Migration of dipropylene glycol diacrylate and tripropylene glycol diacrylate from paper packaging

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Summary

The aims of this study were to investigate the occurence of residual dipropylene glycol diacrylates (DPGDA) and tripropylene glycol diacrylates (TPGDA) in three original paper stick packages of crystaline saccharose and in the packaged saccharose, and to evaluate the efficiency of low density polyethylene (LDPE) coating on the decrease of DPGDA and TPGDA into food simulants: 10%, 50% and 95% ethanol solutions, 3% acetic acid, olive oil, sorbent Tenax, saccharose and NaCl. LDPE layer efficiency against migration of acrylates was compared with their migration from plain paper. Using gas chromatography-mass spectrometry, DPGDA was found in two packages in contents of 4 $mg \cdot kg^{-1}$ and 443 $mg \cdot kg^{-1}$, while TPGDA was found in all packages at levels of 40 $mg \cdot kg^{-1}$, 52 $mg \cdot kg^{-1}$ and 222 $mg \cdot kg^{-1}$. Concerning the transfer of diacrylates into food simulants at 40 °C, the highest levels of migration were found for 95% ethanol when more than 80% of TPGDA and 30% of DPGDA were transported from the packaging via LDPE into the simulant. The levels of migration into the other liquid simulants were much lower. The study proved that the layer of LDPE is a functional barrier against penetration of diacrylates from packagings into food simulants.

Keywords

paper packaging; migration; diacrylates; printing ink; gas chromatography-mass spectrometry

Some years ago, the cause of off-odour (unpleasant smell after acrylates or organic chemicals) of crystalline saccharose in 4 g paper stick packages from a Czech producer was analysed in our laboratory. The packaging material consisted of paper coated with low density polyethylene (LDPE). As we had not found any information on the transfer of substances from packaging materials into food in available scientific literature, we decided to study this problem. The contamination of saccharose with dipropylene (DPGDA) and tripropylene glycol diacrylate (TPGDA) was identified as the source of the sensory defect [1]. These substances are used as components of printing inks intended for the non-food contact surface of food packages. TPGDA and DPGDA are defined as an energy-curing monomers and they are classified as stenomeric acrylates with low molecular weight, often called as "reactive diluents" or "monomers" in practice [2–4].

A lot of information is available on migration of components of paper-based packaging materials into food including several recent reviews and articles on screening of chemicals potentially present in paper and paperboard [5–9]. The mechanism of migration from paper differs from that

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from polymers. Paper and paperboard materials are heterogenous, consisting of fibres with pores. Migration of molecules is controlled by adsorption and desorption processes on the fibre, transfer through the fibre and pores [10]. In this case, the course of migration generally depends on many factors including the type of contact of packaging material and food and/or food simulant (direct or indirect), properties of food and/or food simulant, paper characteristics such as thickness, grammage, porosity, content of mechanical processed pulp or content of recycled fibre, chemical nature of the migrant (molecular weight and structure, polarity, vapour pressure, partition coefficient) and contact conditions (time, temperature) [10–14]. The penetration of paper constituents through polymer layers of packaging materials, which can act as functional barriers [15], is influenced by their thickness, solubility of the migrant in the polymer, by the content of the migrant in paper and by temperature. Generally, polyolefins, including polyethylene, are not an efficient functional barrier that would prevent the paper constituent from transfer into packaged food [10, 16, 17]. Already described was the transfer of various constituents of printing inks, namely, mineral oil residues [18–22], plastificators [23, 24], photoinitiators [25] and solvents [13, 26, 27]. However, no information is available on the migration of diacrylates from packaging materials into food or food simulants.

DPGDA and TPGDA are components of printing inks, which are not allowed to be used on food contact surfaces of packaging materials. Therefore, the application of these substances is not mentioned in specific EU legislation for food contact materials [28], it must only meet the requirements of general EU legislation, which states that "materials and articles do not transfer their constituents to food in quantities which could endanger human health; bring about an unacceptable change in the composition of the food; or bring about a deterioration in the organoleptic characteristics" [15] and that all food contact materials including paper and paperboard have to be manufactured in accordance with good manufacturing practice [29]. The application of DPGDA as energy-curing monomer into printing inks for food packaging is allowed by Swiss legislation [30] in the list of non-evaluated solvents, i.e. without the value of specific migration limit. This regulation does not mention the application of TPGDA. Some important parameters of both diacrylates are summarized in Tab. 1. Diacrylates belong to additives that should not be present in the packaging material after ultraviolet curing and in food after their migration from packaging. No data on systemic toxicity test for DPGDA are available in the literature. TPGDA has an inherent potential to be genotoxic and was found to cause a significant, dose-dependent increase in the percentage of peripheral blood polychromatic erythrocytes [31].

Due to a lack of information on migration of DPGDA and TPGDA, the aims of this study were (i) quantification of the residues of DPGDA and

Tab. 1. Characteristics of diproplyleneglycol diacrylate and triproplyleneglycol diacrylate.

Substance	Diproplyleneglycol diacrylate (DPGDA)	Triproplyleneglycol diacrylate (TPGDA)
CAS number	57472-68-1	42978-66-5
Molecular formula	$C_{12}H_{18}O_5$	$C_{15}H_{24}O_6$
Chemical name (IUPAC)	Oxybis(methyl-2,1-ethanediyl) diacrylate	2-[2-(2-(Acryloyloxy)-1-methylethoxy)-1-methylethoxy]-methylethyl acrylate
Molecular weight	242.27 g·mol^{-1}	300.35 g·mol^{-1}
Density	1.050 g·cm^{-3} at 20 °C	1,040 g·cm^{-3} at 20 °C
Vapour pressure	0.085 Pa at 20 °C	0.0044 Pa at 20 °C
Boiling temperature	104 °C at 2.05 hPa (self-ignition at 240 °C at 1013.25 hPa)	> 120 °C at 1013.25 hPa (decomposition)
Water solubility	5.2 g·l^{-1} at 20 °C	4.0 g·l^{-1} at 20 °C
Log $P_{O/W}$	0.01–0.39 at 24 °C	2 at 25 °C
Health effect	No available data about carcinogenicity; both substances can cause eye, dermal and respiratory irritation as well as an allergic skin reaction. Tolerable daily intake: 0.1 mg·kg^{-1} body weight Median lethal dose (LD_{50}): 4600–6800 mg·kg^{-1}	

Log $P_{O/W}$ – Logarithm of the partition coefficient octanol/water corresponding to product's ability to bioaccumulate through the food chain, as measured by its bio-concentration factor.

Tab. 2. Parameters of packaging materials and the original content of diacrylates in them.

Code	Parameters					DPGDA [mg·kg^{-1}]	TPGDA [mg·kg^{-1}]
	Type	Paper	LDPE	Total thickness	Recycled fibres		
P1	Printed packaging material	50 g·m^{-2}	20 g·m^{-2}	75 μm	0 %	443 ± 11	40 ± 3
P2						4.0 ± 0.4	52 ± 3
P3						< *LOQ*	222 ± 7
Laminate A	Unprinted packaging material	60 g·m^{-2}	40 g·m^{-2}	86 μm	10 %	–	–
Laminate B		50 g·m^{-2}	20 g·m^{-2}	57 μm	10 %	–	–
Control	Unprinted filter paper	100 g·m^{-2}	–	95 μm	0 %	–	–

LDPE – low-density polyethylene, DPGDA – diproplyleneglycol diacrylate, TPGDA – triproplyleneglycol diacrylate, *LOQ* – limit of quantification (for DPGDA 0.3 mg·kg^{-1}).

TPGDA in original packaging materials intended for the production of paper stick packages and in the packaged saccharose, (ii) characterization of the course of migration of DPGDA and TPGDA from original as well as laboratory-spiked packaging materials into different food simulants and (iii) evaluation of the barrier efficiency of the LDPE layer against the transfer of diacrylates.

MATERIALS AND METHODS

Materials

DPGDA (oxy-bis(methyl-2,1-ethanediyl) diacrylate, CAS No. 574-68-1, 98%) and TPGDA ((1-methyl-1,2-ethanediyl)bis[oxy(methyl-2,1-ethanediyl)] diacrylate, CAS No. 42978-66-5, 99%) and sorbent Tenax (poly(2,6-diphenyl-*p*-phenylene oxide, 0.177–0.841 mm) were obtained from Sigma Aldrich (St. Louis, Missouri, USA). Potato starch (p.a.), saccharose (p.a.), NaCl (p.a.), acetic acid (99%) and ethanol (HPLC) were obtained from Penta Chemicals (Prague, Czech Republic). Acetone and methanol (both for gas chromatography, SupraSolv) were obtained from Merck (Darmstadt, Germany). Unprinted papers coated with low density polyethylene (LDPE) were obtained from the company Martin Peroutka (Martin Peroutka, Buštěhrad, Czech Republic) and were designated as laminate A and B in the following text. Three types of paper/LDPE laminate intended for use as stick packages of crystalline saccharose (materials P1–P3, unknown producer), as well as the ready packages made of the laminate P1 filled with saccharose, were obtained from a Czech food producer and differed only in the printing design. Tab. 2 shows the parameters of analysed packaging materials. As plain paper, laboratory filter paper (Paper mill Pernštejn, Pernštejn, Czech Republic) was used as a reference material for the preparation of control/comparative packaging. Moisture content of all packaging materials was less than 8 %.

Determination of diacrylates in packaging materials

The packaging material (2.5 g) was cut into pieces and extracted with 50 ml of 95% ethanol at 40 °C overnight. The extract (1 μl) was directly injected, using an auto-injector, into the gas chromatograph Hewlett-Packard 6890 Series coupled with HP 5973 mass-selective detector (Agilent, Santa Clara, California, USA). Chromatographic conditions were: column HP-5MS (30 m × 0.2 mm × 0.25 μm); column temperature program: 60 °C (2 min), rate 10 °C·min^{-1} to 250 °C (3 min); injector temperature: 240 °C; carrier gas He, constant flow 1.4 ml·min^{-1}, average velocity: 43 cm·s^{-1}; split 1:10. Detection in selected ion mode (SIM) followed the acryloyl ion (m/z = 55, $[CH_2{=}CH\text{-}C{=}O]^+$) and the acryloyl propyloxy ion (m/z = 113, $[CH_2{=}CHCO\text{-}O\text{-}CHCH_3CH_2]^+$). Limits of quantification of the used method for DPGDA and TPGDA were 0.3 mg·kg^{-1} and 0.1 mg·kg^{-1}, respectively. Recoveries for five replicates of three levels of diacrylates in fortified samples (1 mg·kg^{-1}, 50 mg·kg^{-1} and 500 mg·kg^{-1} in packaging, food or food simulant, respectively) were in the range of 70–120 % and relative standard deviations were less than 15 %. Repeatability and reproducibility of the used methods were calculated from five replicates with one level of diacrylates in fortified samples (50 mg·kg^{-1} in packaging, food or food simulant) and were more than 95 %.

Determination of diacrylates in saccharose

Saccharose (1.5 g) was extracted with 5 ml of acetone in an ultrasonic bath (20 min, 25 °C). The extracts were centrifuged using Hettich Universal 320R centrifuge (Hettich, Tuttlingen, Germany)

at 1677 ×*g* for 2 min. Supernatant was directly injected into gas chromatograph and analysed as described above.

Determination of the migration of diacrylates into food or food simulants

Migration from packaging materials P1 and P2

Packaging materials were tested in migration cells according to EN 1186-1:2002 [7] using one side contact of the packaging material (1.92 dm^2) with following food simulants (125 ml): 10%, 50% and 95% ethanol, 3% acetic acid (v/v) and olive oil. The migration tests were done at 40 °C for 10 days. Packaging material P3 was excluded from this determination, because amount of sample was insufficient.

Diacrylates were isolated from olive oil by Gilson Automated GX-271 GPC Clean-up System (Gilson, Middleton, Wisconsin, USA) and a Phenomenex EnviroSep-ABC column (Phenomenex, Torrance, California, USA). A mixture of ethyl acetate and cyclohexane (1:1, v/v) was used as a mobile phase at aflow rate of 5 $ml \cdot min^{-1}$, the injection volume of the sample was 2 ml.

Extraction of diacrylates from 10% ethanol and 3% acetic acid was achieved by liquid-liquid extraction. The food simulant (125 ml) was evaporated by vacuum rotary evaporator IKA RV 10 (IKA-Werke, Staufen, Germany) to the volume of approximately 50 ml and extracted by dichloromethane (100 ml). After shaking for 5 min, the dichloromethane layer was separated and dichloromethane was evaporated to dryness by vacuum rotary evaporator. The 50% and 95% ethanol samples were directly evaporated to dryness by vacuum rotary evaporator without extraction to dichloromethane. Dry extracts were dissolved in 5 ml of methanol, directly injected into gas chromatograph and analysed as described above.

Migration from spiked packaging materials

The outer paper layer of laminates A, B and plain paper was spiked (uniformly sprayed) with the ethanol solution of DPGDA or TPGDA and dried (25 °C, 2 h). The final contents of DPGDA and TPGDA in the packaging materials were 4.2 ± 0.6 $mg \cdot dm^{-2}$ and 4.1 ± 0.5 $mg \cdot dm^{-2}$, respectively. The flat sachets (5 cm × 10 cm) were thermally sealed from spiked laminates, filled with 25 ml of one of the liquid food simulant mentioned above or with 4 g of Tenax or 5 g of saccharose or 5 g of NaCl. The sachets from plain paper could not be sealed by heat, so they were glued using a solution of pure potato starch for food purposes in distilled water (15 g of starch in 250 ml of distilled water, gelatinized by heating). Finally, the completed sachets were placed into a thermostat at 40 °C. The samples for determination of the content of diacrylates in food or food simulant were taken in chosen intervals during the storage lasting up to 24 h (sampling after 0.5, 1, 1.5, 3, 5, 7, 10 and 24 h) for liquid simulants and up to 96 h (sampling after 0.5, 1, 1.5, 3, 5, 6, 12, 24 and 96 h) for solid simulants.

The determination of diacrylates in liquid simulants was done as mentioned above. The solid simulants were placed into a centrifuge tube and extracted with 5 ml of the solvent (methanol for Tenax, acetone for saccharose and NaCl) in an ultrasonic bath (20 min, 25 °C). The extracts were centrifuged using the Hettich Universal 320R centrifuge at 1677 ×*g* for 2 min. The supernatants were directly injected into gas chromatograph. The GC-MS analyses were performed at the same conditions as given previously.

Statistical analysis

All analyses were performed in two replications. Data were subjected to statistical analysis using SPSS software (version 16 for Windows XP; SPSS, Chicago, Illinois, USA) for the analysis of variance (ANOVA). Duncan's new multiple range test was used to analyse differences between samples. Mass transfer from paper-based materials (especially sigmoidal-shape of the migration curves) into food and food simulants is not sufficiently described by models based on Fick's 2nd law solutions. Weibull model is a good alternative [10, 14, 32]. The coefficients of the Weibull model τ and β were estimated using a non-linear estimation and the least squares method as a loss function in the software Statistica (StatSoft, Tulsa, Oklahoma, USA).

RESULTS AND DISCUSSION

Determination of diacrylates in original packaging materials

The contents of diacrylates determined in packaging materials are given in Tab. 2. The content of DPGDA in saccharose packaged in the stick packages made of material P1 was in the range of 0.17–0.23 $mg \cdot kg^{-1}$, the content of TPGDA was lower than the detection limit of the used method, i.e. lower than 0.1 $mg \cdot kg^{-1}$, which corresponds to the ten times lower content of TPGDA in material P1 compared with that of DPGDA. Level of DPGDA migration was higher than the specific migration limit of 0.01 $mg \cdot kg^{-1}$ given by

Tab. 3. Migration of diacrylates from packaging materials P1 and P2 into different simulants at 40 °C after 10 days.

Packaging material		P1	P2
Diacrylates		Dipropylene glycol diacrylate	Tripropylene glycol diacrylate
Content in packaging material [mg·kg^{-1}]		485.7 ± 11.4	75.7 ± 2.9
Maximum quantity allowed [mg·dm^{-2}]		0.34 ± 0.01	0.053 ± 0.002
Migration into simulants [mg·dm^{-2}]	10% ethanol	0.026 ± 0.003	0.022 ± 0.008
	50% ethanol	0.036 ± 0.005	0.028 ± 0.007
	95% ethanol	0.102 ± 0.004	0.047 ± 0.008
	3% acetic acid	0.031 ± 0.008	0.016 ± 0.003
	Olive oil	0.052 ± 0.008	0.019 ± 0.004

Regulation (EC) no. 10/2011 for compounds that are not included in the positive list of this regulation [28].

Migration from packaging materials P1 and P2

Due to the limited available amounts of original packaging materials P1 and P2, the tests using liquid food simulants were performed only, while the available stock of material P3 enabled only the determination of diacrylate content in it but not migration tests. The results of the levels of migration into different simulants at 40 °C after 10 days are given in Tab. 3. Generally, the migration of diacrylates tended to increase with the greater percentage of ethanol in the simulant. A significant difference was found between 95% ethanol and the other simulants for both migrants ($p < 0.05$). The reason could be the high solubility of diacrylates in ethanol. It is also obvious that the transfer of TPGDA into all simulants was more complete compared with DPGDA, e.g. 89% of TPGDA in packaging material migrated into 95% ethanol compared with 30 % of DPGDA. TPGDA was released from the paper materials in similar quantities compared with DPGDA although the total DPGDA content in packaging material was more than six times higher. These findings are in good agreement with results of Song et al. [12] and Huang et al. [16], who found a higher migration of paper constituents through polyethylene or polypropylene layers into 95% ethanol compared with that into 10% ethanol, 20% ethanol or 4% acetic acid.

Despite the hydrophilic character of DPGDA and TPGDA, the level of their migration into olive oil was close to that into 10% ethanol, 50% ethanol or 3% acetic acid. On the other hand, the testifying importance of these results could be questionable as the found levels of migration of TPGDA were close to the limit of quantification of the used method.

Migration from spiked packaging materials

Considering the results of previous experiments in this study, which indicated that there was no significant difference between the transfer of diacrylate into 10% ethanol, 50% ethanol, 3% acetic acid and vegetal oil, migration only into 10% ethanol and 95% ethanol was tested in the following experiments. Moreover, the migration into Tenax sorbent, salt and saccharose was studied as the paper-based packaging materials are intended mainly for solid food products.

Results on the course of migration of both diacrylates into 10% ethanol and 95% ethanol at 40 °C are presented in Fig. 1–2. It can be seen that

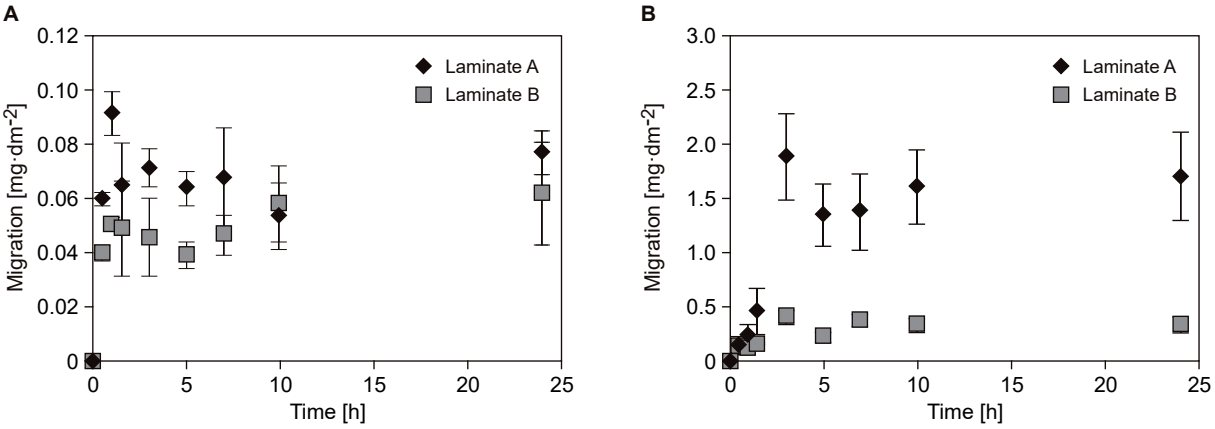

Fig. 1. Migration of diacrylates from two packaging materials into 10% ethanol at 40 °C.

A – dipropylene glycol diacrylate, B – tripropylene glycol diacrylate.

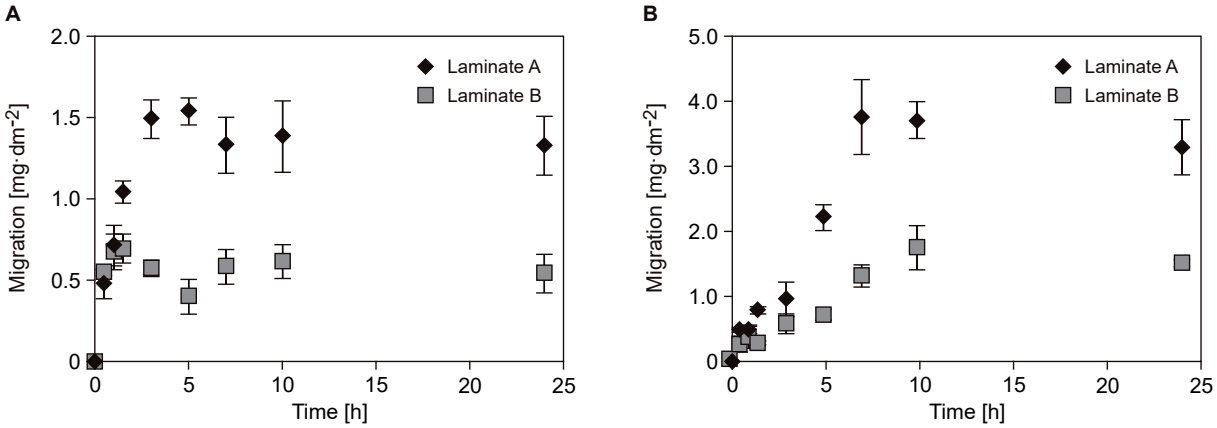

Fig. 2. Migration of diacrylates from two packaging materials into 95% ethanol at 40 °C.

A – dipropylene glycol diacrylate, B – tripropylene glycol diacrylate.

the level of migration of DPGDA into 10% ethanol was quite low, i.e. after 24 h the values were 0.076 ± 0.008 mg·dm^{-2} and 0.061 ± 0.019 mg·dm^{-2} for laminate A and B, respectively. Considering that the original content of DPGDA in the tested laminates was at a level of 4.2 ± 0.6 mg·dm^{-2}, only less than 2% of diacrylate was transferred into food simulant from paper with functional barrier.

A more intensive transfer was found under the same conditions for TPGDA, the original content of which in the tested laminates was at a level of 4.1 ± 0.5 mg·dm^{-2}). In this case, the final levels of diacrylate migration reached the values of 1.6 ± 0.3 mg·dm^{-2} (39% of the substance in the packaging material) and 0.31 ± 0.7 mg·dm^{-2} (7.6% of the substance in the packaging material) for laminate A and B, respectively. Migration of diacrylates into 95% ethanol was much higher, i.e. 31% and 15%, respectively, for DPGDA and more than 80% and approximately 36%, respectively, for TPGDA. The time extent of the experiments was limited by the fact that the first evidence of simulant penetration into outer paper layer was apparent after 24 h.

The results indicate that TPGDA migrated at tested conditions into ethanol simulants more easily compared with DPGDA. This corresponds to results mentioned above for packaging materials P1 and P2. It was surprising that the laminate A, containing thicker layers of paper as

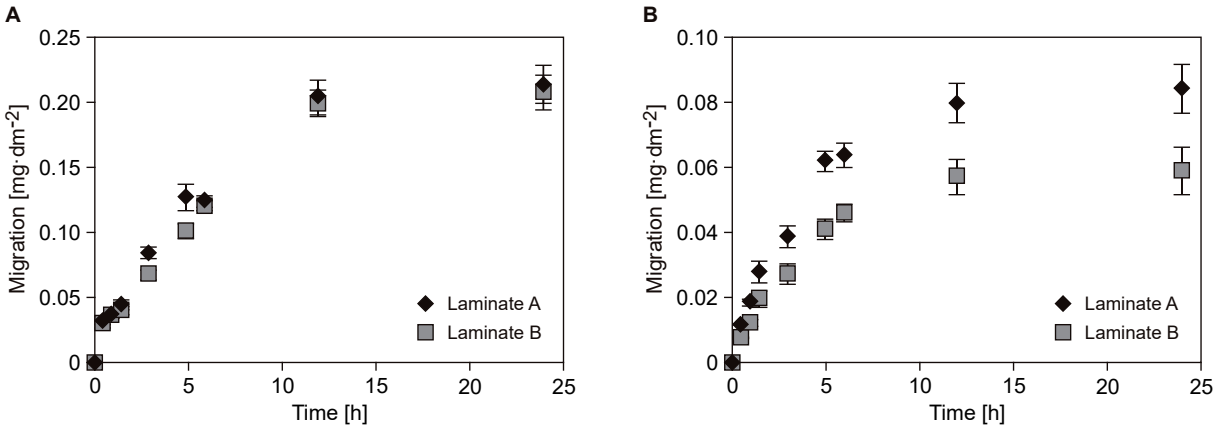

Fig. 3. Migration of diacrylates from two packaging materials into the sorbent Tenax at 40 °C.

A – dipropylene glycol diacrylate, B – tripropylene glycol diacrylate.

After 96 h, the levels of migration of dipropylene glycol diacrylate (DPGA) from laminate A and B were 0.24 ± 0.03 mg·dm^{-2} and 0.23 ± 0.03 mg·dm^{-2}, respectively. For tripropylene glycol diacrylate (TPGA), these levels were 0.096 ± 0.008 mg·dm^{-2} and 0.067 ± 0.007 mg·dm^{-2}, respectively.

After 24 h, the level of migration of DPGA and TPGA from comparative packaging made of filter paper was 1.313 ± 0.012 mg·dm^{-2} and 1.159 ± 0.009 mg·dm^{-2}, respectively.

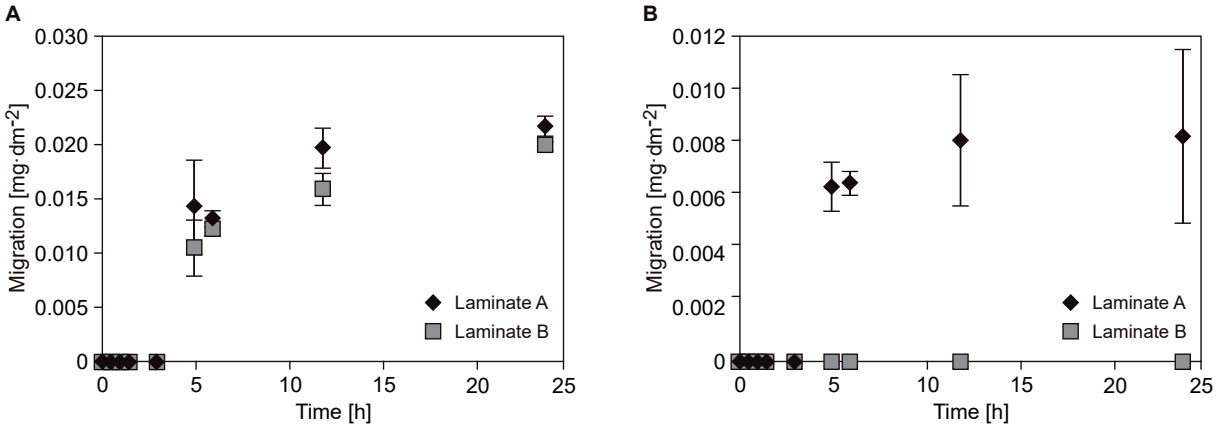

Fig. 4. Migration of diacrylates from two packaging materials into NaCl at 40 °C.

A – dipropylene glycol diacrylate, B – tripropylene glycol diacrylate.
After 96 h, the levels of migration of dipropylene glycol diacrylate (DPGA) from laminate A and B were 0.023 ± 0.003 mg·dm^{-2} and 0.021 ± 0.002 mg·dm^{-2}, respectively. For tripropylene glycol diacrylate (TPGA), these levels were 0.009 ± 0.005 mg·dm^{-2} and 0.006 ± 0.005 mg·dm^{-2}, respectively.
After 24 h, the level of migration of DPGA and TPGA from comparative packaging made of filter paper was 0.108 ± 0.008 mg·dm^{-2} and 0.007 ± 0.001 mg·dm^{-2}, respectively.

well as LDPE, provided poorer barrier against diacrylate transfer than the thinner laminate B. This could be caused by differences in the composition of the packaging materials, i.e. different structure of paper and/or LDPE, presence of an adhesive layer between the two materials and their properties. Unfortunately, the authors have no information about detailed structure of the packaging materials.

The results on migration of diacrylates into solid simulants are given in Fig. 3–5. The levels of migration were much lower compared with those into liquid simulants.

The migration of DPGDA into Tenax was 0.210 ± 0.013 mg·dm^{-2} (i.e. 5.0 % of DPGDA originally present in the packaging material) after 24 h for both laminated packaging materials, while the migration of TPGDA, at the same conditions, was 0.084 ± 0.007 mg·dm^{-2} (2.0 %) and 0.067 ± 0.007 mg·dm^{-2} (1.6 %) for laminates A and B, respectively.

Migration into saccharose was even lower,

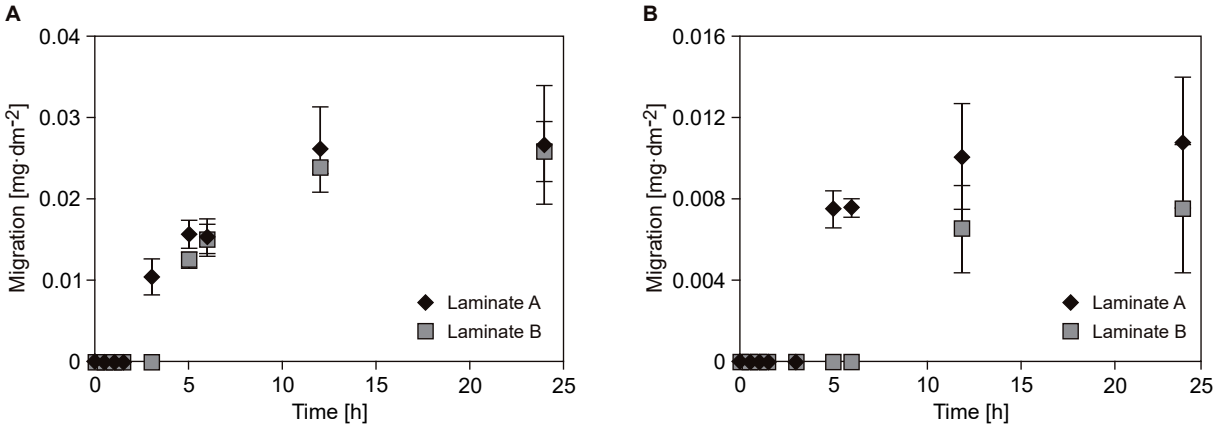

Fig. 5. Migration of diacrylates from two packaging materials into saccharose at 40 °C.

A – dipropylene glycol diacrylate, B – tripropylene glycol diacrylate.
After 96 h, the levels of migration of dipropylene glycol diacrylate (DPGA) from laminate A and B were 0.030 ± 0.005 mg·dm^{-2} and 0.025 ± 0.005 mg·dm^{-2}, respectively. For tripropylene glycol diacrylate (TPGA), these levels were 0.012 ± 0.005 mg·dm^{-2} and 0.008 ± 0.005 mg·dm^{-2}, respectively.
After 24 h, the level of migration of DPGA and TPGA from comparative packaging made of filter paper was 0.166 ± 0.002 mg·dm^{-2} and 0.141 ± 0.007 mg·dm^{-2}, respectively.

i.e. 0.027 ± 0.007 mg·dm^{-2} for DPGDA and 0.011 ± 0.003 mg·dm^{-2} for TPGDA for laminate A after 24 h, and 0.026 ± 0.004 mg·dm^{-2} (DPGDA) and 0.008 ± 0.003 mg·dm^{-2} (TPGDA) for laminate B at the same period.

Migration from laminate A into NaCl after 24 h reached the levels of 0.022 ± 0.001 mg·dm^{-2} and 0.008 ± 0.003 mg·dm^{-2} for DPGDA and TPGDA, respectively. The level of migration of DPGDA from laminate B into NaCl after 24 h was 0.020 ± 0.001 mg·dm^{-2}, while no quantifiable results above the limit of quantification of the used method (0.002 mg·dm^{-2}) were obtained for TPGDA.

Migration of the tested compounds from the filter paper without a functional barrier was higher. Maximum migration levels of DPGDA and TPGDA from plain paper after 24 h were 1.313 ± 0.012 mg·dm^{-2} (31.3 %) and 1.159 ± 0.009 mg·dm^{-2} (28.3 %) into Tenax, 0.166 ± 0.002 mg·dm^{-2} (4.0 %) and 0.141 ± 0.007 mg·dm^{-2} (3.4 %) into saccharose, and 0.108 ± 0.008 mg·dm^{-2} (2.5 %) and 0.007 ± 0.001 mg·dm^{-2} (0.2 %) into NaCl. The stronger adsorption capacity of Tenax sorbent, compared with real food, was reported previously [13, 17]. LDPE layer reduced the migration by up to 92.9 % into Tenax, up to 92.1 % into saccharose and up to 81.0 % into NaCl.

The levels of diacrylate migration after 96 h are also mentioned in the legends of Fig. 3–5. These values did not differ significantly from those after 24 h. It means that equilibrium conditions were stabilized quite rapidly, i.e. in a period shorter than 24 h. This is in agreement with migration methodology given by EU legislation [28] for polymer materials.

DPGDA migrated more easily into solid simulants compared with the transfer of TPGDA. This was an opposite situation of that found with liquid simulants (see above). It can be explained by a higher volatility of DPGDA (see Tab. 1).

The described experiments were done in conditions simulating application of paper-based packages in practice. It means that desorption of diacrylates into the outside atmosphere occurred simultaneously with their penetration into food simulants inside. The losses of both diacrylates during migration tests were not followed. Poças et al. [10] reported that the losses of diethyl phthalate, which has the molecular weight (222.24 g·mol^{-1}) and volatility (vapour pressure of 0.028 Pa at 25 °C [14]) close to DPGDA, were higher than 70 % during a migration test in an open migration cell at 40 °C. Therefore, it can be expected that a significant amount of diacrylates was desorbed into the surroundings of the tested packages during our experiments.

Tab. 4. Parameters of the kinetic model based on Weibull distribution function for dipropylene glycol diacrylate.

Simulant	Laminate A				Laminate B			
	CF_T/CP_0	τ	β	R^2	CF_T/CP_0	τ	β	R^2
Tenax	0.0014 ± 0.0003	9.2 ± 1.5	0.75 ± 0.13	0.989	0.0140 ± 0.0020	7.8 ± 1.3	0.99 ± 0.21	0.986
Saccharose	0.0014 ± 0.0002	8.1 ± 2.2	1.14 ± 0.45	0.963	0.0014 ± 0.0002	8.8 ± 2.4	1.56 ± 0.78	0.956
NaCl	0.0011 ± 0.0003	5.8 ± 0.7	3.18 ± 2.29	0.971	0.0010 ± 0.0001	6.0 ± 0.5	3.51 ± 1.83	0.988
10% Ethanol	0.0005 ± 0.0001	1.0 ± 1.2	0.21 ± 0.16	0.933	0.0004 ± 0.0001	0.3 ± 0.8	0.21 ± 0.16	0.933
95% Ethanol	0.0133 ± 0.0021	1.1 ± 0.3	1.36 ± 0.90	0.958	0.0041 ± 0.0007	0.5 ± 0.1	0.44 ± 0.09	0.996

CF_T – final content of the migrant in the food simulant, CP_0 – initial content of the migrant in the packaging material, τ, β – coefficients of the Weibull model, R^2 – coefficient of determination.

Tab. 5. Parameters of the kinetic model based on Weibull distribution function for tripropylene glycol diacrylate.

Simulant	Laminate A				Laminate B			
	CF_T/CP_0	τ	β	R^2	CF_T/CP_0	τ	β	R^2
Tenax	0.0058 ± 0.0004	6.5 ± 1.3	0.72 ± 0.16	0.983	0.0041 ± 0.0005	5.7 ± 0.8	0.84 ± 0.15	0.990
Saccharose	0.0006 ± 0.0001	5.6 ± 0.8	3.47 ± 3.23	0.943	0.0004 ± 0.0001	–	–	–
NaCl	0.0005 ± 0.0001	5.2 ± 0.5	3.91 ± 2.49	0.973	0.0003 ± 0.0001	–	–	–
10% Ethanol	0.0158 ± 0.0034	2.0 ± 1.4	3.94 ± 9.04	0.932	0.0022 ± 0.0005	1.6 ± 1.0	1.87 ± 2.87	0.803
95% Ethanol	0.0363 ± 0.0028	4.2 ± 1.2	2.39 ± 1.97	0.919	0.0119 ± 0.0024	5.0 ± 1.7	1.39 ± 0.94	0.922

CF_T – final content of the migrant in the food simulant, CP_0 – initial content of the migrant in the packaging material, τ, β – coefficients of the Weibull model, R^2 – coefficient of determination.

The transfer of diacrylate from packaging materials into food simulants was evaluated using a kinetic model based on Weibull distribution function (Eq. 1), which was, for this purpose, proposed by Poças et al. [10, 14].

$$\frac{C_t}{C_\infty} = 1 - exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \quad (1)$$

where C_t is the content of the migrant in the used simulant at time t, C_∞ is this content at an equilibrium, τ and β are the constants characterizing the course of migration.

The experimental data on the migration of diacrylates into ethanol solutions, solid food and Tenax, which are given in Fig. 1–5, were processed using the Statistica software to obtain the parameters of the Weibull kinetic model fitted to the found course of the transfer of diacrylates.

The results are summarized in Tab. 4 and Tab. 5. CF_T is the final content of a migrant in the food simulant (the levels of migration after 96 h and 24 h were used for calculation of this parameter in the case of solid and liquid simulants, respectively), CP_0 is the initial content of the migrant in the packaging material.

The parameters of the kinetic model are not mentioned for migration of TPGDA into saccharose or NaCl. Regarding TPGDA migration into saccharose, the reason was the high level of standard errors as well as the sigmoid shape of the plot of the course of migration. Such course of migration does not fit to the Weibull distribution function. In the case of TPGDA migration into NaCl, the calculated parameters were too high due to the fact that diacrylate in this case was found in the sorbent at a measurable level only after 96 h, and so the kinetic model could be created only on the base of one value.

Considering the migration of diacrylates into solid simulants, the values of the ratio CF_T/CP_0 were quite low, with the exception of DPGDA transfer into Tenax, due to a low portion of diacrylates fixed in the sorbent as mentioned above. The values of parameter τ were relatively low in all cases (in the range from 5.2 to 9.2), which indicated the high process rate in the beginning of the experiment. The values of τ parameters in Tab. 4 are close to that for the transfer of dibutyl phthalate from paper to Tenax at 40 °C referred by Poças et al. [10] and for the transfer of four photoinitiators to Tenax at 20, 40 and 60 °C refered by Cai et al. [32]. No statistically significant differences were found for τ values for DPGDA and TPGDA transfer at the same conditions (α = 0.05). The values found for β parameter ranged from 0.7 to 1.6 for the migration of both diacrylates into Tenax, and for DPGDA transfer into saccharose. The β values of the migration processes in other cases (saccharose – only TPGDA, NaCl, 10% ethanol and 95% ethanol – DPGDA and TPGDA) were in the range from 3.2 to 3.9. The very good agreement between migration data and Weibull model are documented by the high values of coefficient R^2 ranging from 0.943 to 0.990.

The parameters of the Weibull distribution function for diacrylates migration into liquid simulants differed mostly from those mentioned for solid simulants.

The τ values were much lower, i.e. in the range 0.3–2.0, indicating even faster diacrylate transfer in the initial phase of the prosess. Only for the migration of TPGDA into 95% ethanol, the τ values were close to those found for the transfer of diacrylates into solid simulants (τ = 4.2 and 5.0). In these cases, the values of τ parameters were significantly different from values calculated for DPGDA (α = 0.05).

The β parameters calculated for the migration of diacrylates into liquid simulants ranged from 0.21 to 1.36 for DPGDA, and from 1.39 to 3.94 for TPGDA. The statistically significant differences of β parameters were found for DPGDA and TPGDA migration in all cases (α = 0.05). Also in these cases, the very good agreement between migration data and Weibull model were documented by the high values of R^2 ranging from 0.896 to 0.996. A lower value of R^2 was calculated only for TPGDA transfer into 10% ethanol (R^2 = 0.803).

CONCLUSIONS

Migration of DPGDA and TPGDA from packaging materials constituted of paper coated with LDPE into liquid food simulants (10% ethanol, 50% ethanol, 3% acetic acid or olive oil) were much higher compared with the diacrylate transfer into solid simulants or food (Tenax, saccharose or NaCl). The highest level of diacrylates migration was found in the case of 95% ethanol. The levels of TPGDA migration into liquids were higher compared with those of DPGDA, while the results were reverse with solid sorbents. The transfer of diacrylates from paper was higher compared with migration from laminates practically in all cases. The Weibull distribution function closely correlated with the obtained data on migration of diacrylates. The results confirmed that LDPE coating can be considered as a functional layer against migration of diacrylates from packaging materials into solid food. On the other hand, ma-

terials with LDPE which is used for one portion paper stick packages of saccharose still can theoretically change odour in an unacceptable way. Development of new efficient functional barrier materials should be carried out.

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