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MIGRATION OF SUBSTANCES FROM LAYERS CURED BY UV RADIATION

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This paper is focused on migration of substances (photoinitiators and monomers) from formulations cured by UV radiation. The very effective and more often used solution for study of migrating substances into foodstuff is coupling of separation chromatographic techniques (liquid chromatography, gas chromatography) with mass spectrometry. In this work, samples containing only monomer and photoinitiator were cured under different conditions. After evaluation of monomer conversion (FTIR spectroscopy) amount of substances that migrated from cured sample into simulant (acetonitrile) by UV/VIS spectroscopy was estimated. The tested initiators were free radical photoinitiator (1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methylpropan-1-on) and cationic photoinitiator (η^5-2,4-cyclopenta-dien-1-yl)-[(1,2,3,4,5,6-h)-chlorobenzene]-Fe(II)-hexafluorophosphate). Acrylate binder pentaerythritol triacrylate and epoxy binder (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate) were used as monomers. The study proved that UV-VIS spectroscopy is a suitable method for analysis of simple systems consisting of a small number of components (two or three). The disadvantage of this method

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is that in comparison to chromatographic methods it cannot separate and identify a complex mixture of substances. Therefore, UV/VIS spectroscopy is not suitable for evaluation of migrants from commercially available inks and varnishes, which contain a large number of components (monomers, oligomers, initiators and additives).

Introduction

Many chemicals can migrate into foodstuff at different stages of the food chain. These chemicals include food additives, pesticide residues, mycotoxins, but also chemicals from food packaging (unreacted monomers, catalysts, initiators, solvents, plasticizers, antioxidants, dyes, pigments etc.).

General requirements for all types of materials and articles intended to come into contact with food are specified in the Regulation of the European Parliament and Council Regulation EC No. 1935/2004. Another important legislative act is the EC Commission Regulation No. 2023/2006 on good manufacturing practice for materials and substances intended to come into contact with food. It introduces general rules for all business operators in supply chain, and specifies that quality assurance and control systems are established and implemented. All printed inks intended for use on food packaging are in the scope of this Regulation. Both are applied directly in the Czech Republic and other states. There is not yet any specific EU legislation concerning printing inks for food packaging, with the exception of Directive 2007/42/EC relating to materials and articles made of regenerated cellulose film, which states that the printed surface of regenerated cellulose film must not come into contact with food [1]. In April 2010, new provisions came into force in Switzerland (Ordinance on Materials and Articles in Contact with Food, SR 817.023.21) for the use of printing inks and overprint varnishes for coating of food packaging. The ordinance significantly tightens the rules and restricts the permissible substances to defined positive lists (I-V) for evaluated and non-evaluated substances.

Migration usually describes diffusion process, which may be strongly influenced by an interaction of the packaging material with food. Migration data may be obtained from monitoring levels of chemicals in real food systems, but there are major analytical difficulties connected with this approach due to the complexity of the food matrixes and the chemical instability of some migrants. More commonly, migration data are obtained from migration experiment, carried out under controlled condition of time and temperature and contact between the materials and food simulant [2]. According to EU Directive 82/711EEC, the four simulants are water (simulant A) for aqueous foods with a pH above 4.5, 3 % acetic acid in water (simulant B) for acidic aqueous foods (pH below 4.5), 10 % aqueous ethanol (simulant C) for alcoholic products, and olive oil (simulant D) for fatty

foods. There is no simulant for dry food [3]. EU Directive 82/711EEC and its two amendments (Directive 93/8/EEC and 97/48/EC) provide the basic rules on migration testing, including simulants and conditions. Analysis of complex food extracts requires highly selective analytical techniques to characterize and determine targeted compounds and to characterize unknown compounds. Separation technique such as liquid chromatography, gas chromatography and capillary electrophoresis have become techniques used for study of migrating substances into foodstuff. The very effective and more often used approach is coupling of chromatographic techniques with mass spectrometry [4-7].

This work is focused on study of migration of substances (photoinitiators and monomers) from simple formulations (mixture of monomer and photoinitiator) cured by UV radiation at different conditions. The amount of migrated compounds was evaluated by UV/VIS spectroscopy.

Experimental

Materials

Two photoinitiators, free-radical photoinitiator Irgacure 2959 (1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methylpropan-1-one) and cationic photoinitiator Irgacure 261 (η^5-2,4-cyclopentadien-1-yl)-[(1,2,3,4,5,6-η)-(1-methylethyl)benzene]-Fe(II)-hexafluorophosphate) and two monomers: cationically polymerizable monomer Celloxide 2021P (3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexane carboxylate) and radically polymerizable monomer PETIA (pentaerythritol triacrylate) were used in this work. Both photoinitiators were supplied by Ciba Specialty Chemicals and monomers by UCB Chemicals. The formulas of used photoinitiators and monomers are shown in Fig. 1. Acetonitrile (Sigma-Aldrich) was used as a solvent for evaluation of molar absorption coefficients (UV/VIS spectroscopy) of tested substances and also as a simulant for determination of amount of migrated substances from cured samples. Four simulants described in EU Directive 82/711EEC (A, B, C and D) were not used due to their absorption in short wave UV region where also tested monomers and photoinitiators absorbed. Acetonitrile does not absorb in this region.

FTIR Spectroscopy

Polymerization reactions (degree of conversion) were studied by FTIR spectroscopy (specular reflectance). The infrared spectra were recorded with Avatar 320 FTIR spectrometer (Nicolet Instrument Corp., USA) at room temperature.

The concentration of free radical photoinitiator Irgacure 2959 in monomer PETIA was 1.5, 2 and 2.5 molar % and for cationic photoinitiator Irgacure 261 in monomer Celloxide 2021P 1, 2, 3 and 5 molar %. The samples were prepared by coating thin layer of curing mixture (liquid monomer with photoinitiator) on aluminium foil. For observation of cationic polymerization the samples were measured by FTIR before exposure and then after one passage through UV tunnel (medium pressure mercury lamp). Samples were measured in defined time lags up to 180 minutes (UV dose 175 mJ cm^{-2}, measured by radiometer UV Integrator, f. UV-technik). For observation of free radical polymerization the samples were measured by FTIR before exposure and then after 1, 5 and 10 passages through UV tunnel. The UV dose was set at 175 mJ cm^{-2} after 1 passage through UV tunnel (measured by radiometer UV Integrator, f. UV-technik). The disappearance of the functional groups was monitored by selecting the IR wave number where these functional groups exhibit their absorption bands: 809 cm^{-1} for acrylate double bond (PETIA) and three overlapping bands (788, 798 and 808 cm^{-1}) for epoxy rings of Celloxide 2021P. The degree of conversion (X) was calculated from the decrease in IR absorbance after a given exposure (free-radical polymerization) or defined time lag (cationic polymerization) by equation

$$X = 1 - \frac{A_t}{A_0} \tag{1}$$

where A_0 is the quotient measured band (acrylate or epoxide group) and internal standard without UV exposure and A_t is the quotient measured band and internal standard after UV exposure. Carbonyl group was chosen as an internal standard (1 738 cm^{-1} for acrylate monomer and 1 727 cm^{-1} for epoxide monomer).

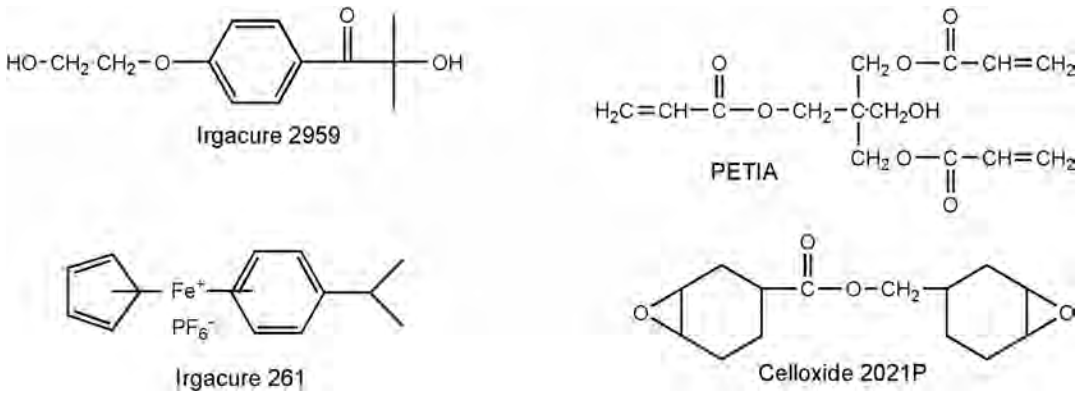


Fig. 1 Studied photoinitiators and monomers

UV-VIS Spectroscopy

UV-VIS absorption spectra were recorded by UV-VIS spectrometer Specord 210 (Analytik Jena AG, Germany) in acetonitrile at room temperature. The molar absorption coefficients were calculated using the Lambert–Beer's law

$$A = \varepsilon c d \tag{2}$$

where A is absorbance, ε is molar absorption coefficient (l $mol^{-1}cm^{-1}$), c is concentration (mol l^{-1}) and d is thickness of cuvette (cm). Circular pieces (diameter 11 mm) were cut out from samples (aluminium foil with thin layer of curing mixture) cured in UV tunnel and then soaked in 4 ml of acetonitrile in a small glass bottles for 1, 3, 5 and 24 hours. Five pieces were put into every bottle. After extraction, the absorption spectra of migrants in acetonitrile were measured by UV/VIS spectroscopy. Subsequently, the concentrations of migrants were evaluated by applying Lambert– Beer's law. The amount of migrants dissolved in acetonitrile is given as amount of specific migrant (mg) per gram of cured sample (extracted samples were weighed before extraction).

Results and Discussion

FTIR Spectroscopy

The reached degree of conversion of acrylate monomer PETIA with photoinitiator Irgacure 2959 (concentration 1.5, 2 and 2.5 molar %) after UV exposition are presented in Fig. 2a and for epoxy monomer Celloxide 2021P with photoinitiator Irgacure 261 (1, 2, 3 and 5 molar %) in Fig 2b.

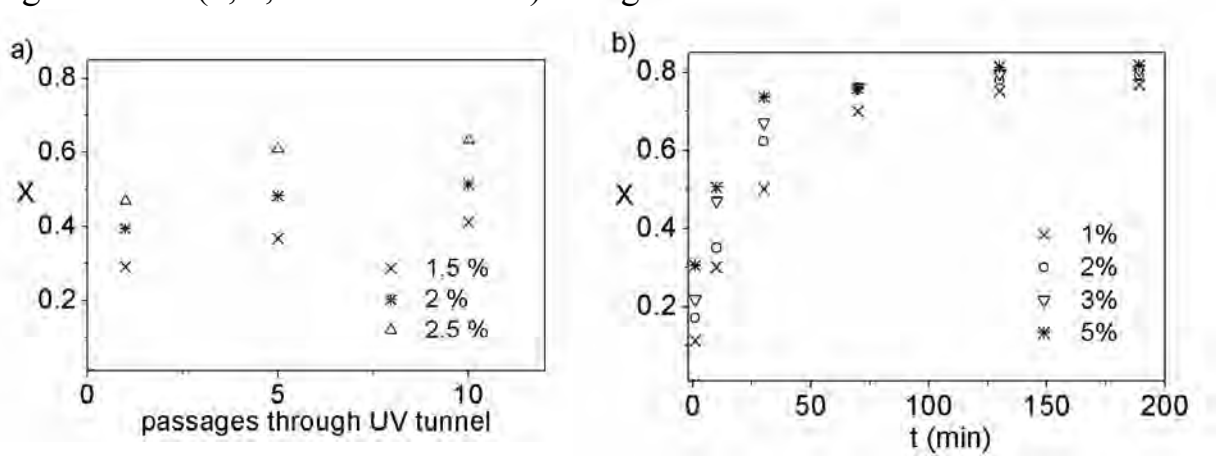


Fig. 2 The conversion curves of acrylate monomer PETIA with initiator Irgacure 2959 (a) and cationic monomer Celloxide 2021P with initiator Irgacure 261 (b)

The achieved degree of conversion of acrylic monomer PETIA varies according to content of photoinitiator and number of passages through UV tunnel (1, 5 or 10). In contrast, the cationic polymerization of binder Celloxide 2021P after 180 minutes after UV exposition achieved approximately the same degree of conversion (around 78 %) regardless of the amount of photoinitiator. The concentration of photoinitiator (Irgacure 261) affected the achieved degree of conversion primarily at the initial stage. The difference in degree of conversion of monomer Celloxide 2021P between samples containing 1 or 5 molar % of initiator was almost 20 %. The degree of conversion was also measured 24 hours after UV exposition, and the achieved degree of conversion was only about 2-4 % higher than the degree of conversion achieved after 3 hours (depending on concentration of photoinitiator).

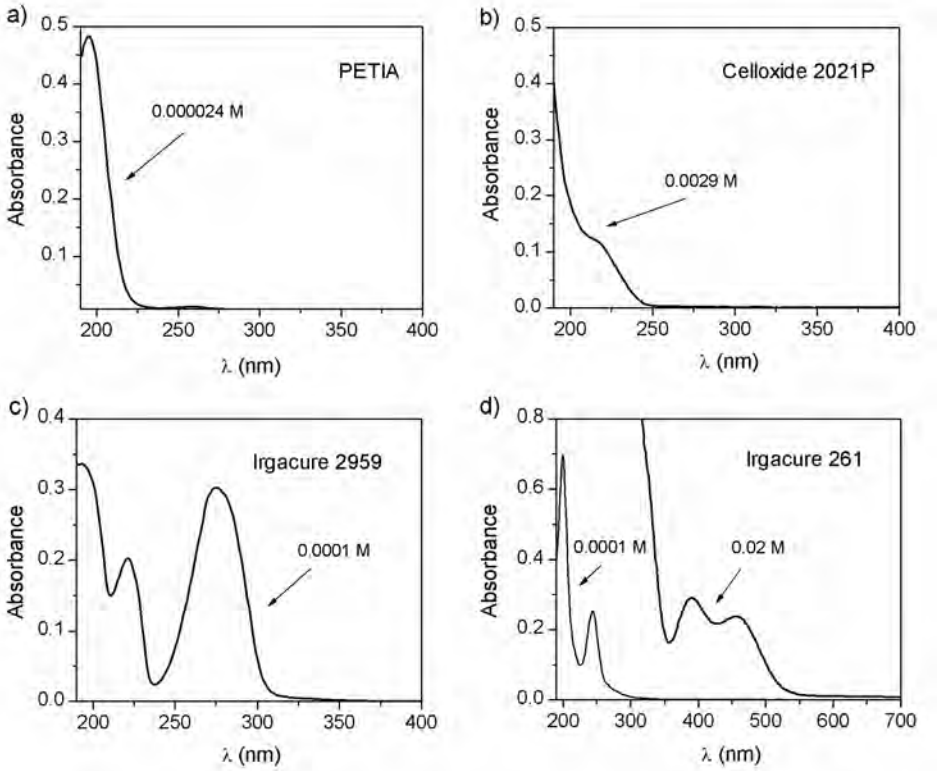


Fig. 3 UV-VIS spectra of PETIA (a), Celloxide 2021P (b), Irgacure 2959 (c) and Irgacure 261 (d)

UV-VIS Spectroscopy

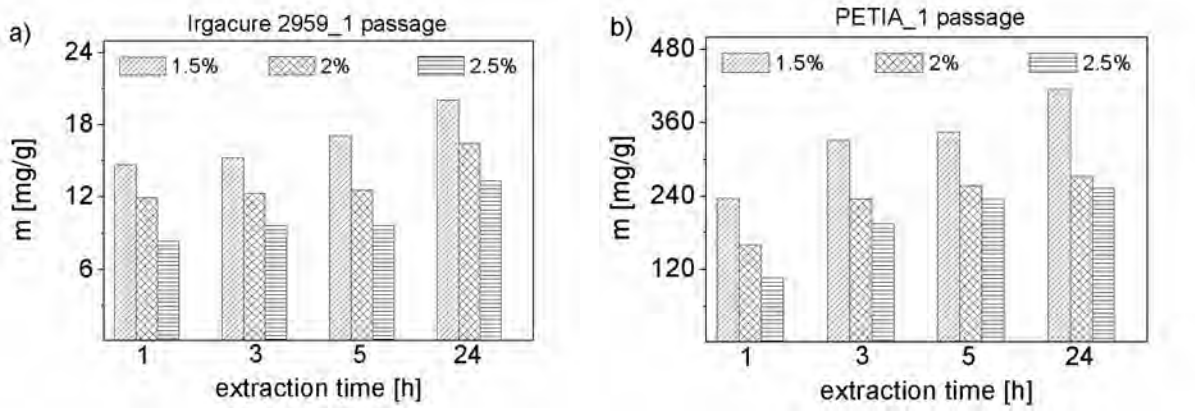
UV-VIS spectra of studied photoinitiators and monomers are shown in Fig. 3 and evaluated molar absorption coefficients are summarized in Table I (determined concentrations of tested substances migrated from cured samples into acetonitrile were evaluated for these specific wavelengths). Concentration of free radical initiator Irgacure 2959 in solution after extraction was evaluated at 271 nm, where monomer PETIA does not absorb. Monomer PETIA absorbs in all areas as initiator

Irgacure 2959. For evaluation of PETIA concentration in extracts, wavelength 194 nm was chosen. To be able to evaluate concentration of monomer PETIA, the absorbance of extract at 194 nm had to be corrected. The correction consisted in subtraction of absorbance of Irgacure 2959 (absorbance of Irgacure 2959 at 194 nm was computed using the concentration evaluated for wavelength 271 nm) from extract absorption spectra. Similarly, concentration of initiator Irgacure 261 was evaluated at 244 nm and monomer Celloxide 2021P at 199 nm (again with correction to absorbance of initiator Irgacure 261 at this wavelength). The amount of substances dissolved in acetonitrile is given as amount of substance (mg) per gram of cured sample.

Table I Molar absorption coefficients ε of substances studied in acetonitrile for specific wavelength (λ)

Substances	λ_1 nm	ε_1 l mol^{-1} cm^{-1}	λ_2 nm	ε_2 l mol^{-1} cm^{-1}	λ_3 nm	ε_3 l mol^{-1} cm^{-1}
Irgacure 2959	194	16 712	221	10 621	271	15 661
Irgacure 261	199	36 229	244	13 157	-	-
PETIA	194	35 955	-	-	-	-
Celloxide 2021P	199	214	-	-	-	-

Figure 4 shows migration of free radical photoinitiator Irgacure 2959 and acrylate monomer PETIA under different conditions (number of passages through UV tunnel and extraction time). With increasing concentration of photoinitiator in sample the amount of released monomer is reduced (Fig. 4b, d, f). The amount of migrating monomer ranges from 7 to 400 mg g^{-1} and for photoinitiator Irgacure 2959 (Fig. 4a, c, e) from 0.9 to 20 mg g^{-1}.



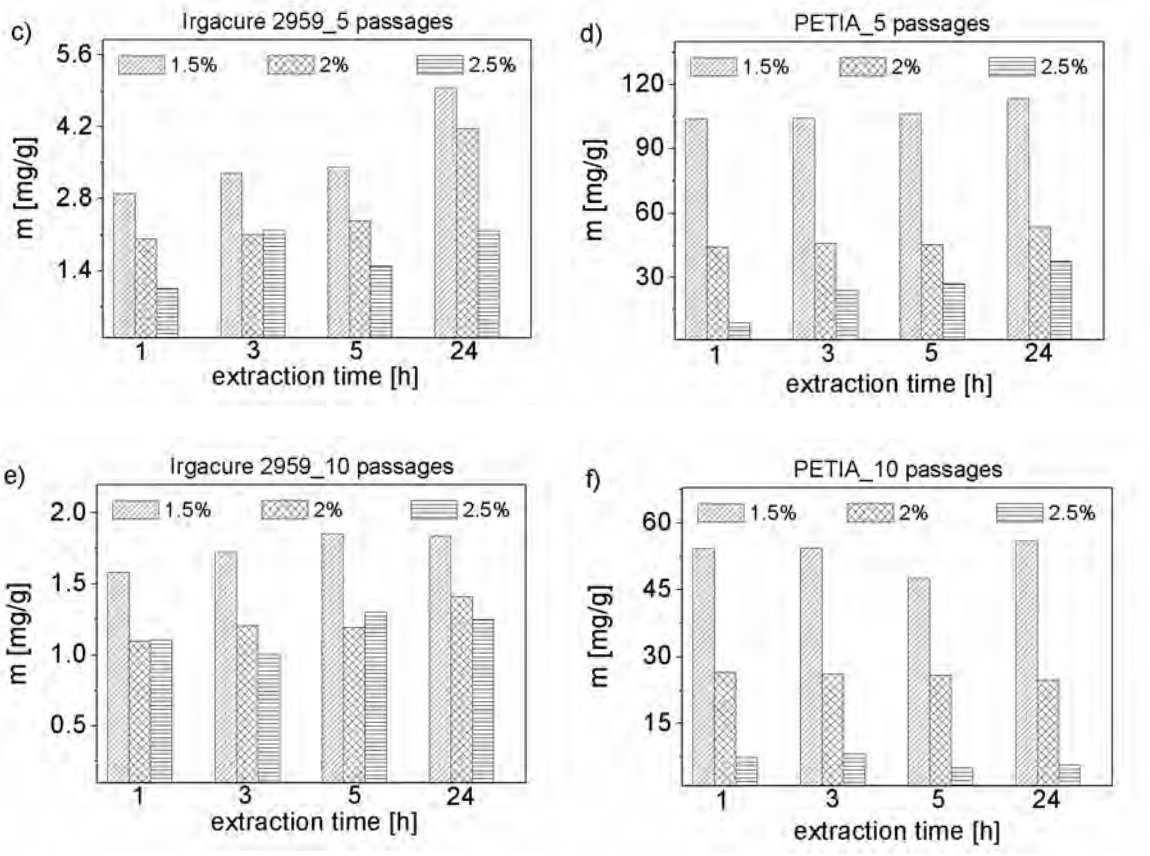


Fig. 4 The migration of Irgacure 2959 (a, c, e) and monomer PETIA (b, d, f) from the cured samples into acetonitrile for the extraction times of 1, 3, 5 and 24 hours

The difference between the amount of substances migrating from samples for 5 and 10 passages through UV tunnel is significantly lower than for 1 and 5 passages through UV tunnel, which is consistent with the degree of conversion. The migration of monomer PETIA from the samples containing 2.5 mol.% of photoinitiator Irgacure 2959 after 1 passage through UV tunnel (degree of conversion 0.47, extraction time 24 hours) was 255 mg g^{-1}, compared to 10 passages through UV tunnel (degree of conversion 0.63), where the migration was only 8 mg g^{-1}.

Similarly, with increasing concentrations of photoinitiator in samples a smaller amount of photoinitiator is extracted (Figs 4a, c, e). The degree of conversion significantly affects the amount of extracted photoinitiator Irgacure 2959. The samples containing 1.5 mol. % of photoinitiator Irgacure 2959 (10 passages through UV tunnel, extraction 24 hours, degree of conversion 41 %) shows migration of 1.8 mg g^{-1} (15 % of photoinitiator in extracted sample), the samples containing 2 mol. % of photoinitiator (degree of conversion 52 %) 1.5 mg g^{-1} (10 %) the and samples containing 2.5 mol. % of photoinitiator (degree of conversion 63 %) 1.3 mg g^{-1} (6 %).

Figures 5 and 6 show migration of epoxide monomer Celloxide 2021P and cationic photoinitiator Irgacure 261 under different conditions (polymerization

time after UV exposition — 0, 1, 3 and 5 hours (before extraction) and extraction time — 1, 3 and 24 hours). Large amount of monomer Celloxide 2021P was extracted from almost all samples except those that polymerized 5 hours (Fig. 5d). Extracted amount of monomer was between 550-970 mg g^{-1} depending on concentration of photoinitiator and polymerization time (Figs 5a, b, c). After 5 hours of polymerization, approximately 8 times less monomer was extracted from samples containing 5 mol. % of photoinitiator than from samples with shorter time of polymerization.

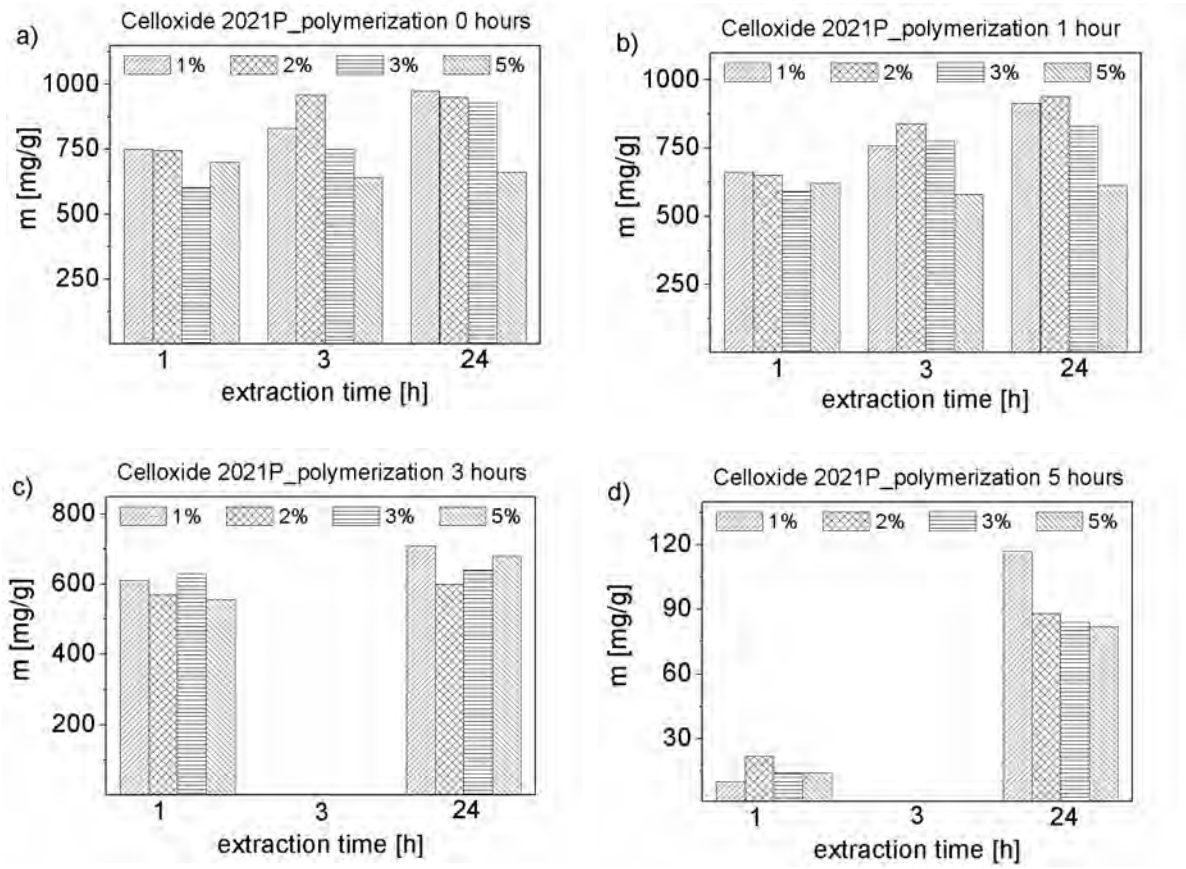


Fig. 5 The migration of monomer Celloxide 2021P from the cured samples into acetonitrile for the extraction times of 1, 3 and 24 hours

The amount of extracted cationic photoinitiator Irgacure 261 is proportional to concentration of photoinitiator in sample (Fig. 6), which is in contrast to the free radical initiator Irgacure 2959. The best results were achieved after 5 hours of polymerization (Fig. 6d), where the samples containing 1 mol. % of Irgacure 261 (extraction time 24 hours) show migration 4.2 mg g^{-1} (26 % of photoinitiator in extracted sample), sample containing 3 mol. % of photoinitiator 7.9 mg g^{-1} (18 %), and sample containing 5 mol. % of photoinitiator 12.1 mg g^{-1} (16 %).

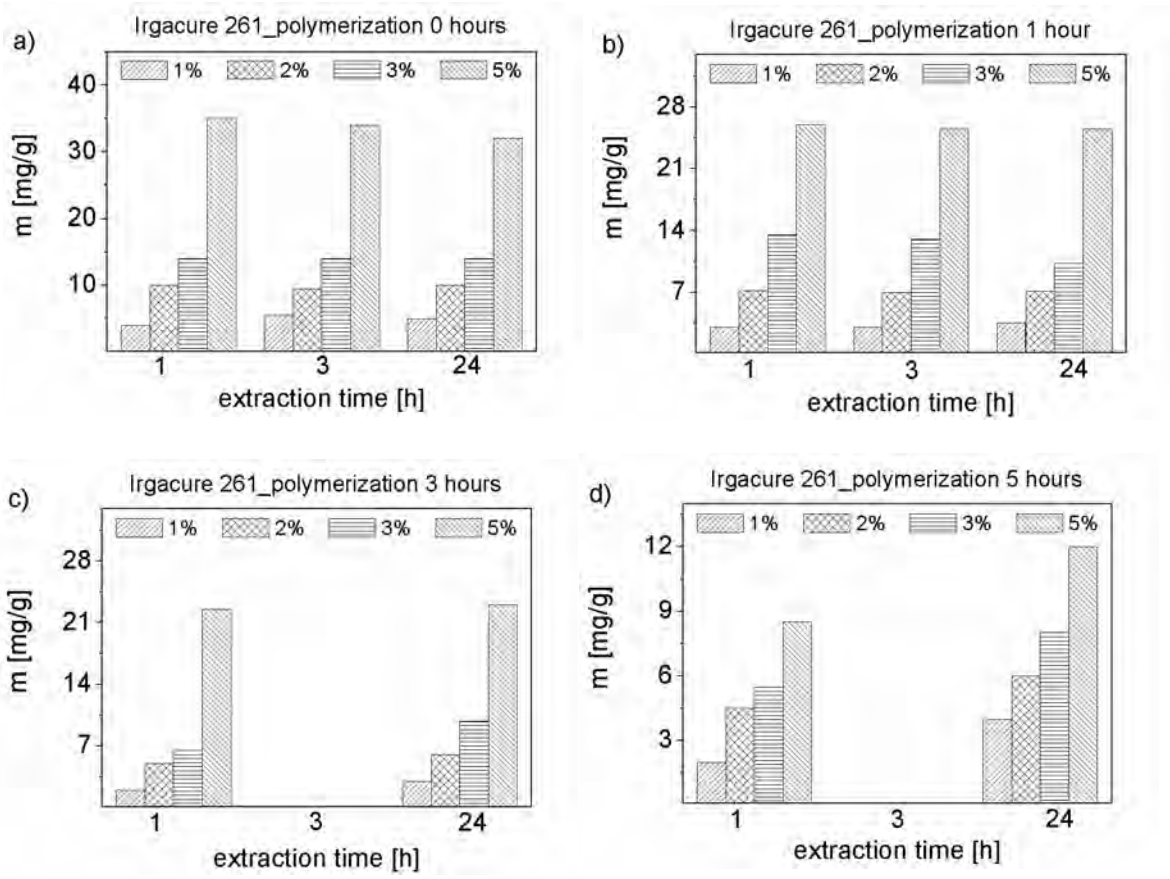


Fig. 6 The migration of photoinitiator Irgacure 261 from the cured samples into acetonitrile for the extraction times of 1, 3 and 24 hours

Conclusion

The aim of this work was to study the migration of substances from UV cured systems (under different conditions) by UV/VIS spectroscopy. The most often used method for evaluation of migrants from cured samples is mass spectrometry connected with liquid or gas chromatography as separation technique. The study proved that UV-VIS spectroscopy is suitable method for analysis of simple systems consisting of a small number of components (two or three). The disadvantage of this method is that in comparison to chromatographic methods it cannot separate and identify a complex mixture of substances. Therefore, UV/VIS spectroscopy is not suitable for evaluation of migrants from commercially available inks and varnishes, which contain a large number of components (monomers, oligomers, initiators and additives).

The measurements showed that from "fully cured samples" (radical polymerization, extraction time 24 hours, system PETIA/Irgacure 2959) 1.22-1.78 mg g^{-1} of initiator Irgacure 2959 and 8-54 mg g^{-1} of monomer PETIA (depending on the concentration of photoinitiators) were released. For cationically

polymerizable systems (Celloxide 2021P/Irgacure 261, 5 hours polymerization, extraction time 24 hours) 4.2-12.1 mg g^{-1} of initiator Irgacure 261 and 83-116 mg g^{-1} of monomer Celloxide 2021P (depending on initiator concentration) were released. The comparison of cationically and radically cured system is difficult, since they differ in many parameters (such as total UV-dose, polymerization time, functionality of monomers, etc.)

The present study shows several difficulties connected with measurement of substance migration from UV cured systems by UV-VIS spectroscopy. In the future more detailed research has to be carried out to study the potential of this approach.

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