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Research article

The kinetics of swelling and migration: A case study of plasticized polylactic acid food contact plastics tested with ethanolic food simulants

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Abstract. The effect of swelling and plasticizer content of a plastic, as well as the ethanol content of the food simulant on the migration kinetics of three stabilizer-type additives from polylactic acid (PLA)-based food contact plastics has been investigated. The results proved that the parameters that affect the diffusion of substances inside the polymer matrix, *i.e.*, swelling, plasticization, and the size of migrants, are the decisive factors in the migration from PLA to ethanolic food simulants. Both swelling and migration were negligible when ethanol 10% (v/v) was used. Contrarily, the specific migration limits of Commission Regulation (European Union, EU) No. 10/2011 were exceeded in ethanol 50% (v/v) for all investigated stabilizers. Migration was promoted by plasticization, but this effect could only be observed when the applied food simulant swelled the plastic (at least 20% (v/v) ethanol content). The dependence of the plasticizer's migration-enhancing effect on the swelling has not been shown before. When the plasticization caused increased migration, it also led to specific migration limit exceeding within a shorter period of time. It happens even if PLA-based plastics are dedicated to the storage of hydrophilic food, which is the most common application area of these products. These results can support the improvement of both consumer safety and active packaging development.

Keywords: *poly(lactic acid), plasticizer, food contact plastic, additive, bio-based, biopolymer*

1. Introduction

In the market of biobased and biodegradable plastics, polylactic acid (PLA) is one of the most popular polymers due to its relatively low price and advantageous mechanical and optical properties [1]. The application field of PLA is versatile: the polymer gained its popularity as the raw material of 3D printing and medical implants. However, its position in the food packaging industry is more relevant today.

Potentially harmful compounds (*e.g.*, starting materials, additives, impurities) can be released from the packaging as they come in contact with food [2, 3]. The mass transport process of different substances from the plastic and their dissolution in the contacting

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food is called as migration [4–6]. To ensure food quality and consumer safety, it is necessary to eliminate those migrating substances that risk human health. From a toxicological point of view, migrants with less than 1000 Da molecular weight can pose a risk, as these tend to be absorbed in the gastrointestinal tract [7]. At the same time, the controlled release of active ingredients is the principle of many active packaging [8]. Therefore, understanding those effects that promote or reduce migration is essential [9].

Even though, as a raw material, PLA has numerous advantageous characteristics, some of its properties (*e.g.*, barrier properties, ductility, or heat resistance) should be improved with additives [1, 10–18] or blending [19]. The rigidity of PLA can be decreased with the addition of plasticizers [11–13], while elevated heat resistance can be achieved with crystallization, *e.g.*, by the application of nucleating agents [14, 15]. For the improvement of polymer chain stability, stabilizers (*e.g.*, antioxidants, UV-absorbers, anti-hydrolysis agents) should be applied [16–18]. The screening migration tests of PLA-based products prove that antioxidants, UV-stabilizers, flame retardants, slip agents, and plasticizers are indeed often used [20–23]. At the same time, the manufacturers must follow the recommendations of Commission Regulation 10/2011 (*of 14 January 2011 on plastic materials and articles intended to come into contact with food*) [24] in the European Union (EU) to ensure that the usage of their products does not risk consumer safety and food quality. According to the regulation, the overall migration must be below 10 mg/kg (food or its simulants) or 60 mg/dm^2 (contact surface area). For some substances even lower, specific migration limits (SMLs) have been set by the regulation.

The main condition of migration tests (*e.g.*, contact temperature) and the substituents of food (food simulants) are also determined in the Commission Regulation (EU) No. 10/2011 [24]. For the laboratory scale testing of migration, circumstances must be chosen to model the worst foreseeable conditions of storage. Therefore, PLA is usually tested at 40 °C contact temperature (or below) [25–35] since this is the maximum applicable temperature for uncrystallized PLA-based products. Considering any polymer–migrant–food simulant system (unless degradation happens), the rate of migration and the concentration of released compounds increase with increasing temperature [30, 31, 35, 36].

The development of PLA-based active packaging focuses on the thorough investigation of migration kinetics and the migration influencing parameters. The most important parameters of migration, such as the polymer's molar weight, the properties of the contacting medium (*i.e.*, food or food simulants), and the physico-chemical properties of the migrating substances have already been inspected in many studies [27, 29, 32–34, 37]. The physico-chemical properties with the most decisive influence are the size and polarity of migrant molecules and the available functional groups that affect the possible migrant–polymer, and migrant–food simulant interactions. Iñiguez-Franco *et al.* [29] and Mascheroni *et al.* [34] both assumed the nexus between the number of hydroxyl groups and the migration affinity. Later also investigated the effect of methylation of a hydroxyl group on migration. Stoll *et al.* [27] described the different migration behaviour of two carotenoids with the same molecular formula but different molecular flexibility. Kirchkeszner *et al.* [33], Petrovics and coworkers [32, 37], and Jamshidian *et al.* [31] explained the different migration behaviour of additives with the molecular sizes (molar weight (M_w) or molecular volume).

According to Commission Regulation (EU) 10/2011, real food can be substituted with food simulants in migration tests that can mimic the physico-chemical properties of different types of food [24]. Most of the liquid food simulants are ethanol-containing solutions (ethanol 10, 20, 50, and 95% (v/v), also called as food simulant 'A', 'C', 'D1' and alternative 'D2', respectively), beyond that acetic acid 3% (w/v) (food simulant 'B') and vegetable oil (and its other alternative, isooctane; food simulant 'D2') are determined. Since the active compounds – migrants from active packaging, usually antioxidants – and plastic additives are often hydrophobic substances, higher migration was measured to food simulants with less water content, *e.g.*, [29, 35, 38]. At the same time, the interaction between the polymer and the food simulant can influence the kinetics of migration, too. Several studies mentioned that ethanol – due to its similar polarity to PLA – can swell the polymer [25, 28–35, 37, 39]. As a result of solvent uptake, both the distance between polymer chains and the flexibility of chains increase – this way, the penetrated solvent acts as a plasticizer. Therefore, the diffusivity of compounded substances gets higher, which results in increased migration. Kirchkeszner

et al. [33] found a strong linear correlation between the kinetics of swelling and migration of six plastic additives in a series of migration tests from polypropylene (PP) and from PLA, carried out in isooctane and in ethanol 95% (v/v), respectively. The ethanol accessibility to PLA could be further increased by elevating the contact temperature and with the compoundation of PLA with tributyl acetyl citrate (TBAC) plasticizer and/or with multiple stabilizer-type additives at the same time [32]. However, swelling-reducing parameters are also known, such as a high degree of crystallinity [37].

Just like the swelling caused by plasticization, the compoundation of plasticizer-type additives can significantly increase the migration of substances [26, 32, 34]. Stoll *et al.* [26] investigated the migration of bixin from PLA (plasticized with TBAC) into ethanol 95% (v/v) and reported a sixfold increase in the overall mass transfer coefficient due to plasticization. However, the migrated concentration of bixin after reaching the equilibrium was lower, which was explained by the decreased stability of the carotenoid in the presence of TBAC. Mascheroni *et al.* [34] applied polyethylene glycol plasticizer for the production of a PLA-based composite. From this composite, the active ingredient was released in a higher quantity compared to unplasticized PLA (with no filler). A more detailed investigation was carried out by Petrovics *et al.* [32] on the plasticization-affected migration from PLA and PP-containing plastics at four different plasticizer levels. With an increasing plasticizer content (from 0 to 10% (w/w)), an increased migration (by a factor of 1.17–3.52) of different stabilizers from PLA to ethanol 95% (v/v) at 40 °C was reported. Moreover, a correlation between the plasticizer concentration of plastics and the migration rate or the maximum migrated concentration was proven. The similar effect of plasticization and contact temperature on migration mechanism was discussed with the conclusion of migration being more affected by contact temperature than plasticization. Besides the mentioned studies, the effect of plasticization on the migration from PLA-based food contact plastics (FCPs) is scarcely investigated so far.

The aim of this study was to investigate the effect of plasticization on the kinetics of both swelling and migration in ethanol 10, 20, and 50% (v/v) food simulants with PLA-based plastics. Since the relation of plasticization and migration has only been reported in ethanol 95% (v/v) so far, the possible outcome of this interaction is still unknown in food simulants with lower ethanol content, though PLA-based FCPs are usually made for this purpose. For the experiments, PLA-based plastics were injection molded with 0, 5, and 10% (w/w) TBAC concentrations, along with three stabilizer-type additives. An ultra-high performance liquid chromatographic – tandem mass spectrometric (UHPLC–MS/MS) method was developed and validated for the quantitative analysis of these additives. For the kinetic study, a 13 day long migration experiment was performed. The results were evaluated with the determination of the maximum migrated concentrations and the two main parameters of the Fickian mathematical model (diffusion (D_P) and partition coefficients ($K_{P/F}$)).

2. Materials and methods

2.1. Materials

During the experiments and analysis, the following solvents were used: methanol (≥99.9%, PanReac AppliChem, Darmstadt, Germany), absolute ethanol (≥99.9%, Merck KGaA, Darmstadt, Germany), and ethanol 96% (v/v) (Thomasker Finechemicals Ltd., Budapest, Hungary). Ammonium-formate (≥99.0%) was the product of Merck KGaA. Ultrapure water (MQ water) was produced with a Millipore Direct 8 (Merck KGaA) water purification system. Ethanol 96% (v/v) and ultrapure water were used to prepare the food simulants for the experiments, *i.e.*, ethanol 10% (v/v) (food simulant 'A'), ethanol 20% (v/v) (food simulant 'C') and ethanol 50% (v/v) (food simulant 'D1'). Gases for the operation of UHPLC–MS/MS instrument – *i.e.*, nitrogen 5.0 and argon 4.6 – were provided by Messer Hungarogáz Kft. (Budapest, Hungary).

For the production of PLA plastic test specimens Ingeo™ 2500 HP polylactic acid (Natureworks LLC Minneapolis, Minnesota, USA); with 0.5% D-lactide content); BHT (2,6-di-*tert*-butyl-4-methylphenol, CAS: 128-37-0), Uvinul 3039 (2-ethylhexyl 2-cyano-3,3-diphenylacrylate, CAS: 6197-30-4), Tinuvin 900 (2-(2H-benzotriazol-2-yl)-4,6-*bis*(1-methyl-1-phenylethyl) phenol, CAS: 70321-86-7) additives and a bioplasticizer, TBAC (tributyl acetyl citrate, CAS: 77-90-7) were used. BHT and TBAC were purchased from Merck KGaA; Uvinul 3039 and Tinuvin 900 were donated by BASF Ltd. (Ludwigshafen, Germany). Some relevant physico-chemical properties of the additives are shown in Table 1.

Table 1. The applied additives and some of their physico-chemical properties.

Name	CAS number	Function	M_w [g/mol]	*van der Waals* volume* [Å^3]	Solubility in water** [µg/L]
Uvinul 3039	6197-30-4	UV absorber	361.5	359.6	23.9
BHT	128-37-0	antioxidant	220.4	244.7	9 187
Tinuvin 900	70321-86-7	UV absorber	447.6	424.8	61.8
TBAC	77-90-7	plasticizer	402.5	396.6	19 713

*the *van der Waals* volume values were calculated with Marvin Sketch
**the additives' solubility in water (at 25 °C) was calculated with MarvinJS Solubility Predictor

The additives' *van der Waals* volume and solubility in water (at 25 °C) were calculated by MarvinSketch (product version: 5.12.1) and MarvinJS Solubility Predictor by ChemAxon Ltd. (Budapest, Hungary), respectively.

2.2. Test specimen production

A detailed description of the production of plastic test specimens can be found in the publication of Kirchkeszner *et al.* [33]. Briefly, the procedure was as follows: after overnight drying, the PLA pellet was compounded with the additives using a Labtech Scientific LTE 26-44 co-rotating twin-screw extruder (Labtech Engineering Co., Ltd., Samutprakarn, Thailand). The diameter of the screws was 26 mm, their rotational speed was set at 50 rpm, and the five heating zones' temperature increased from 170 to 190 °C at 5 °C steps. The formed filaments were ground into 3 mm long pellets. These pellets were then injection molded with an Arburg Allrounder Advance 270S 400-170 instrument (Arburg, GmbH, Lossburg, Germany). Its screw's diameter was 30 mm, which was heated initially to 190 °C that raised in 5 °C steps to 210 °C toward the nozzle. The melt was injected into the 25 °C mold with 50 cm^3/s injection speed. For 20 s, the holding pressure was 500 bar, while for residual cooling time, 40 s was necessary. The resulting injection molded plastic sheets' dimensions were 80×80×2 mm.

The Uvinul 3039, BHT, and Tinuvin 900 content of each injection molded plastic sheet was 1% (w/w). As for their TBAC content, three different variations of sheets were prepared containing 0, 5 or 10% (w/w) TBAC. As a reference sample, neat PLA (without any additives) was extruded and injection molded. The same samples have been investigated by Petrovics *et al.* [32], previously.

2.3. Characterization of the test specimens

To prove the success of plasticization, the produced granules' and plastic sheets' melt flow index (MFI) and differential scanning calorimetric (DSC) analysis have been performed. For MFI determination a CEAST 7027.000 (Instron, Norwood, Massachusetts, USA) instrument has been used. The MFI values were measured according to standard ISO 1133-2:2011 [40], *i.e.*, with a 2.16 kg nominal load and at 190 °C plasticization temperature. The DSC measurements have been performed with a Q2000 type instrument of TA Instruments (New Castle, Delaware, USA). Approximately 5 mg pieces of test specimens were measured in heat/cool/heat cycles. The heating and cooling ranges varied between 0 and 200 °C at a heating and cooling rate of 5 °C/min. From the resulting thermograms, the glass transition (T_g), cold-crystallization (T_{cc}), and melting (T_m) temperatures were determined, along with the enthalpies of cold-crystallization (ΔH_{cc}) and fusion (ΔH_m). The degree of crystallinity (X%) of plastics was between 18.1±0.7 and 26.2±0.3%, and it increased along with the amount of plasticizer. The rheological and thermal properties of the test specimens can be found in Table 2.

Table 2. Thermal and flow characteristics of the injection molded sheet test specimens.

	MFI [g/10 min]	T_g [°C]	T_m [°C]	T_{cc} [°C]	X [%]
Reference	7.2±0.1	62.3±0.4	175.6±0.3	95.4±0.5	21.3±1.4
L0	8.6±0.1	62.3±0.4	174.3±0.3	90.6±0.8	18.1±0.7
L5	14.6±0.1	56.5±0.2	172.7±0.3	84.7±0.3	23.0±0.5
L10	20.6±0.1	49.7±0.2	171.8±0.4	79.3±0.2	26.2±0.3

Abbreviations: MFI: melt flow index, T_g: glass transition temperature, T_m: melting temperature, T_{cc}: cold crystallization temperature, X%: degree of crystallinity. Measurements were performed in triplicates.

These results have been determined by Petrovics *et al.* [32].

2.4. The UHPLC–MS/MS analytical method

For the quantitative analysis of target compounds, the UHPLC–MS/MS analytical technique with multiple reaction monitoring (MRM) data acquisition method was used. An UltiMate 3000-RS UHPLC system (Thermo Scientific Inc., Waltham, Massachusetts, USA) and an Acquity UPLC HSS C18 analytical column (1.8 µm particle size, 2.1 mm I.D. ×100 mm length; (Waters Corporation, Milford, Massachusetts, USA) were used for the chromatographic separation. A TSQ Fortis (Thermo Scientific Inc., Waltham, Massachusetts, USA) triple quadrupole mass spectrometer equipped with a heated electrospray ion source (H-ESI) was coupled to the UHPLC system for the detection of compounds. The sheath, aux, and sweep gases were nitrogen (purity: 5.0), while argon (purity: 4.6) was used as collision gas. Data evaluation was performed with Chromeleon 7.3 software (Thermo Scientific Inc., Waltham, Massachusetts, USA).

The chromatographic parameters of the analytical method were the following. As eluents, MQ water (with 1 mM ammonium-formate modifier) and methanol were used. During the analysis, the flow was set at 200 µL/min, and the injected sample volume was 10 µL. The column thermostat was set at 40 °C. The gradient program started with 25% initial methanol content, which increased to 80% at a rate of 18.3%/min. After reaching the 80% methanol ratio, the gradient rate was decreased to 5.0%/min until the eluent consisted of only methanol. The 100% methanol content was maintained for 9 min before the eluent composition was set back to the initial 25% methanol (in 1 min). Despite the decreased gradient rate after 3 min, the peaks of BHT and Uvinul 3039 could not be separated. This phenomenon did not cause any problems in the quantitative analysis of the two additives due to the selectivity of the triple quadrupole (QQQ) analyzer. The final gradient program, along with the extracted ion chromatograms, can be seen in Figure 1. The asymmetry factor (calculated with Chromeleon 7.3, Asymmetry (EP) algorithm) of compounds was between 0.95–1.19.

The detailed settings of the mass spectrometric ionization and detection method can be found in Table 3. H-ESI ion source parameters were optimized in both positive and negative ionization modes to achieve the highest possible intensity for each target compound. The presence of ammonium-formate in the eluent significantly helped the ionization of two target compounds, BHT and Uvinul 3039. To build up the MRM method, the two most intensive quantifier–qualifier ion transitions of each target compound were used.

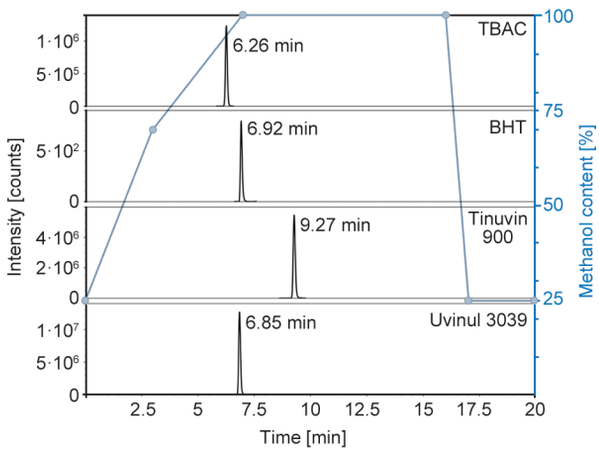

Figure 1. Extracted ion chromatograms of the target compounds from a 0.5 mg/L concentration solution overlayed with the gradient program.

2.5. Swelling and migration kinetic experiments

From the injection molded PLA sheets, (length × width × thickness) 30×10×2 mm test specimens were cut out. After the surface contaminations were removed (with triplicate immersion into *n*-hexane), the accurate dimensions and mass (m_{dry}) of each specimen were determined with Vernier calipers and an analytical balance (VWR LA 124i, VWR International LLC (Radnor, Pennsylvania, USA)). The test specimens were placed into glass vials containing preheated food simulants. The vials were then placed into a laboratory incubator (POL-EKO-APARATURA sp.j. (Wodzisław Śląski, Poland)) with its temperature set at 40 °C. In this study, the ethanolic food simulants of Commission Regulation (EU) No. 10/2011 were investigated, *i.e.*, food simulant 'A' (ethanol 10% (v/v)), 'C' (ethanol 20% (v/v)) and 'D1' (ethanol 50% (v/v)) [24]. Experiments were prepared with three replicates.

The prescribed test specimen surface–food simulant volume ratio is 0.6 cm^2/g [24], which resulted in the application of a 12.7 g food simulant. This meant 13–13 mL of ethanol 10% and 20% (v/v), and 14 mL of ethanol 50% (v/v) (densities of solutions were 0.982, 0.969 and 0.914 kg/L, respectively). Samples were taken after 1, 6, and 10 h, then on a daily basis until 13 days of contact time. At the given sampling times, the test specimens were removed from the

Table 3. Parameters of the mass spectrometric ionization and detection mode.

Settings of H-ESI ion source						
Sheath gas flow	[L/min]		5.58			
Aux gas flow	[L/min]		11.69			
Sweep gas flow	[L/min]		3.75			
Collision gas pressure	[mTorr]		1.5			
Spray voltage	[V]	positive mode	+4500			
		negative mode	–4150			
Ion transfer tube temperature	[°C]		275			
Vaporizer temperature	[°C]		350			
Detection parameters						
			TBAC	**Uvinul 3039**	**BHT**	**Tinuvin 900**
Retention time	[min]		6.26	6.85	6.92	9.27
Ionization mode			+	+	–	+
Precursor ion *m*/*z*			403.3	379.2	219.2	448.3
Adduct type			$[M+H]^+$	$[M+NH_4]^+$	$[M–H]^–$	$[M+H]^+$
Product ion *m*/*z**			185.2	232.1	163.2	91.1
			259.2	**250.1**	**203.2**	**370.2**
Collision energy	[V]		18.4	23.2	25.1	46.1
			14.1	12.0	26.7	21.1
Dwell time	[ms]		300	150	300	300
Tube lens voltage	[V]		84	41	81	83
Source fragmentation voltage	[V]		0	1.6	16.3	0

*boldly written product ion *m*/*z* values belong to the quantifier ions.

vials, the remaining liquid was wiped off of their surface, and the swelled weight ($m_{swelled}$) was measured as soon as possible. No sample enrichment was necessary prior to the UHPLC–MS/MS analysis, as the migrated concentration of the additives was in the working range of the analytical method. Therefore, 1 mL aliquot of the food simulants was pipetted into 2 mL vials for analysis. For some samples, dilution was necessary to get into the working range. In these cases, 10 times dilution was applied.

2.6. Evaluation of swelling and migration kinetic experiments

The swelling of test specimens was characterized by the adjusted swelling degree (*ASD*%), which was introduced by Kirchkeszner *et al.* [33], according to the Equation (1):

$$ASD\% = \frac{m_{swelled} + \sum c_{i,V} \cdot V_s - m_{dry}}{m_{dry}} \cdot 100 \qquad (1)$$

where $c_{i,V}$ is the concentration of the migrated *i* additive referred to the volume of food simulant [mg/L], and V_s is the volume of food simulant [L].

The concentration ($c_{i,V}$) of migrated additives in the food simulants was determined by using the above-described UHPLC–MS/MS method. For the quantitative analysis of target compounds, their ethanolic solutions in the concentration range of 5 µg/L–50 mg/L were measured at 13 concentration levels. In the individual working ranges of each target compound, linear or quadratic polynomial curves were fitted to the calibration points. The goodness of fitting was always verified with the inspection of R^2 values and residuals.

So that the errors of test specimen cutting could be eliminated, the results of migration measurements were normalized to the accurate surface of test specimens (Equation (2)):

$$c_{i,A} = \frac{c_{i,V} \cdot V_s}{A} \qquad (2)$$

where $c_{i,A}$ is the migrated concentration of *i* additive referred to the accurate surface of the test specimen [µg/dm^2] or [mg/dm^2], and *A* is the accurate surface of the test specimen [dm^2].

Kinetic curves were made by plotting the mean of three parallel results of *ASD*% or $c_{i,A}$ measurements as the function of contact time. As numerical representations of kinetic curves, the maximums of adjusted swelling degree ($ASD\%_{max}$) and migrated concentrations ($c_{i,A,max}$) were given. $ASD\%_{max}$ and $c_{i,A,max}$ are the average of measured *ASD*% and $c_{i,A}$ values

after reaching the steady-states of swelling and migration process, respectively. Each $ASD\%_{max}$ and $c_{i,A,max}$ results were calculated from at least 4 points. To characterize the kinetics of migration, the Fickian model (based on Fick's 2nd law) can be used by determining two key parameters of the process, *i.e.*, the diffusion (D_P) and partition ($K_{P/F}$) coefficients. For the calculation of D_P and $K_{P/F}$ the following formulas were used (Equation (3)–(5)) [4].

$$\frac{M_{F,t}}{M_{F,\infty}} = (1-\alpha)\left[1 - e^{\left(\frac{\tau}{\alpha^2}\right)}\operatorname{erfc}\left(\frac{\tau}{\alpha^2}\right)^{0.5}\right] \quad (3)$$

Where

$$\alpha = \frac{1}{K_{P/F}} \cdot \frac{V_F}{V_P} \quad (4)$$

and

$$\tau = \frac{D_P \cdot t}{L_P^2} \quad (5)$$

and $M_{F,t}$, and $M_{F,\infty}$ are the amount of migrated substance in the food simulant at time t and equilibrium, respectively [mg]; α is the mass ratio of migrated substance in food simulant to that in plastic at equilibrium; $K_{P/F}$ is the partition coefficient of migrated substance between the plastic and the food simulant; V_F and V_P are the volumes of food simulant and plastic, respectively [cm^3] and L_P is the thickness of the test specimen [cm]. To measure the fit between the calculated and the measured data, the root of mean square percentage error (*RMSE*%) was calculated according to Equation (6). Using the Microsoft Excel Solver, parameters of calculated data were iterated until *RMSE*% reached its minimum [41, 42]:

$$RMSE\% = \frac{1}{M_{P,0}} \cdot \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left[\left(M_{F,t}\right)_{measured,i} - \left(M_{F,t}\right)_{calculated,i}\right]^2} \cdot 100 \quad (6)$$

where $M_{P,0}$ is the amount of migrating substance in the plastic initially [mg]; N is the number of measurement points, and i is the number of observations.

3. Results and discussion

3.1. Swelling behaviour of PLA in ethanol 10, 20, and 50% (v/v) food simulants

Considering the previously presented results of Kirchkeszner *et al.* [33] and Petrovics *et al.* [32], the swelling behaviour of PLA in ethanol 10, 20, and 50% (v/v) is not surprising. The food simulant with the least ethanol content hardly swelled the polymer, but the *ASD*% increased with increasing alcohol content (Figure 2). This way, the maximum of *ASD*% elevated from 0.90±0.04% (5% (w/w) TBAC content in ethanol 10% (v/v)) to 1.10±0.05% (10% (w/w) TBAC content in ethanol 20% (v/v)) and 2.39±0.15% (10% (w/w) TBAC content in ethanol 50% (v/v)) (Table 4). When the test specimens contained neither stabilizers nor the plasticizer (reference PLA), the same differentiation was experienced, but to a smaller extent: $ASD\%_{max}$ increased from 0.64±0.03 to 0.92±0.06% in 'A' and 'D1' food simulants, respectively.

According to the results of Petrovics *et al.* [32], higher TBAC contents increased solvent uptake, which resulted in higher $ASD\%_{max}$ values. A similar finding was predicted in the case of ethanol 10, 20, and 50% (v/v) food simulants too. However, the

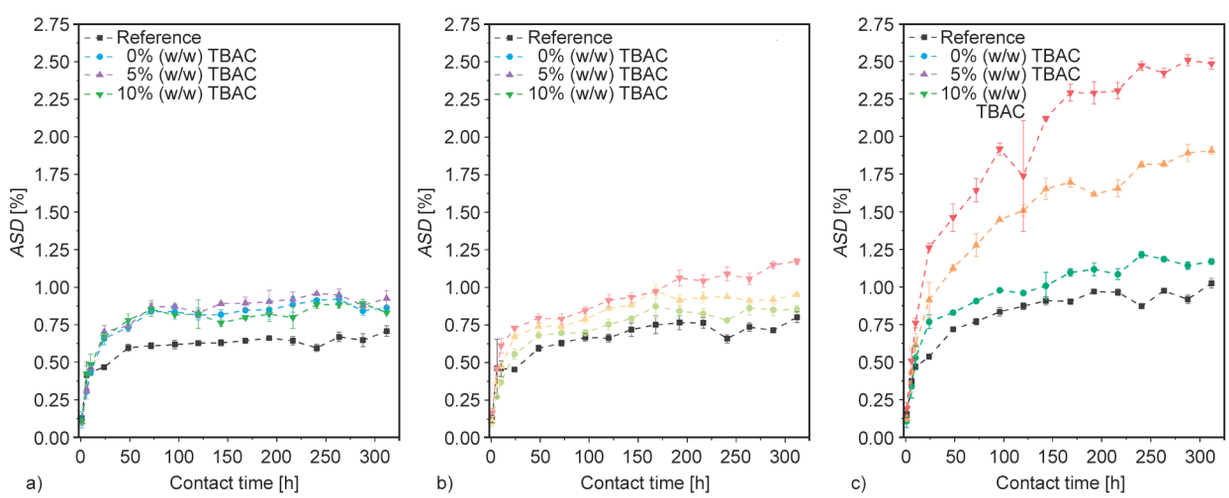

Figure 2. Swelling kinetic curves of PLA-based plastics with different TBAC plasticizer content in a) ethanol 10% (food simulant 'A'), b) 20% (food simulant 'C'), and c) 50% (v/v) (food simulant 'D1') food simulants.

Table 4. Summarized results of the swelling and migration kinetic experiments.

	TBAC content	$ASD\%_{max}$ [%]	Uvinul 3039			BHT			Tinuvin 900		
			$c_{i,A,max}$ [µg/dm²]	D_P^* [cm²/s]	$K_{P/F}$	$c_{i,A,max}$ [µg/dm²]	D_P^* [cm²/s]	$K_{P/F}$	$c_{i,A,max}$ [µg/dm²]	D_P^* [cm²/s]	$K_{P/F}$
Food simulant A	Reference	0.64±0.03	–	–	–	–	–	–	–	–	–
	0% (w/w)	0.86±0.04	2.36±0.40	–	$8.57 \cdot 10^5$	23.5±2.76	–	$8.59 \cdot 10^4$	0.56±0.06	–	$3.63 \cdot 10^6$
	5% (w/w)	0.90±0.04	2.45±0.38	–	$8.24 \cdot 10^5$	76.6±54.0	–	$2.63 \cdot 10^4$	0.78±0.03	–	$2.58 \cdot 10^6$
	10% (w/w)	0.83±0.04	1.86±0.30	–	$1.08 \cdot 10^6$	64.8±28.1	–	$3.11 \cdot 10^4$	0.98±0.15	–	$2.06 \cdot 10^6$
Food simulant C	Reference	0.72±0.05	–	–	–	–	–	–	–	–	–
	0% (w/w)	0.84±0.03	15.1±0.67	$2.14 \cdot 10^{-11}$	$1.34 \cdot 10^5$	41.2±3.42	$5.99 \cdot 10^{-11}$	$4.90 \cdot 10^4$	1.84±0.08	$1.33 \cdot 10^{-12}$	$1.10 \cdot 10^6$
	5% (w/w)	0.94±0.02	13.9±1.04	$7.94 \cdot 10^{-11}$	$1.45 \cdot 10^5$	152±9.90	$1.46 \cdot 10^{-10}$	$1.32 \cdot 10^4$	1.20±0.09	$3.07 \cdot 10^{-12}$	$1.68 \cdot 10^6$
	10% (w/w)	1.10±0.05	34.2±1.62	$4.89 \cdot 10^{-11}$	$5.90 \cdot 10^4$	273±23.6	$3.16 \cdot 10^{-10}$	$7.37 \cdot 10^3$	4.56±0.66	$4.30 \cdot 10^{-12}$	$4.43 \cdot 10^5$
	TBAC content	**$ASD\%_{max}$ [%]**	**Uvinul 3039**			**BHT**			**Tinuvin 900**		
			$c_{i,A,max}$ [mg/dm²]	**D_P^* [cm²/s]**	**$K_{P/F}$**	**$c_{i,A,max}$ [mg/dm²]**	**D_P^* [cm²/s]**	**$K_{P/F}$**	**$c_{i,A,max}$ [mg/dm²]**	**D_P^* [cm²/s]**	**$K_{P/F}$**
Food simulant D1	Reference	0.92±0.06	–	–	–	–	–	–	–	–	–
	0% (w/w)	1.18±0.03	0.48±0.01	$3.32 \cdot 10^{-10}$	$4.19 \cdot 10^3$	0.78±0.05	$3.89 \cdot 10^{-10}$	$2.57 \cdot 10^3$	0.13±0.01	$1.66 \cdot 10^{-10}$	$1.61 \cdot 10^4$
	5% (w/w)	1.86±0.05	2.18±0.23	$2.08 \cdot 10^{-9}$	$9.03 \cdot 10^2$	3.19±0.22	$2.09 \cdot 10^{-9}$	$6.10 \cdot 10^2$	0.35±0.05	$4.40 \cdot 10^{-10}$	$5.82 \cdot 10^3$
	10% (w/w)	2.39±0.15	2.83±0.24	$2.53 \cdot 10^{-9}$	$6.92 \cdot 10^2$	4.57±0.63	$2.56 \cdot 10^{-9}$	$4.20 \cdot 10^2$	0.36±0.07	$6.33 \cdot 10^{-10}$	$5.64 \cdot 10^3$

$ASD\%_{max}$: maximum of adjusted swelling degree
$c_{i,A,max}$: maximum of the migrated concentration (of *i* additive)
D_P: diffusion coefficient
$K_{P/F}$: partition coefficient between the polymer (P) and the food simulant (F)
Food simulant A: ethanol 10% (v/v) food simulant
Food simulant C: ethanol 20% (v/v) food simulant
Food simulant D1: ethanol 50% (v/v) food simulant
*Diffusion coefficient values were not determined in ethanol 10% (v/v) food simulant because the migration process did not follow the Fickian model.

results only partially met the expectations. The ethanol 50% (v/v) food simulant behaved similarly to ethanol 95% (v/v): the $ASD\%_{max}$ value of the unplasticized, but stabilizer containing PLA was about half of the 10% (w/w) TBAC containing PLA (Table 4). In contrast, in ethanol 10% (v/v) food simulant, the presence of plasticizer did not result in any increase in the degree of swelling, while in ethanol 20% (v/v), any change could hardly be recognized (0.26% increase due to 10% (w/w) plasticizer). This means that the swelling-promoting effect of plasticization only reveals if the ethanol content of the medium exceeds a critical level. According to our results, this effect has been noticed in ethanol 20% (v/v) first, and even at this ethanol content, approximately 10% (w/w) plasticizer is necessary for the considerable swelling induced mass increase of PLA. The comparison of $ASD\%_{max}$ results with fixed plasticizer content supports this assumption: with 0 and 5% (w/w) TBAC concentration, the swelling kinetic curves practically showed no difference in ethanol 10 and 20% (v/v) food simulants (Figure 2).

3.2. Effect of swelling, plasticization, and the ethanol content of food simulants on the migration kinetics

Kirchkeszner *et al.* [33] proved a good linear correlation between the PLA's swelling and the migration of additives since swelling – due to the loosened polymer chains – makes it easier for the compounded substances to migrate out of the polymer into the surrounding medium. In ethanol 10% (v/v) food simulant, the $ASD\%_{max}$ values were moderate (less than 1%), and the swelling kinetic curves were similar to each other regardless of the plasticizer content (Figure 2a). In the migration kinetic curves to ethanol 10% (v/v), the same pattern can be seen. As an example, the results of Uvinul 3039 can be seen in Figure 3a. Technically, the migrated concentration of additives was independent of the concentration of TBAC in the plastics. This observation proves that, generally, the presence of the plasticizer affects the solvent uptake of the polymer, but on its own (without the polymer swelling), it hardly influences the migration of substances into the liquid medium.

Conclusively, the plasticization of PLA promotes the migration of additives, but only indirectly: the presence of plasticizer can only promote the migration of additives if the applied food simulant is able to swell the polymer. It has not been proved by Kirchkeszner *et al.* [33] or Petrovics *et al.* [32], because ethanol 95% (v/v) was the applied food simulant in both studies. This phenomenon has not been reported yet, as previous studies usually do not interpret polymer swelling results in aqueous food simulants.

In the case of food simulants with low ethanol content, a possible migration-inhibiting effect must be considered, too, *i.e.*, the solubility of additives. Limited solubility could be a possible explanation for the lack of migration-promoting effect of plasticization in ethanol 10% (v/v). Yet, this hypothesis can be dismissed, based on the analytical performance characteristics determination of the UHPLC–MS/MS method (data not shown). In these measurements, solutions of target compounds in ethanol 10% (v/v) were examined, but no solubility problems were experienced at the migrated concentration levels. The additives' volume normalized maximum migrated concentrations were 14.3±2.22, 448±316 and 5.73±0.88 µg/L for Uvinul 3039, BHT and Tinuvin 900, respectively (calculated from the $c_{i,A,max}$ results, see in Table 4). The upper limit of quantitation (*i.e.*, the highest concentration level, where the target compounds could be measured with good accuracy (80–120%) and precision (relative standard deviation, *RSD*% < 20%)) in ethanol 10% (v/v) exceeded the measured $c_{i,A,max}$ values, with at least a 4 times factor. Additionally, the solubilities of additives in water at 25 °C were predicted with MarvinJS Solubility Predictor. The results can be found in Table 1. It can be seen that the measured $c_{i,A,max}$ values were below the predicted solubility values, too. Therefore, solubility could not have been a determining factor in the performed experiments. This is a piece of relevant information because in ethanol 10% (v/v) food simulant, the migrated concentration of additives

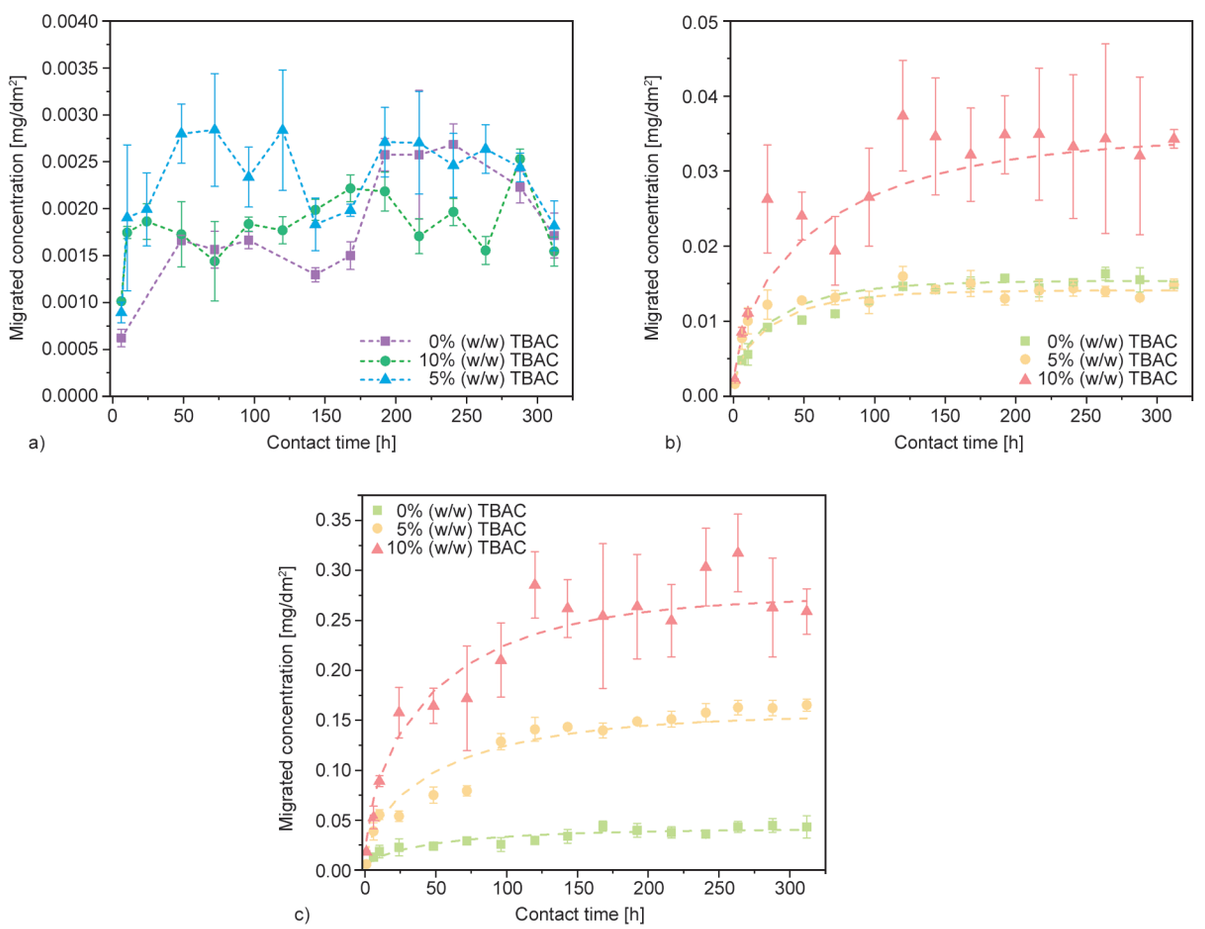

Figure 3. Migration kinetic curves of Uvinul 3039 in a) ethanol 10% and b) 20% (v/v) food simulants; and c) BHT in ethanol 20% (v/v), with different TBAC plasticizer content. For the ethanol 20% (v/v) kinetic curves, the Fickian curves have been fitted.

seems to be barely dependent on the contact time: the dynamic range of curves is quite short, and the migrated concentration hardly increases with contact time. Because of this uncorrelation, the Fickian model was not fitted to these data. The fast steady-state set can be explained: since low swelling was measured, and the test specimens were relatively thick (2 mm), migration supposedly took place only in the surface layer of the plastics, and the additive diffusion from the bulk material was negligible [33]. This way, not only could the equilibrium be reached in a short time, but the migrated concentration of additives remained low, too. For BHT, similarly low migrated amounts were measured by Jamshidian *et al.* [31] to ethanol 10% (v/v). Moreover, the migration of BHT remained below the limit of quantitation after 100 days long contact time in the study of Ortiz-Vazquez *et al.* [43].

In Figures 3b and 3c migration, kinetic curves of Uvinul 3039 and BHT can be seen, respectively, in ethanol 20% (v/v) food simulant. Noticeable differences can be found in the migration behaviour of the BHT and Uvinul 3039 (results of Tinuvin 900 are not shown, but its curves were very similar to those of Uvinul 3039). In the case of BHT, distinct kinetic curves were measured based on the plasticizer content of the plastics. This means, that the $c_{i,A,max}$ result from unplasticized plastic was the lowest, followed by the 5% (w/w) and eventually the 10% (w/w) TBAC containing test specimens. Accordingly, the $K_{P/F}$ values decreased with the increasing plasticizer content. Diffusion coefficients reveal, that not only the amount of migrated BHT, but also the speed of migration increased with the TBAC content, as almost ten-times increase in D_P values was experienced (Table 4).

This is not the case for Uvinul 3039 and Tinuvin 900. Their kinetic curves of migration from plastics 0 and 5% (w/w) plasticizer content overlap each other, while the ones from plastics with 10% (w/w) TBAC clearly exceeds them. The observed anomalous behaviour of Uvinul 3039 and Tinuvin 900 can be explained by their significantly higher *van der Waals* volumes compared to BHT (Table 1). The *van der Waals* volume is a parameter that characterizes the size of molecules, and it is the minimal amount of space occupied by molecules [44]. As can be seen in Table 1., BHT is the molecule with the smallest *van der Waals* volume, while Uvinul 3039 and Tinuvin 900 are at least 1.4× larger substances (a similar trend can be seen in the case of M_w, too). Polymer swelling was moderate in ethanol 20% (v/v) (0.84±0.03, 0.94±0.04 and 1.10±0.05% for 0, 5 and 10% (w/w) TBAC content, respectively), though noticeably raised with the plasticizer content. As mentioned before, in the swelled polymer, the macromolecular chains loosen and block the path of migrating substances less. Apparently, such a small difference in swelling was enough for the smallest molecule additive (BHT) to produce distinct migration kinetic curves. Contrarily, in the case of Uvinul 3039 and Tinuvin 900, the highest plasticizer content was necessary to achieve such a level of swelling, where migration was unquestionably facilitated.

In ethanol, 50% (v/v) food simulant, the migration-promoting effect of plasticization can be clearly seen (Figure 4). The comparison of $c_{i,A,max}$ values (Table 4) reveals, that the increasing TBAC concentration in the plastics promotes the migration of additives – similarly to the *ASD*%. Constant increases in D_P values were also seen as the result of plasticization. In the case of BHT and Uvinul 3039, a more than sixfold increase was found in the speed of migration. The same result for Tinuvin 900 was a 3.8× increase. Jamshidian *et al.* [31] also measured the migration of BHT into ethanol 50% (v/v) food simulant at 40 °C contact temperature. They calculated $2.7 \cdot 10^{-9}$ cm^2/s D_P, which is almost an order of magnitude larger than our D_P result ($3.89 \cdot 10^{-10}$ cm^2/s) from unplasticized PLA. The reason for this difference is probably the various thicknesses of the test specimens: Jamshidian *et al.* [31] worked with approx. 160 µm thick PLAs, while ours had 2 mm thickness. Garde *et al.* [5] also experienced significant D_P decrease (up to a factor of 100), as the thickness of tested PP films increased. As the TBAC content was increased to 10% (w/w), the D_P also grew to the same level as the one measured by Jamshidian *et al.* [31]. Though the rate of migration could be elevated to the same level with plasticization, the $K_{P/F}$ results remained different: Jamshidian *et al.* [31] reported that 60% of the BHT remained in the film, while our measurements resulted in 420 $K_{P/F}$ value (approx. 99.75% of the BHT could not migrate into the food simulant). This is at least two orders of magnitude difference. Such enormous discrepancy in equilibrium concentrations must originate from the different thicknesses again.

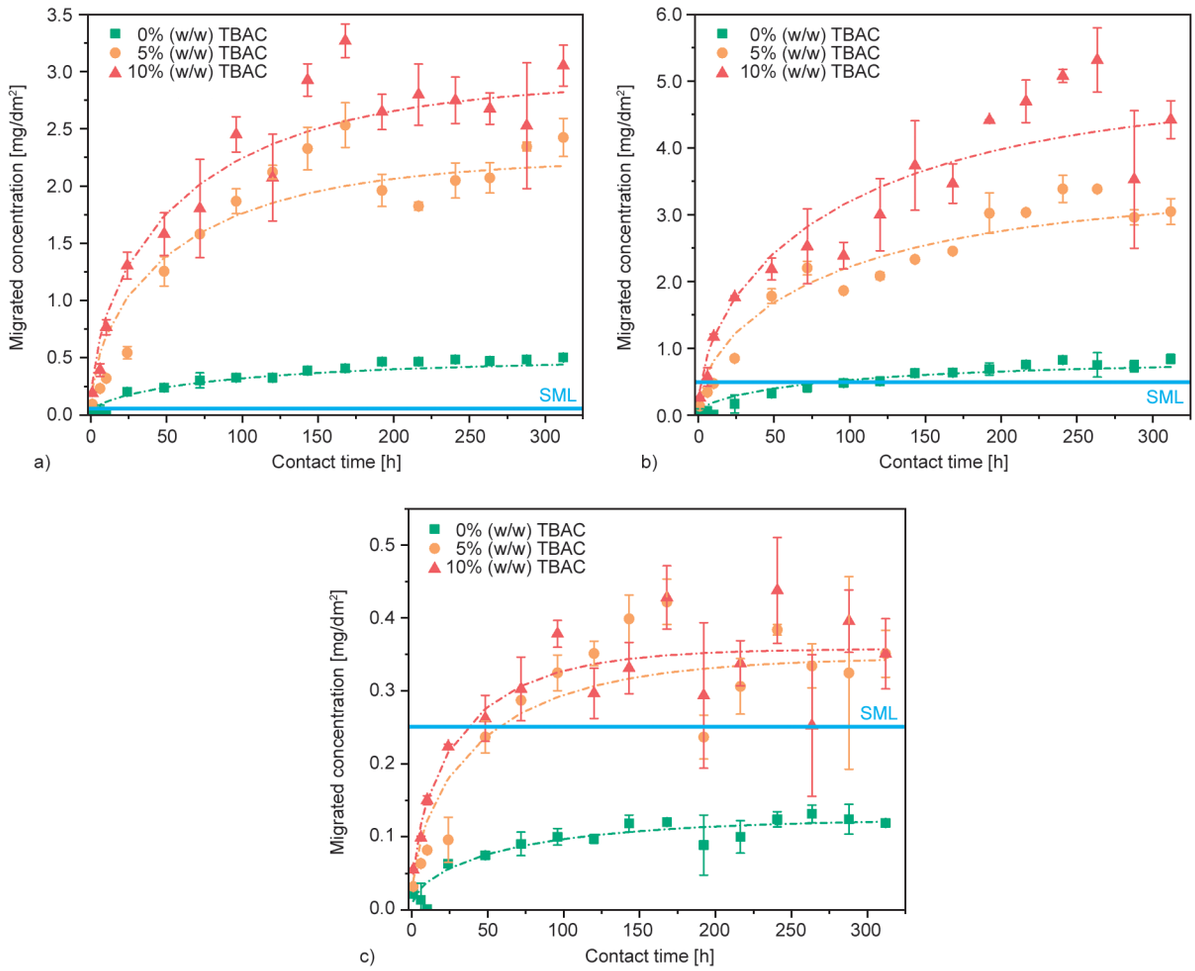

Figure 4. Migration kinetic curves of a) Uvinul 3039, b) BHT, and c) Tinuvin 900 in ethanol 50% (v/v) food simulant, with different TBAC plasticizer contents. For the measurement points the Fickian curves have been fitted. Regulated specific migration limits (SML) of each additive were marked with blue straight lines.

3.3. Evaluation of the quantitative results of migration experiments

In Table 4, the detailed numerical results of migration kinetic experiments are shown. The comparison of investigated plastic additives with each other (under given experimental circumstances) reveals the dominance of BHT over Uvinul 3039 and Tinuvin 900 from a migration perspective. BHT always resulted in the highest $c_{i,A,max}$, followed by Uvinul 3039, and eventually by Tinuvin 900, regardless of the ethanol content of the food simulant or the plasticizer content of the plastics. A similar trend can be discovered related to the D_P values. This consistency in the migrated concentrations and D_P can be related to the size of the molecules. Additives with smaller molecular sizes tend to diffuse out of the polymer matrix more since their way is less obstructed. The steric hindrance of polymer macromolecules is less notable. For the characterization of additive molecular sizes, the *van der Waals* volumes were predicted. To gain information about the relation of molecular size and migrated concentration, *Pearson's* linear correlation test was performed for each examined test condition. The test results – expressed with Pearson's correlation coefficient (PCC) – proved the linear correlation between these parameters. PCC results were above 0.9381 in all cases (the lowest value was calculated for the 10% (w/w) TBAC sample in ethanol 10% (v/v)). Since it still exceeds 0.9000, a strong linear correlation can be assumed.

As the ethanol content of food simulants increased, the migrated amount of plastic additives increased too, but to various extents. Changing from 10 to 20% (v/v) ethanol content caused the increase in migration, but only 1.7–18.4× change was observed. The same comparison, however, revealed 16.7–288× higher migrated concentrations when the ethanol 20% (v/v) was changed to ethanol 50% (v/v). This

increase results from the simultaneous effect of increased solubility and polymer swelling. Similarly, the plasticization also caused a notable increase in $c_{i,A,max}$: 2.2–6.7× elevation was found in both ethanol 20 and 50% (v/v) food simulants when the 0 and 10% (w/w) TBAC containing samples were compared.

The Commission Regulation (EU) No. 10/2011 sets the allowed specific migration limits (SML) of Uvinul 3039, BHT, and Tinuvin 900 at 0.05, 3, and 1.5 mg/kg, respectively [24]. Assuming that 1 kg food or food simulant can be packed into a 6 dm^2 surface area of packaging, the SMLs can be converted to 0.083, 0.5, and 0.25 mg/dm^2. Comparing the surface referred SMLs with the measured $c_{i,A,max}$ results (Table 4), it can be seen that in ethanol 10 and 20% (v/v) food simulants, the migration levels remain below the SMLs, even at long contact times. However, in ethanol 50% (v/v) food simulant, the migrated concentration of additives exceeded the regulatory limits (Figure 4, the surface referred SMLs were marked with a blue line). Uvinul 3039 is the most critical additive: the SML was exceeded in less than 24 h, even in the case of unplasticized PLA. As the TBAC content increased to 5 and 10% (w/w), the SML was reached in less than an hour. The results of BHT and Tinuvin 900 perfectly represent the potential risk of plasticization. The migration of Tinuvin 900 from the plasticizer-free sample stayed below the SML in the 13 day long experiment. But, as TBAC was compounded along with the stabilizers, in 72 and 48 h contact times, the migrated level of Tinuvin 900 crossed the SML in the case of 5 and 10% (w/w) TBAC content, respectively. In the case of BHT, the migrated concentration exceeded the SML after 120 h of contact when the plastic contained no plasticizer. The presence of plasticizer decreased this 'safe time' to 24 and 6 h, when the concentration of TBAC was 5 and 10% (w/w), respectively.

Considering the currently available PLA-based FCPs (*e.g.*, cups, straws, cutlery, or meal containers), the 1–6 h long contact times are absolutely lifelike conditions of storage. The validity of longer contact times at 40 °C is also explicable, because these substitute storage at refrigerated conditions (5 °C). For example, 72 h long contact time at 40 °C mimics 145 days at 5 °C [24], which is conceivable for the storage of dairy, and (more than 20% (v/v)) alcohol-containing products. Similarly, the 48 h long contact of food simulant with the test specimen at 40 °C substitutes the storage for 97 days.

4. Conclusions

In the present work, the swelling and migration kinetics of three stabilizer-type additives were investigated from polylactic acid-based plastics in 10, 20, and 50% (v/v) ethanolic food simulants. These measurements were performed to show the effect of plasticization in contact with the mentioned food simulants since plasticization can essentially determine the swelling of the polymers and the migration of additives [32, 37]. To enable this, plastics with three different TBAC plasticizer content were injection molded [33].

Between the polymer swelling and the migration of additives strong correlation was found. In the case of ethanol 10% (v/v) food simulant, both swelling and migration remained low, while in ethanol 50% (v/v), the swelling and the migration increased, and differentiation – based on the plasticizer content – was observed. In ethanol 50% (v/v) food simulant, the migrated concentration of additives exceeded their specific migration limits (SMLs), laid down in Commission Regulation (EU) No. 10/2011 [24]. Based on our results, the application of Uvinul 3039 in PLA-based FCPs should be strictly restricted. In the case of BHT and Tinuvin 900, limited contact times are recommended if the PLA contains a plasticizer, too.

Technically, ethanol 20% (v/v) was the transition between the other two food simulants, considering the effects of examined parameters. Swelling of the plastics remained moderate, but the effect of plasticization on the migration was noticeable. In the case of BHT, the plasticizer-caused differentiation was unquestionable at all three TBAC concentrations. In comparison, the migration of Uvinul 3039 and Tinuvin 900 increased only when the highest, 10% (w/w) plasticizer concentration was applied. These results proved that the presence of a plasticizer can only promote the migration of additives if the applied food simulant is able to swell the polymer.

The cause of differences in migration to ethanol 20% (v/v) between BHT and Uvinul 3039 or Tinuvin 900 was the size of the molecules. Due to the moderate swelling, the diffusion of BHT (which bears the smallest *van der Waals* volume) in the polymer matrix was facilitated, but the larger molecule additives movement remained inhibited. The

measured maximum of migrated concentrations and the calculated diffusion and partition ($K_{P/F}$) coefficients of additives always followed the order of molecular sizes.

With the increase of ethanol content in the food simulants, the values of $K_{P/F}$ decreased. Obviously, the higher ethanol content increased the solubility of additives in the food simulant, which promoted the migration, too. At the same time, the plasticization also decreased the $K_{P/F}$, which implies that solubility was not the determining factor in the additive migration. Since the process of migration into ethanol 10% (v/v) has not followed the Fickian mechanism, this trend was not obvious in the case of this food simulant. The decisive parameters from the migration's point of view were the ones that helped or obstructed the substances' diffusion inside the polymer, *i.e.*, the swelling of the polymer, plasticization, and the size of migrants.

Our results have different messages for manufacturers of traditional and active packaging. It was proved that the migration of substances could be relevantly increased from PLA-based packaging with plasticization, even if the product was meant to be used as hydrophilic FCP. This can be either an opportunity to facilitate the active ingredient release from active packaging or a possible safety concern in the case of traditional FCPs.

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