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Application of FT-IR spectroscopy to the specific migration study of an organotin heat stabilizer from rigid poly(vinyl chloride) into food simulants

Summary — The specific migration of an organotin heat stabilizer (Irgastab 17 M0K) from rigid poly(vinyl chloride) (PVC) into food simulants is investigated. For that purpose, two fatty simulants were used: hexane and ethanol. The test conditions were 15 days at 4 °C and 40 °C and 3 hours at 70 °C. The rate of the mass variation of the films was followed as a function of time. FT-IR spectroscopy was used to investigate the migration phenomena and to estimate the diffusion coefficients by using mathematical models. The influence of various parameters such as temperature, time of contact and the nature of food simulant was considered.

Keywords: organotin stabilizer, migration, food simulant, FT-IR spectroscopy.

ZASTOSOWANIE SPEKTROSKOPII FT-IR DO BADAŃ MIGRACJI SPECYFICZNEJ ORGANOCYNOWEGO STABILIZATORA Z TWARDEGO POLI(CHLORKU WINYLU) DO PŁYNÓW SYMULUJĄCYCH ŻYWNOŚĆ

Streszczenie — Zbadano specyficzną migrację organocynowego stabilizatora termicznego (Irgastab 17 M0K) z twardego poli(chlorku winylu) (PVC) do płynów symulujących żywność. Zgodnie z unijną dyrektywą, do badań zastępczych wybrano substytuty takich płynów — heksan i etanol. Test migracji, w temp. 4 °C i 40 °C w ciągu dwóch tygodni oraz w temp. 70 °C przez 3 h, prowadzono przy użyciu próbek cienkiej folii wykonanej z PVC z dodatkiem Irgastab 17 M0K. Szybkość zmian masy folii wyznaczano jako funkcję czasu (rys. 1). Metodą FT-IR potwierdzono zachodzące zjawisko migracji (rys. 2), a pomiary absorbancji posłużyły do obliczenia, według dwóch modeli matematycznych: Arheniusa i Fick'a, współczynnika dyfuzji *D* (rys. 3, tabela 1). Stwierdzono, że na wielkość oznaczanej migracji specyficznej istotny wpływ wywiera zarówno temperatura i czas kontaktu, jak i rodzaj płynu symulującego żywność.

Słowa kluczowe: organocynowy stabilizator, migracja, symulant żywności, spektroskopia FT-IR.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most important and widely used thermoplastics due to its many valuable properties like low price, good processability, chemical resistance and low flammability. It is approved for use as films and gaskets for bottles corks in general contact applications. Its principal drawback, however, is low thermal stability at processing temperature. To increase the heat stability of PVC, different metal soaps like Pb, Cd, Ca and Zn carboxylates and some di- and mono-alkyltin compounds are used [1]. Furthermore, various additives such as plasticizers and lubricants are generally incorporated. The addition of such substances is necessary for processing and for achieving the desired chemical and mechanical properties [2]. However, despite their high compatibility with PVC, these low molecular weight additives possess a high mobility and, in contrast to the macromolecules, are capable of migrating from the packaging material into the packed product [3]. Some of the migrants may affect the quality of the packed product as exhibited by sensorily determinable changes (odour and/or taste) or by toxicological symptoms from ingestion [4]. According to the EC regulation, the detection and the quantification of contaminants migrating from the polymers are essential for the safety assessment of food contact plastic packaging materials.

The aim of the present work is to carry out a kinetic study of the specific migration of an organotin heat stabilizer from rigid PVC films into food simulants (ethanol and hexane) by FT-IR spectroscopy and to estimate the diffusion coefficients by using mathematical models. The toxicity of organotin compounds is associed with impuri-

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ties, such as the dialkyl and tetra alkyl-tin; they affect the cerebral and renal systems. Furthermore, the tin can compete with the calcium in the bones [5, 6].

The liquids chosen for migration testing simulate the fatty foods like olive oil or sunflower oil. As recommended guidelines directives 82/711/EEC and 97/48/EC (Official Journal of the European Communities' No L 222/10): conventional simulants substitutes can be chosen when the conventional test conditions proved not feasible for technical reasons related to the method of analysis. Also, the FT-IR spectroscopy cannot follow the kinetics of migration in olive oil or sunflower oil because it is difficult to remove the traces of oil that has diffused in the PVC films. Furthermore, these oils and organotin compounds (here Irgastab 17 M0K) have the C=O bonds which overlap, thus masking the real migration.

Mathematical modeling of migration processes may be carried out at different levels of description. It concerns small or large molecules, into, through or from a packaging material and may be described by the second Fick's law [7]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2} \tag{1}$$

where: C — *the additive concentration in the plastic at time t and distance x, D — diffusion coefficient or diffusivity of the substance.*

The solutions for a large number of diffusion problems were provided by Crank [7]. The amount of migrant is given by the following convergent series:

$$\frac{M_t - M_\infty}{M_\infty} = \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n+1)^2}\cdot \exp\left[-\frac{D(2n+1)^2\pi^2}{L^2}t\right] \tag{2}$$

where: M_t — *amount of substance transferred,* M_∞ — *amount of substance at equilibrium, L — sheet thickness.*

For long times, only the first term is significant and the eq. (2) becomes:

$$\frac{M_t - M_\infty}{M_\infty} = \frac{8}{\pi^2}\exp\left[-\frac{D\pi^2}{L^2}t\right] \tag{3}$$

For short times, when $M_t/M_\infty < 0.6$

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{D}{\pi}\right)^{\frac{1}{2}}\cdot\sqrt{t} \tag{4}$$

Diffusion coefficients are estimated graphically by plotting $\log[(M_t - M_\infty)/M_\infty]$ and M_t/M_∞ as a function of time and square root of time, respectively.

Then, for long times:

$$f(t) = \log\frac{M_t - M_\infty}{M_\infty} = \log\frac{8}{\pi^2} - \frac{D\pi^2}{L^2}$$

The slope of the curve is

$$S = \frac{D\pi^2}{L^2} \tag{5}$$

And for short times: $f(\sqrt{t}) = M_t / M_\infty$; the slope of the curve is

$$S^2 = \frac{16}{L^2\pi}\cdot D \tag{6}$$

Temperature, migrant concentration and nature of the food simulator are parameters which influence the diffusivity. The dependency of the diffusion coefficient on temperature is described by the Arrhenius equation [8]:

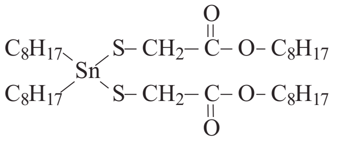
$$Dp = D_0 \exp - (E/RT) \tag{7}$$

where: D_0 — *the hypothetical diffusion coefficient at very high temperature, E — the activation energy of diffusion (J/mol), R — the gas constant (J/mol K), T — the temperature (K),* D_0 *and E can yet only be obtained by fitting with experimental data.*

EXPERIMENTAL

Materials

Commercial grade PVC from Sheintech with *K* value 70.2—72.0 and the heat stabilizer Irgastab 17 M0K, a yellowish liquid with 15.3 ± 0.5 wt. % of tin and 28.8 ± 3.0 wt. % of monooctyl tin), from Ciba Geigy were used as received. The chemical structure of Irgastab 17 M0K is the following:


(I)

Tetrahydrofuran (99.5 % of purity), ethanol (96 % of purity), and hexane (98.5 % of purity), were purchased from Prolabo and used as received.

PVC films preparation

Generally, a heat stabilizer concentration lower than 5 wt. % is used in industrial formulations. In this work, a formulation containing 4.5 wt. % of Irgastab 17 M0K was prepared by dissolving completely the compounds in tetrahydrofuran. The solvent was evaporated at room temperature during 24 h, and then the film was dried at 50 °C in a thermostatically controlled chamber for 2 h. Square films [2 x 2 (cm^2)] with 120 μm of thickness were cut and used.

Migration testing

For analytical feasibility reasons, migration tests were carried out by using two fatty food simulants, 96 % ethanol and hexane. Testing conditions were chosen according to EU Directives 82/711/EEC and 85/572 EEC. Test temperatures and times were two weeks at 4 °C, and two weeks at 40 °C and 3 hours at 70 °C. Before analysis, the films were wiped and dried at 50 °C in a thermostatically controlled chamber for 24 h to desorb the liquid simulators. The weights of the films were 0.0540 ± 0.0041 g. The mass variation (σ, %) was calculated according to the following relation:

$$\sigma = \frac{m_t - m_0}{m_0}\cdot 100 \tag{8}$$

where: m_0 — *initial mass before immersion*, m_t — *mass of the film at the time t after wiping and drying.*

Methods of testing

The IR spectra of the PVC films were taken using a Shimadzu FT-IR 8000 PC infrared spectrophotometer with 40 scans per sample and a resolution of 2 cm^{-1}. The KBr pellets were used for organotin heat stabilizer. IRsolution software was used for spectra processing data. IRsolution is Shimadzu's FT-IR instrument control and data analysis software. IRsolution Ver.1.20 and later works with Windows 2000 or Windows XP Professional, and allows the user to measure IR spectra by connecting to the FT-IR-8000 series or IRPrestige series Fourier Transform Infrared Spectrophotometers, and the AIM-8800 Infrared Microscope (optional).

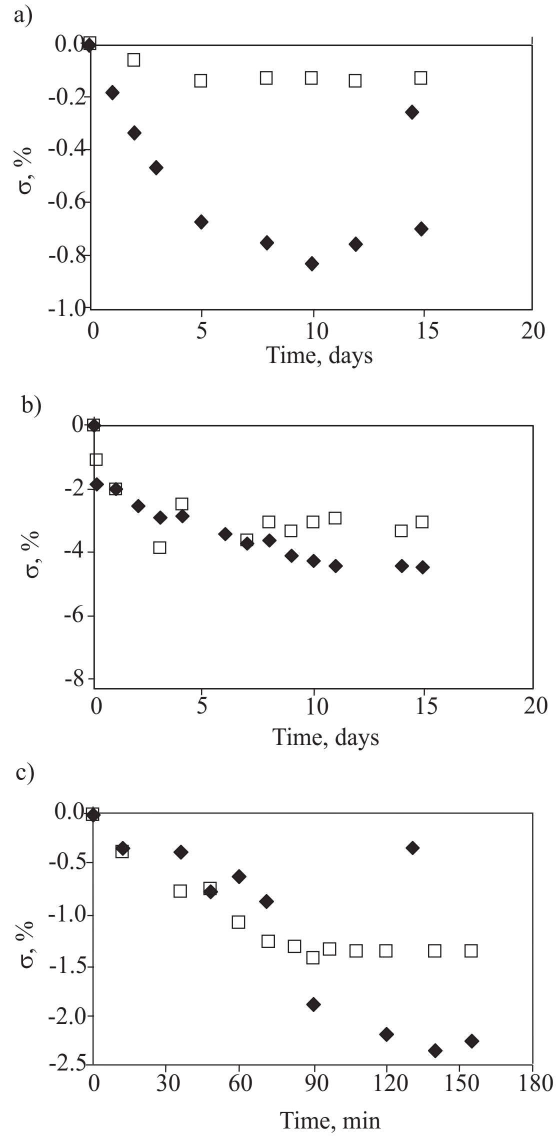


Fig. 1. Effect of the temperature and nature of the food simulant on the rate of mass variation for rigid PVC: a) temp. 4 °C, b) temp. 40 °C, c) temp. 70 °C; ◆ — hexane, □ — ethanol

RESULTS AND DISCUSSION

The rate of mass variation

The mass loss gives information about the phenomenon which occurred between the samples and the liquid simulants. It can be noted (Fig. 1) that the mass variation decreased in both simulants and for all the considered temperatures. This means that the migration of Irgastab 17 M0K occurred in the two considered fatty simulants. The highest rates of mass loss were observed at 40 °C. At equilibrium, Fig. 1 shows that the highest rates of mass loss occurred in hexane for the three temperatures: 0.65 %, 4.63 % and 2.27 % of mass loss were obtained at 4 °C, 40 °C and 70 °C, respectively. In ethanol, however, the rates were 0.13 %, 3.19 % and 1.37 %, respectively, for the same temperature order. This might be attributed to the better solubility of Irgastab 17 M0K in hexane.

FT-IR investigation of the PVC films before migration testing

The spectrum (Fig. 2) of the organotin heat stabilizer shows C=O group stretching vibration at 1730 cm^{-1} and CO stretching vibrations at 1540 and 1380 cm^{-1}. The C-S group absorbs at 1293 and 2854 cm^{-1} while the C-Sn group absorbs at 1184 cm^{-1} [9]. The comparison of the three spectra shows the presence of the bands at 1540, 1732 and 2854 cm^{-1} due to the organotin stabilizer in the spectrum of PVC containing this stabilizer. Then, a modification of the intensity of these bands after migration testing can be correlated to a phenomenon of organotin migration. The presence of a band at 1065 cm^{-1} is to be noted. It is due to the residual THF used as the solvent for films casting.

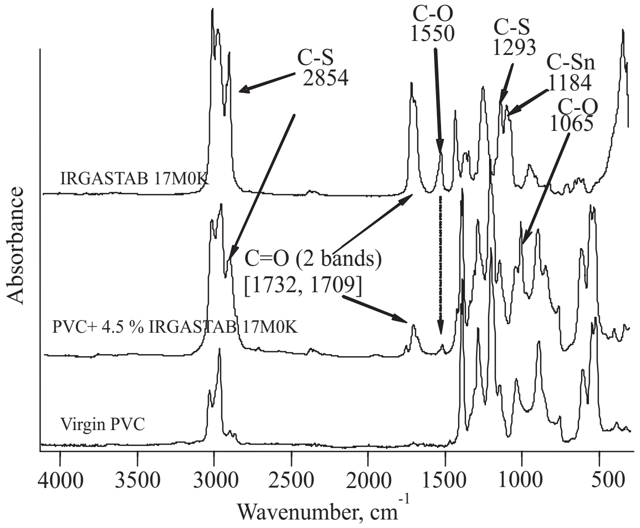


Fig. 2. FT-IR spectra of: rigid PVC films, PVC + 4.5 wt. % Irgastab 17 M0K and organotin stabilizer Irgastab 17 M0K

FT-IR investigation of the PVC films after migration testing

The comparison of PVC films spectra before and after all migration testing shows a decrease of the carbonyl band at 1732 cm^{-1} with time. This was attributed to the Irgastab 17 M0K migration in the considered liquid simulants. A quantitative estimation of this additive migration was carried out. For that purpose, the area's ratios A_{1732}/A_{1432} were calculated as a function of time. The band at 1432 cm^{-1} is due to the vibration of CH_2 of PVC and was taken as a reference band [10].

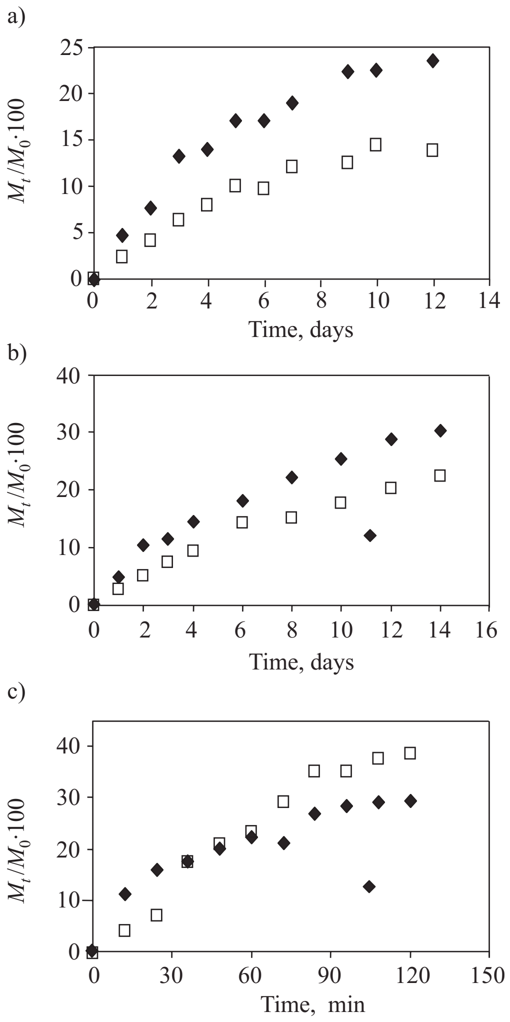


Fig. 3. Effect of the nature of food simulant and the temperature on the migration of Irgastab 17 M0K; a) temp. 4 °C, b) temp. 40 °C, c) temp. 70 °C; ◆ *— hexane,* ☐ *— ethanol*

The migrant levels (M_t) of Irgastab 17 M0K were calculated by using a calibration curve. The obtained rates of migration (M_t/M_0) are given in Fig. 3, where M_t and M_0 corresponding to migrated and initial amount of the Irgastab 17 M0K, respectively. It can be observed that the additive migration is related to the nature of the food simulant and the temperature.

Determination of the diffusion coefficients

The experimental diffusion coefficients $D_{\exp}$ were evaluated according to the equations (5) and (6) and compared to the theoretical values given by the equation (7) (Table 1). The diffusion coefficient increased with temperature. Therefore, the higher coefficients correspond to 70 °C in ethanol and hexane. At this temperature, Arrhenius model gives values of coefficients ten times lower than in Fick's model. This model gives close values for the temperatures 4 °C and 40 °C in the two simulants. This is due to the fact that the values are estimated by considering the linear part of the migrating curve which corresponds to the first samples where the migrated quantities are low and then the relative error would be important.

T a b l e 1. Values of Irgastab 17 M0K diffusion coefficients at various temperatures

Mathematical models	Hexane	Ethanol
Fick:		
— For T = 4 °C and 40 °C	$D_{4\,°C}$ = 3.09E-11	$D_{4\,°C}$ = 3.33E-11
$S = D\pi^2/L^2$	$D_{40\,°C}$ = 3.43E-11	$D_{40\,°C}$ = 3.53E-11
— For T = 70 °C	$D_{70\,°C}$ = 3.36E-09	$D_{70\,°C}$ = 4.84E-09
$S^2 = (16/L^2\pi)\cdot D$		
Arrhenius	$D_{4\,°C}$ = 1.26E-11	$D_{4\,°C}$ = 6.76E-11
$Dp = D_0 \exp - (E/RT)$	$D_{40\,°C}$ = 1.69E-10	$D_{40\,°C}$ = 6.38E-10
	$D_{70\,°C}$ = 1E-09	$D_{70\,°C}$ = 4.06E-09

The Arrhenius model shows well the influence of the temperature on the phenomenon of migration.

CONCLUSIONS

The mass variations of the films during food simulants contact decreased with time indicating the migration of the stabilizer in the two food simulants considered. The migration phenomenon is influenced by the nature of the food simulant, the temperature and the time of contact. The migration is more important at high temperatures. At 4 °C and 40 °C, hexane appears to be the simulant where the additive diffusion is better than ethanol. The obtained diffusion coefficients increased with temperature.

Finally, it can be stated that in comparison with GC, the FT-IR spectroscopy is a simple, low-cost and rapid method which can be used to investigate the migration phenomena.

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