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EFFECT OF CONCENTRATION OF IRON-ARENE PHOTOINITIATOR ON ITS MIGRATION FROM CURED POLYMER FILM

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Nowadays, UV curable systems (inks, varnishes) are frequently used in printing industry. Their unquestionable advantages are the absence of volatile organic compounds, good chemical resistance and short curing times (fractions of second). A disadvantage of a UV-cured system is the possibility of migration of unreacted photoinitiators, monomers and other substances from the cured polymeric film. This parameter is of high importance in food packaging industry. In most cases, migration is an unwanted effect during which the unreacted photoinitiator or binder can be released from the package, contaminate and affect the food. In some cases, slow migration of antioxidants from packages to food is used intentionally. In this case, the antioxidants act positively on the food quality. This paper is aimed at research of curing and migration of substances from a cationically polymerizable system containing iron-arene photoinitiator Irgacure 261 and epoxidic binder Celloxide 2021P. The curing of systems was monitored at different concentrations of photoinitiator via infrared spectroscopy. By UV/VIS

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spectroscopy, migration of photoinitiators was monitored under different curing conditions and times of extraction. The results show that the greatest effect on the extracted amount of photoinitiator was exhibited by the concentration of the photoinitiator in the curing systems. With increasing curing time, the amount of extracted photoinitiator decreased, but this decrease was not significant. The UV/VIS spectroscopy data analysis is generally suitable for the determination of migration of substances from simple systems (two or three components), but for more complex systems is not appropriate. With larger number of components (commercial inks and varnishes), there will be overlap between the absorption spectra of individual components, and thus it will be impossible to determine their concentration in the extract.

Introduction

Nowadays, curing of inks and varnishes by the help of energy rich radiation is increasingly applied in printing industry. Inks and varnishes can be divided according to the type of radiation into heatset inks (curable by IR radiation or hot air), UV curable inks and inks cured by the help of electron beam. UV curable systems can be classified according to the type of polymerization reactions leading to complex polymerization of monomers and oligomers into three groups; they are free radical, ionic or hybrid.

The unquestionable advantages of these systems are the absence of volatile organic compounds (VOCs), good chemical resistance and short curing times (fractions of second). One of disadvantages of UV cured systems is the possibility of migration of unreacted photoinitiators, monomers and other substances from the cured polymeric film (especially at insufficient curing of the inks or varnishes). Migration of substances from the cured ink or varnishes is important in food packaging industry where such substances can contaminate packaged food. This contamination can affect not only odour or taste change of food, but there is also possibility of negative impact on the human body. These circumstances lead to the research and development of new highly efficient monomers and photoinitiators systems. One possibility how to reduce the amount of migrating initiators from cured film is their structure modification and increasing of their molecular weight [1,2].

In practice, to assess the overall migration of substances, gas chromatography, liquid chromatography, mass spectrometry, gravimetry or a combination of mentioned methods are frequently used [3]. This work is aimed at studying the effect of concentration of irone-arene photoinitiator on its migration from the cured two-component system (photoinitiator/monomer), by using spectroscopy in the ultraviolet and visible spectral region (UV/VIS spectroscopy) at different stages of curing. The degree of curing the binder film was studied by Fourier transform infrared spectroscopy (FTIR).

Experimental

Materials and Instruments

Photoinitiator: As photoinitiator, (η^6-Chlorobenzene) (η^5-cyclopentadienyl) iron hexafluoro-phosphate was used, which is commercially available cationic photoinitiator (Irgacure 261) of organo-metallic (irone-arene) type. This photoinitiator is mainly suitable for curing of vinyl ethers and epoxides monomers.

Resin: The (3'-4'-epoxycyclohexane)methyl 3'-4'-epoxycyclohexyl-carboxylate epoxy resin supplied by UCB Chemicals under commercial name Celloxide 2021P was used.

Solvent: Acetonitrile supplied by TJ Blaker was the solvent used for the measurement of absorption spectra of substances and for the extraction of migrants from the cured film in the UV/VIS.

UV Source: For curing of samples, UV tunnel (Miniterm UV 220 Q Super, Aeroterm) which is equipped with medium pressure mercury lamp, was used. UV dose was 400 mJ cm^{-2} (measured by radiometer UV-integrator from uv-technik).

FTIR spectrometer: FTIR spectrometer Avatar 320 (Nicolet) was used to study the conversion degree. The process of polymerization was monitored in the mid-infrared region (400-4000 cm^{-1}), at a resolution of 4 cm^{-1} averaging 32 scans. The polymerization was monitored by the decrease of absorption band of epoxy group and the absorption band of selected inner standard (carbonyl group). The evaluation of the absorption bands areas was done employing Omnic E.S.P 5.2 software package.

UV/VIS spectrometer: For the determination of spectral dependencies of molar absorption coefficients in UV/VIS spectral region, spectrometer Specord 210 (Analytic Jena AG) was used. For the measurements, cuvettes with thickness of 2, 5 and 10 mm were used. The used resolution and scanning speed were 1 nm and 10 nm s^{-1}, respectively.

Experiment Workflow

Preparation of samples: Three mixtures of photoinitiator and monomer with molar concentration of photoinitiator 2, 3 and 5 % were prepared. Thin layers (12-15 :m) of prepared mixtures were applied on aluminium foil.

Measuring of conversion degree: Immediately after application of the sample on aluminium foil, IR spectra were measured. After UV irradiation, series of IR spectra were recorded each two minutes for 2 hours. Due to the "living polymerization", another IR spectra of samples were measured after 24 and 48 hours.

Polymerization of Celloxide 2021P resin was monitored by the decrease of absorption bands with maxima at ~ 788 cm^{-1}, 798 cm^{-1} and 808 cm^{-1} that correspond to the deformation vibrations of the epoxide group. As a reference band (inner standard), carbonyl group characteristic vibration peaking at ~ 1723 cm^{-1} was chosen. This band was chosen due to its stability during the polymerization reaction (the change of carbonyl band area during the polymerization was not higher than 5 %). The degree of conversion was calculated from equation

$$X(\%) = \frac{A_0 - A_t}{A_0} 100 \tag{1}$$

where A_0 is an area quotient of measured band of reactive group and chosen inner standard before exposure with UV radiation, A_t is a quotient of measured bands of reactive group and chosen inner standard in different time lags after exposure with UV radiation [4].

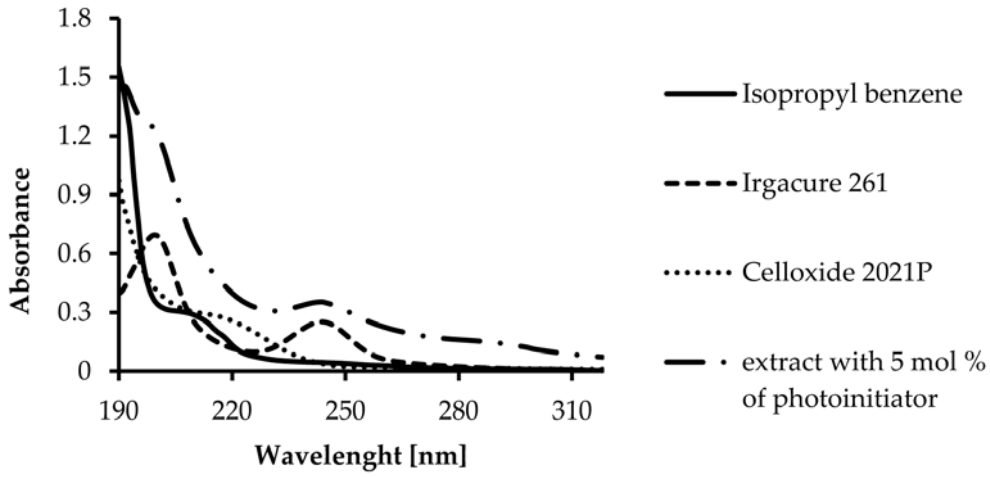

Fig. 1 Absorption spectra of isopropylbenzene (C = 1×10^{-4} mol l^{-1}), photoinitiator Irgacure 261 (C =1×10^{-4} mol l^{-1}), monomer Celloxide 2021P (C =1.9×10^{-2} mol l^{-1}) and extract of sample with molar concentration of photoinitiator 5 % (curing time 2 h, extraction time 24 h)

Determination of molar absorption coefficient: Molar absorption coefficients in UV-VIS spectral region were calculated according to Lambert–Beer law. For photoinitiator Irgacure 261, the wavelength of 244 nm was chosen because it

corresponds to the maximum of its absorption band. Monomer Celloxide 2021P and isopropylbenzene (product of photoinitiator decomposition) do not absorb in this spectral region (see Fig. 1) [4]. The value of the molar absorption coefficient for Irgacure 261 for 244 nm is 1 298.1 m^2 mol^{-1}.

Determination of migrants concentration: Prepared layers (on aluminium foil) were cured and after that, from every series, 10 circle samples (diameter of 12 mm) for extraction in acetonitrile were cut out. Circular samples were weighted and then extracted (vial with 6 ml of acetonitrile for 1 and 24 hours). Extracts from samples were measured by means of a UV/VIS spectrometer in 190-318 mm wavelength range.

From the measured absorbances of extracts at 244 nm and molar absorption coefficient of the photoinitiator, the concentration of photoinitiator in the extract was calculated.

Further, from the concentration of the photoinitiator and known volume of the sample, weight of the photoinitiator in the extract was calculated, which was consequently recalculated to the mass extracted from 1g sample (m_{1g}) and the percentage of photoinitiator extracted from the original amount of initiator in the sample ($m_{1\%}$).

The amount of released monomer was calculated only from the weight decrease of the sample before and after extraction (the amount of photoinitiator was subtracted). Finally, the amount of migrating monomer was recalculated as the percentage of extracted monomer from the original sample amount ($m_{po\%}$). However, we note that such a determination is rather tentative. The amount of released monomer cannot be calculated based on the measured absorption spectra due to the overlap of absorption bands of monomer, photoinitiator and isopropyl-benzene (product of photoinitiator decomposition). It was not possible to determine what proportion belongs to the photoinitiator and to isopropylbenzene (see Fig. 1).

Results and Discussion

Conversion Degree

Average values of conversion degrees of prepared samples with molar concentration of photoinitiator 2, 3 and 5 % are shown in Fig. 2. It is worthy noting that each concentration was measured three times. The conversion degree of sample with photoinitiator molar concentration of 2 % is ~ 59 % two hours after UV exposure. Further, for samples with photoinitiator molar concentrations of 3 and 5 %, conversion degrees were found to be ~60 and 68 %, respectively. The average values of conversion degrees of prepared samples at 2, 24 and 48 hours after exposure are given in Table I.

Table I Average values of conversion degrees of prepared samples with photoinitiator molar concentration of 2, 3 and 5 % for 2, 24 and 48 hours after UV exposure

Time after exposure, h	Molar concentration of photoinitiator, %		
	2	3	5
	Conversion degree, %		
2	58.9 ± 1.0	60.1 ± 0.9	68.0 ± 0.6
24	64.7 ± 1.6	64.8 ± 1.5	72.8 ± 1.0
48	66.4 ± 1.8	65.3 ± 1.9	73.3 ± 0.9

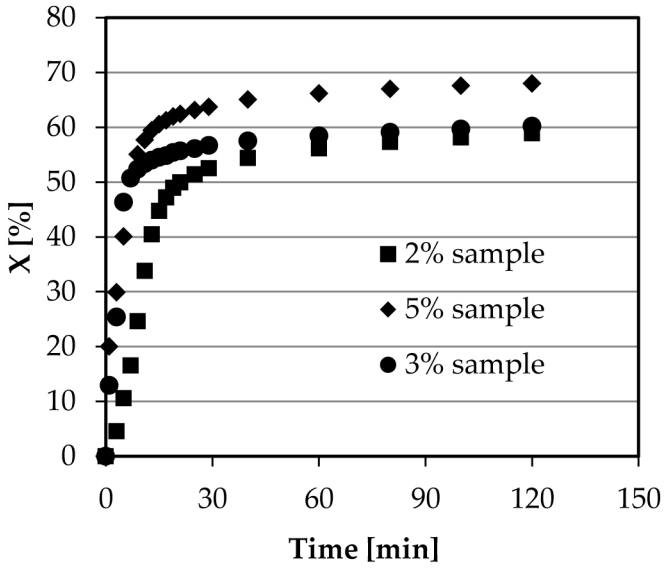

Fig. 2 Conversion degrees of samples with molar concentration of photoinitiator 2, 3 and 5 %

Extraction

Table II summarizes average values (from 3 measurements) of extracted monomer and photoinitiator from samples with various concentration of photoinitiator, different conditions of curing time and extraction time.

Figure 3 shows extracted amount of photoinitiator from various samples. It is obvious that curing time has positive effect on extracted amount of photoinitiator. Longer curing time means lower extracted amount of photoinitiator due to increasing of degree of conversion. Samples with 2 molar % of photoinitiator have the degree of conversion higher by about 7.5 %, samples with 3 molar % of photoinitiator about 5.2 % and samples with 5 molar % of photo-

Table II Average values of extracted amount of photoinitiator and monomer from cured samples

	Curing time 2 h, extraction time 1 h			Curing time 2 h, extraction time 24 h		
sample	m_{1g}, mg g^{-1}	$m_{1\%}$, %	$m_{po\%}$, %	m_{1g}, mg g^{-1}	$m_{1\%}$, %	$m_{po\%}$, %
2 molar %	6.7 ±1.1	21.8 ±2.9	31.5 ±1.7	7.0 ±0.3	22.9 ±1.0	38.3 ±2.4
3 molar %	9.5 ±0.7	19.9 ±1.7	35.9 ±3.9	11.1 ±1.2	24.8 ±2.4	37.6 ±1.4
5 molar %	22.8 ±0.9	30.5 ±1.0	38.1 ±0.9	24.0 ±0.5	32.8 ±0.4	47.3 ±2.2
	Curing time 24 h, extraction time 1 h			Curing time 24 h, extraction time 24 h		
sample	m_{1g}, mg g^{-1}	$m_{1\%}$, %	$m_{po\%}$, %	m_{1g}, mg g^{-1}	$m_{1\%}$, %	$m_{po\%}$, %
2 molar %	4.3 ±0.2	14.7 ±0.4	35.0 ±3.0	5.2 ±0.5	15.1 ±0.4	39.7 ±0.1
3 molar %	11.2 ±1.1	22.7 ±1.2	29.3 ±2.0	11.8 ±0.8	26.3 ±1.9	35.2 ±0.1
5 molar %	20.9 ±0.4	28.0 ±0.5	35.7 ±0.5	23.7 ±2.1	31.3 ±2.4	41.7 ±3.2
	Curing time 48 h, extraction time 1 h			Curing time 48 h, extraction time 24 h		
sample	m_{1g}, mg g^{-1}	$m_{1\%}$, %	$m_{po\%}$, %	m_{1g}, mg g^{-1}	$m_{1\%}$, %	$m_{po\%}$, %
2 molar %	4.1 ±0.3	13.8 ±0.6	33.1 ±6.1	4.7 ±0.3	16.2 ±0.7	35.0 ±3.3
3 molar %	8.1 ±0.4	18.0 ±0.8	36.4 ±0.8	7.5 ±0.4	16.7 ±1.0	43.0 ±0.6
5 molar %	19.6 ±0.9	27.1 ±1.3	32.1 ±1.3	21.0 ±0.5	28.1 ±0.5	31.0 ±4.1

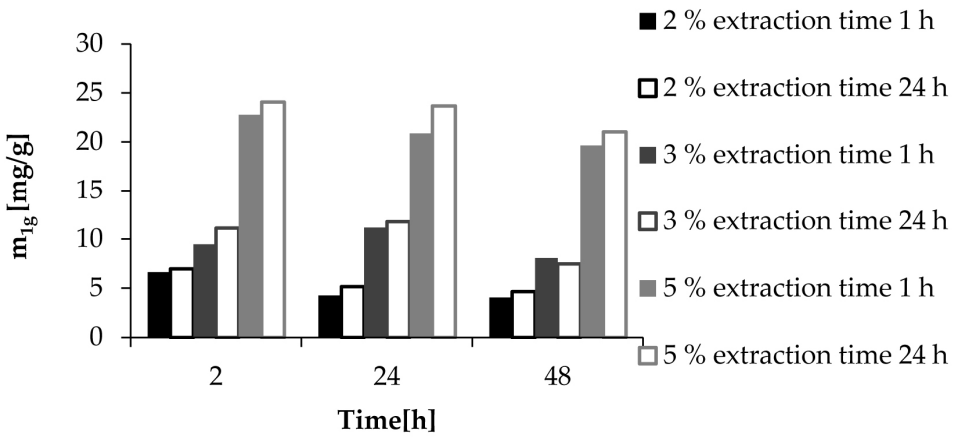

Fig. 3 Dependence of extracted amount of photoinitiator on curing and extraction time

initiator about 5.3 % (in all cases there is a difference between conversions for curing times 2 and 48 hours, see Table I). These increases in the degree of conversions correspond to the reduction of migrating photoinitiator about 8 % (samples with concentration of photoinitiator 2 molar %), 1.9 % (samples with concentration of photoinitiator 3 molar %) and 3.4 % (samples with concentration of photoinitiator 5 molar %) (see Table II, parameter $m_{1\%}$). Overall migration of

photoinitiator (see Table II, parameter m_{1g}) is due to its higher concentration more pronounced. For example, the amounts extracted from the samples with 2 mol. % and 5 mol. % concentrations of photo-initiator (curing time 48 hours, extraction time 1 hour) were 4.1 mg g^{-1} and 19.6 mg g^{-1}, respectively.

The released amount of monomer was almost in all cases in the range of 31-41 % and there was no trend. As it was mentioned above, this determination of extracted amount of monomer is rather tentative (evaluated based on weight loss).

Conclusion

From the measured values of extracted photoinitiator can be seen that increasing degree of conversion declines extracted amount of photoinitiator, but this decline is not too pronounced. When degree of conversion increased about 5 % (samples with concentration of photoinitiator 5 mol. %, curing time 2 and 48 hours, extraction time 1 hour), the amount of extracted photoinitiator decreased only about 3.3 mg g^{-1}, which is 3.4 % of original amount of photoinitiator. The differences in the amount of extracted photoinitiator between different extraction times (1 and 24 h) are very small (in most cases, the amount of extracted photoinitiator with longer extraction increased).

From the samples with the photoinitiator concentration of 5 mol. % were extracted 2.8 times more photoinitiator than from the samples with a photoinitiator concentration of 3 mol. %. In comparison of samples containing 5 and 2 mol. % of photoinitiator it was 4.6 times more. From these results it can be seen important influence of photoinitiator concentration on its extraction.

The UV/VIS spectroscopy data analysis is generally suitable for the determination of migration of substances from simple systems (two or three components), but for more complex systems is not appropriate. With larger number of components, there will be overlap of the absorption spectra of individual components and thus not possible to determine their concentration in the extract.

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