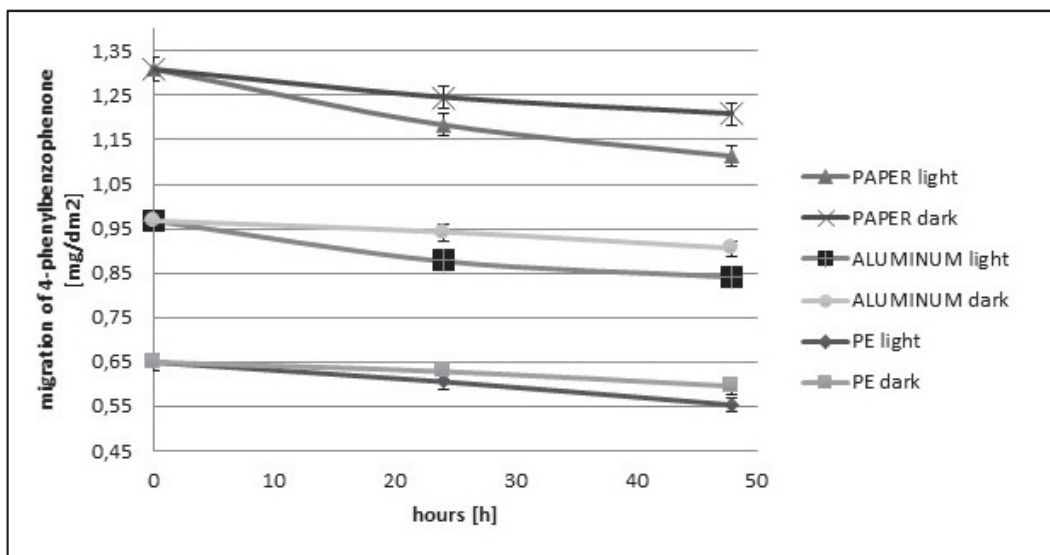


Fig. 2. Migration of a stored reprint from 6  $\mu\text{m}$  layer after 24 and 48 hours in a darkened room and exposed to UV light.

As can be seen from the data presented, the migration of 4-PBZ from the varnish coating is observed in the case of reprints stored in a shaded room as well as reprints subjected to UV radiation. This is

due to further cross-linking of the varnish surface. It is worth noting here even bigger decline is observed in the case of varnish subjected to UV radiation, which to a certain extent would most probably confirm the earlier thesis.

#### 4. CONCLUSIONS

At present a lot of attention is paid to polygraphic varnishes, whose task is both to protect the packaging from external factors and to give clarity and depth to the colors used. Due to the excellent aesthetic qualities, UV varnishes have gained enormous popularity. However, it should be noted here that in their composition they often contain harmful photoinitiators that can migrate to the protected product.

This paper attempts to investigate the type of substrate used and the method of storing the varnish layer on the degree of migration of a 4-PBZ photoinitiator into a food product. As it results from the presented research findings, the type of substrate used has a key impact on reducing migration of the photoinitiator from the polygraphic varnish layer. The smallest amount is emitted from the PE substrate, the largest of paper (relative increase in 4-PBZ migration by approx. 55%). In addition, in the case of reprints stored for 48 hours with additional exposure to UV light, a significant decrease in the emission of the photoinitiator was observed. Therefore, in order to reduce the emission of harmful photoinitiators from food packaging, and thus reduce the risk of negative impact of these substances on human health, it is recommended to use a polyethylene substrate and additionally "lagering" of reprints before using them for food packaging

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