



Effect of temperature and plasticizer content of polypropylene and polylactic acid on migration kinetics into isooctane and 95 v/v% ethanol as alternative fatty food simulants

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ABSTRACT

Plasticizers are commonly used plastic additives. Deep understanding of their effect on the migration of other substances is essential, especially for food contact materials. The migration kinetics of four stabilizer-type additives from polypropylene (PP) and polylactic acid (PLA) with different tributyl acetyl citrate plasticizer content were investigated. The results confirm that the presence of plasticizer in the plastics enhances swelling, and thus the migration of additives. The plasticizer content is in strong correlation with migration rate for all additives, except for PLA-Irgafos 168 samples. Migration kinetic experiments conducted at different contact temperatures showed that the role of temperature apparently exceeds that of plasticization. Nevertheless, hierarchical cluster analysis revealed similarity in the migration mechanisms of stabilizers from plastics with low plasticizer content at high temperature, to that at low temperature from plastics with high plasticizer content.

1. Introduction

Due to their versatility and relatively low price, plastics are unavoidable in our everyday life. To facilitate efficient and affordable manufacturing, polymers are often modified with additives, i.e., with plasticizers, nucleating agents, lubricants, etc. Also, this way the products' mechanical and thermal properties can be optimized for their potential application. Furthermore, with other types of additives, such as antioxidants, light stabilizers, anti-hydrolysis agents, etc., the final products' resilience can be increased.

Despite the advantageous effects of additives on plastic products,

these substances might pose a risk to users. Small molecules are capable to diffuse across polymer chains, and dissolve in the matrix which contacts the plastic. This migration process is critical when the material in contact with the plastic is food. Along with the possible decrease of food quality, the continuous intake of migrating additives can be harmful for human health. Standardized circumstances of migration testing are established in [Commission Regulation \(EU\) No 10/2011 \(2011\)](#) (of 14 January 2011 on "Plastic materials and articles intended to come into contact with food"). In general, conditions of migration tests must be chosen to model the worst-case scenario of migration. To achieve this, typically three parameters are adjusted: contact time,

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contact temperature and type of food simulant. With the variation of contact time and temperature, all kinds of storage scenarios can be modeled. Whereas food simulants are prescribed for the substitution of real food to simplify the testing. These food simulants mimic the physico-chemical properties of foodstuff with various characteristics – i. e., acidity, alcohol content and lipophilicity of the food. The latter must be modeled with any vegetable oil, containing less than 1% unsaponifiable matter, or (when it is technically not feasible) with alternative food simulants, 2,2,4-trimethylpentane (isooctane) and ethanol 95 v/v %.

Migration is a complex process, influenced by many parameters: the mobility of the migrant in the polymer matrix (characterized with the diffusion coefficient, D_p) and in the food simulant, the partition coefficient of the migrant ($K_{p/F}$) and the boundary resistance at the polymer and food simulant boundary. While food safety can be ensured by testing migration with specific contact times representing the worst-case scenarios, deeper understanding of the migration process can only be achieved through kinetic measurements. Evaluation of the kinetic measurements usually focus on the determination of D_p and $K_{p/F}$ based on Fick's second law (Bodai et al., 2015; Iñiguez-Franco et al., 2012; Sanches Silva et al., 2008; Tehrani & Desobry, 2004). This approach is so widely accepted, that it is often applied even when non-Fickian behavior is apparent on some of the migration curves (extent of migration vs. time) (Iñiguez-Franco et al., 2012; Jamshidian et al., 2013; Li, 2019; Samsudin et al., 2014) or when swelling is indicated as a reason for an elevated migration rate (Garde et al., 2001; Iñiguez-Franco et al., 2012; Li, 2019; Ramos et al., 2014).

Contact temperature is undoubtedly among the most important and widely observed influencing factors of migration tests. Even if the investigation of its influence is not directly targeted, measurements are often conducted at different temperatures, because diffusivity is enhanced and solubility is changed by the increasing contact temperature and thus, migration rate and the amount of migrated compounds are bound to change. This phenomenon is frequently observed through the increase of the diffusion coefficients and the decrease of the partition coefficient of the migrant between the polymer and food simulant (Heydari-Majd et al., 2019; Iñiguez-Franco et al., 2012; Jamshidian et al., 2013; Li, 2019; Manzanarez-López et al., 2011; Soto-Valdez et al., 2011) at higher temperatures.

Obviously, the characteristics of the polymer, the migrating additive and the food simulant also have significant influencing effects. First off, migration occurs predominantly in the amorphous phase of polymers. Microcavities are formed there, and migrants are dissolved in these small void volumes (Limm & Hollifield, 1996). Therefore, both polymer structure (morphology, crystallinity, etc.) and migrant characteristics (shape, size, etc.) fundamentally determine migration process. The complexity of this topic is unquestionable, as demonstrated by numerous studies for different polymers, extensive information on PP and PLA is also available. Samsudin et al. (2014) examined the migration of astaxanthin from polylactic acid (PLA) to ethanol 95 v/v%. After comparing the release rate of astaxanthin with that of other antioxidants (e.g., 2,6-di-*tert*-butyl-4-methylphenol (BHT), resveratrol, catechin), they found that BHT had the highest diffusivity. Their explanation for this phenomenon was the non-bulky structure of BHT, however, the structure of BHT or other additives were not characterized with any quantitative parameter. Contrarily, Jamshidian et al. (2012a) studied the correlation between the physicochemical properties (polarity, $\log P$, M_w and molecular volume) of four synthetic phenolic antioxidants and their release rates from PLA to food simulants with various ethanol content. They proved, that both size and polarity of the additive are decisive factors in the time dependence of migration. Wang et al. (2018) investigated migration of five stabilizers from polypropylene (PP) film into 50 v/v% ethanol and isooctane food simulants at different temperatures. The migration of additives was simulated – based on experimental results – using molecular dynamics simulation technique. This study also highlighted that migration of additives is strongly influenced

by their structure, especially by the van der Waals volume, gyration radii and ratio of inertia moments of molecules.

Besides the solely polymer or additive inherent factors the polymer–additive interactions are also decisive in migration (Limm & Hollifield, 1996; Wang et al., 2018). Unfortunately, hardly any study targets the effect of these interactions. Iñiguez-Franco et al. (2012) investigated the migration of catechin and epicatechin from PLA to 95 v/v% ethanol. By comparing the observed diffusion coefficients with that of resveratrol (measured by Soto-Valdez et al., 2011) and BHT (measured by Ortiz-Vazquez et al., 2011) they showed that the increasing number of hydroxyl groups inhibit the migration from PLA. This conclusion, however, contradicts the results of Jamshidian et al. (2012a), as in their experiments propyl gallate with three hydroxyl groups had the highest migration rate, and BHT with only one hydroxyl group had the lowest.

Among the polymer–additive interactions to be considered the effect of plasticization is essential. The presence of plasticizing agents in the polymer matrix enhances the segmental mobility of chains, therefore it changes the mechanical, thermal, and other properties of plastics. Plastics containing plasticizers have lower glass transition (T_g) and melting temperatures (T_m). The changing crystallinity and morphology have various consequences, e.g., better processibility, tensile and impact strength, rigidity. For example, neat, amorphous PLA is a rigid raw material with low impact strength, therefore the possibilities of its plasticization have been thoroughly researched (Tábi et al., 2021). Besides T_g and T_m reduction, the PLA's cold-crystallization temperature (T_{cc}) also decreases with plasticization (Martin & Avérous, 2001; Sawalha et al., 2010).

In some cases, comparable change of thermal properties was found, when not plasticizers, but antioxidants or other stabilizers were compounded with PLA. In the study of Hwang et al. (2012) resveratrol and α -tocopherol (AT) were added to PLA in different proportions (overall 5 w%), which caused approximately 5 °C decrease in both T_g and T_m . To a greater extent, but similar findings were reported by Sawalha et al. (2010) for PLA films casted from solutions containing various oils. Contrarily, only slight decrease or no change was observed after the addition of 1.49 nominal w% marigold flower extract (Samsudin et al., 2014), 1 w% or 2 w% of synthetic antioxidants (Gonçalves et al., 2013; Jamshidian et al., 2012b, respectively), as well as 2.58 w% AT (Manzanarez-López et al., 2011). Gonçalves et al. (2013) also observed that PLA films with 4 and 10 w% antioxidant content showed 2–9 °C decrease in T_m . These data show clearly that the impact of additives on thermal properties are highly dependent on their amount in the plastics.

Polymer–additive interactions can have major effects even with nearly unaffected thermal properties. For example, Zhang et al. (2010) reported that the blending a small amount (2 w%) of silicon oil with PP significantly changes the polymer's rheological properties. The viscosity of this PP/silicon oil blend was 10 times lower than that of the silicon oil-free PP. On the other hand, in the work of Fasihnia et al. (2020) the effect of BHA, BHT and TBHQ antioxidants in different concentrations (1, 2 and 3 w%) on the tensile strength of PP-based active composites were investigated. It was found that all concentrations of BHT, 2 and 3 w% butylated hydroxyanisole (BHA), and 3 w% *tert*-butylhydroquinone (TBHQ) significantly increased the tensile strength of the composite PP films compared to that of an additive-free or a reference PP film. The effect of additives on crystallinity degree (X_c) is rather varied. Some substances increase its value, while others decrease it. In PLA, eugenol (Sawalha et al., 2010) and AT (Gonçalves et al., 2013) promote the crystallization process, whereas BHT, TBHQ (Gonçalves et al., 2013; Jamshidian et al., 2012b), BHA (Jamshidian et al., 2012a) and limonene (Sawalha et al., 2010) inhibit it.

Besides polymer–additive interactions, the polymer–food simulant interaction is also worth considering. It is known that polymers are capable of uptaking small molecular solvents, especially when their polarity is similar, which leads to changes in the polymer structure. Among food simulants, isooctane can swell polyethylene (PE) (Helmroth et al., 2002) and PP (Kirchkeszner et al., 2022), while PLA is capable of

absorbing ethanol from ethanol 50 v/v% and 95 v/v% food simulants (Iñiguez-Franco et al., 2016; Kirckeszner et al., 2022). Iñiguez-Franco et al. (2016) proved that the swelling of PLA by ethanol causes T_g decrease, hence crystallization is promoted, even at a relatively low temperature (40 °C). Through the plasticization of polymers, swelling promotes the migration of additives (Feigenbaum et al., 2000; Iñiguez-Franco et al., 2017; Kirckeszner et al., 2022; Samsudin et al., 2014). Chang et al. (1988) and Reynier et al. (2002) both presented theoretical methods to consider the dependence of diffusion coefficients on the food simulant concentration in the plastic at each time and distance from the surface of the specimen. Furthermore, strong linear correlation between solvent absorption and additive migration into ethanol 95 v/v% and isooctane – from PLA and PP, respectively – have been demonstrated (Kirckeszner et al., 2022). Also, Helmroth et al. (2002) proved that the mechanism of migration was Fickian when PE was in contact with non-swelling solvents. However, plasticization occurred in contact with e.g., isooctane, which significantly increased the diffusion rate of Irganox 1076.

As it can be seen, many aspects and decisive parameters of small molecule migration from PLA- and PP-based food contact plastics (FCPs) have already been examined in details. But the polymer-additive interactions in the aspect of migration tests have hardly been investigated, even though additives often change the plastics' thermal and mechanical properties or crystallinity significantly. Therefore, the aim of this work was to study the effect of increasing amount of a plasticizer (tributyl acetyl citrate, TBAC) on the swelling and migration kinetics for four common stabilizers from PLA and PP to ethanol 95 v/v% and isooctane food simulants, respectively. Since ethanol swells PLA and isooctane swells PP, the typical approach assuming that Fick's second law applies, was dismissed. Instead, variography – which had previously been successfully applied in migration studies by Bodai et al. (2015) and Kirckeszner et al. (2022) – was used for the determination of the starting points of steady-states appearing on the kinetic curves. Migration tests were performed at three different contact temperatures. This way the effect of contact temperature and plasticization on migration rate and mechanism could be confronted.

2. Materials and methods

2.1. Materials

For the investigation of migration and swelling kinetics, injection molded plastic sheets were produced. Polypropylene (Tipplen H145F, MOL Group (Budapest, Hungary)) and polylactic acid (0.5% D-lactide content, Ingeo™ Biopolymer 2500HP, NatureWorks LLC (Minnetonka, Minnesota, USA)) were compounded with overall five different plastic additives – four stabilizers (antioxidants and UV absorbers) and a plasticizer. The investigated antioxidants were BHT (2,6-di-*tert*-butyl-4-methylphenol, CAS: 128-37-0) and Irgafos 168 (*tris*(2,4-di-*tert*-butylphenyl) phosphite, CAS: 31570-04-4). As UV absorbers Uvinul 3039 (2-ethylhexyl 2-cyano-3,3-diphenylacrylate, CAS: 6197-30-4) and Tinuvin 900 (2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl) phenol, CAS: 70321-86-7), while as plasticizer TBAC (tributyl acetyl citrate, CAS: 77-90-7) were applied. BHT, Irgafos 168 and TBAC were the products of Merck Life Science Co. (Budapest, Hungary), whilst Uvinul 3039 and Tinuvin 900 were donated by BASF Hungary Ltd. (Budapest, Hungary). Based on the polymers' technical data sheets and Commission Regulation (EU) No 10/2011 (2011), all the above-mentioned materials are allowed to be used intentionally in FCPs.

In the migration tests, the two alternatives of food simulant D2 (vegetable oil with less than 1 % unsaponifiable matter), isooctane (2,2,4-trimethylpentane, CAS: 54-84-1) and ethanol 95 v/v% (CAS: 64-17-5) – products of Thomasker Finechemicals Ltd. (Budapest, Hungary) – were used. Before analysis, migration media were spiked with internal standards (ISTDs): mirex (perchloropentacyclodecane, CAS: 2385-85-5) and *n*-hexadecane (CAS: 544-76-3). Both chemicals

were the products of Merck Life Science Co. (Budapest, Hungary).

2.2. Plastic production and characterization

Plastic test specimens for migration and swelling kinetic tests were produced and characterized with the same settings and process that have previously been described by Kirckeszner et al. (2022). Therefore, here only a brief description of them is given. PP and PLA neat polymers were compounded with the additives by means of a twin-screw extruder. The mass ratio of stabilizers added to the plastic sheets were constant (1–1 w% for each antioxidant and UV absorber), but the amount of plasticizer changed from sample to sample: 0, 2.5, 5 or 10 w% TBAC was compounded with the polymers, besides the 4 w% sum of added stabilizers. However, it must be noted that PP test specimens contained some surplus of Irgafos 168, as neat Tipplen H145F PP already contains approximately 0.5 w% of it. PLA samples were marked as L0, L2.5, L5 and L10, and the notation of PP plastics were P0, P2.5, P5 and P10 in accordance with the amount of added TBAC. The extruded filaments were shredded and injection molded into 80 mm × 80 mm × 2 mm (height × width × thickness) plastic sheets. Besides the spiked polymers, reference sheets (with no additives) were prepared from both PLA and PP (LR and PR, respectively) with the same process.

Plastics were characterized based on their mechanical and thermal properties. For mechanical specification, melt flow rate (MFR) was determined according to ISO 1133-2:2011 standard (ISO 1133-2:2011, 2011) with 2.16 kg nominal load at 190 °C. Thermal properties of plastic specimens were determined with differential scanning calorimetric (DSC) analysis. From the thermograms data on the plastics' glass transition temperature (T_g), cold crystallization temperature (T_{cc} – for PLA only), melting temperature (T_m), enthalpy of cold-crystallization (ΔH_{cc} – for PLA only) and enthalpy of fusion (ΔH_m) were obtained. From the results, crystallinity degree (X%) could be calculated based on the following formula:

$$X\% = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f} \cdot (1 - \alpha) \cdot 100, \quad (1)$$

where ΔH_f is the melting enthalpy of 100 % crystalline polymer (theoretical data, 93.0 J/g for PLA (Battagazzore et al., 2011) and 207.1 J/g for PP (Wunderlich & Wunderlich, 2005)), and α is the summarized mass ratio of additives in the plastic. Both MFR and DSC measurements were performed in triplicates.

2.3. Migration tests

Test specimens with dimensions of 30 × 10 × 2 mm (height × width × thickness) were cut with a table saw from the injection molded plastic sheets. Then the accurate weight and geometrical properties of each specimen were measured using a VWR LA 124i analytical balance and Vernier calipers. In the migration tests, a nominal 0.6 cm²/g plastic surface to food simulant mass ratio was applied. The test specimens were immersed into pre-heated food simulants that are alternatives for food simulant D2 – i.e., 95 v/v% ethanol in the case of PLA, whereas isooctane in the case of PP. The choice between the two food simulants was based on their ability to swell the polymers (Kirckeszner et al., 2022). Volumes of food simulants were set to fulfill the 0.6 cm²/g ratio (surface of FCP to amount of food simulant) recommended by Commission Regulation (EU) No 10/2011 (2011), therefore 16 mL of ethanol 95 v/v% and 18 mL of isooctane ($\rho_{\text{ethanol, 95 v/v\%}} = 0.79 \text{ g/cm}^3$ and $\rho_{\text{isooctane}} = 0.69 \text{ g/cm}^3$ at 20 °C) were applied. Sampling times were 5 and 30 min; 1, 2, 6, 12 h; 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 days; for every sampling time 5 individual replicates were prepared and measured. Migration tests were performed at three contact temperatures, 20 °C and 40 °C (both PLA and PP); and 60 °C (only PP). Since semi-crystalline PLA is recommended to contact only cold or room temperature food (below 40 °C), the 60 °C migration test was not

carried out with PLA-based plastics. The constant temperature for migration tests was provided by a POL-EKO ST2 laboratory incubator (Pol-Eko-Aparatura, Wodzisław Śląski, Poland). After the defined contact times, the plastic test specimens were removed from the food simulant, they were dried by wiping, and their swelled weights (m_{swelled}) were recorded.

2.4. GC-MS and GC-FID analysis

The migrated concentration of additives from PLA was typically smaller compared to that from PP, therefore lower LOQ was necessary for their quantitative analysis (Kirchkeszner et al., 2022). Thus, ethanol samples (originating from PLA) were measured with a gas chromatograph coupled with single quadrupole mass spectrometer (GC-MS), just like in a previous publication (Kirchkeszner et al., 2022). On the other hand, to ease the demand on the operating time of the GC-MS, isooctane samples (originating from PP) were quantified with a gas chromatograph coupled with flame ionization detector (GC-FID). Detailed information on the operational settings of both instruments, along with the method and ranges of calibration are specified in Chapter 1 of Supp. Inf.

2.5. Calculation of adjusted swelling degree, surface normalized concentration and migration rate

2.5.1. Adjusted swelling degree

Adjusted swelling degree (ASD%) was used to describe the swelling of plastics as defined by Kirchkeszner et al. (2022). With this approach the weight loss caused by the migrating chemical compounds is also considered. ASD% was calculated using the following formula:

$$ASD\% = \frac{(m_{\text{swelled}} + \sum_i c_{V,\text{mig},i} \cdot V_{\text{simulant}}) - m_{\text{dry}}}{m_{\text{dry}}} \cdot 100 \quad (2)$$

where m_{swelled} is the mass of the test specimen after removal from the food simulant, m_{dry} is the mass of the test specimen before immersing into the food simulant, $c_{V,\text{mig},i}$ is the mass concentration of i additive (mass of migrated i additive divided by the volume of food simulant) and V_{simulant} is the volume of the food simulant.

2.5.2. Surface normalized concentration

The result of GC-FID or GC-MS analysis was the mass concentration of i migrated additive in the food simulants ($c_{V,\text{mig},i}$). For the more representative determination of i additive's migrated concentration, its amount was related to the accurate surface of plastic specimens, this way surface normalized concentration ($c_{A,\text{mig},i}$) was calculated as shown in Eq. (3):

$$c_{A,\text{mig},i} = \frac{c_{V,\text{mig},i} \cdot V_{\text{simulant}}}{A_{\text{specimen}}} \quad (3)$$

in which V_{simulant} is the volume of food simulant (16 mL in case of ethanol 95 v/v%, and 18 mL in case of isooctane) and A_{specimen} refers to the accurate surface of plastic specimens.

On kinetic curves, the time dependence of $c_{A,\text{mig},i}$ is shown. For the characterization of long-lasting steady states on the curves, the arithmetic mean of data points on the plateau was calculated (\bar{c}_{max}). When the migration process did not reach a lasting steady state by the end of experiments, the maximum measured surface normalized concentration (c_{max}) was used for the description of the curve.

2.5.3. Migration rate

In order to gain information about the rate of migration, kinetic curves were transformed to a $c_{A,\text{mig},i} - \sqrt{t}$ function. When the investigated process can be described with Fick's second law, the initial part of the transformed curve is linear, which becomes concave towards the abscissa, and eventually reach the equilibrium value (Crank, 1975). If

the migration process is non-Fickian, distorted curve shapes (e.g., sigmoid or two-stage curve) can be achieved (Crank, 1975). The slope of the initial part of the curve characterizes the rate of migration. So, after the transformation of kinetic curves, the slope values were determined by linear fitting (forced through the origin) to the points belonging to the dynamic range of the migration process. Even in the case of non-Fickian migration curves, these slope values give good indication of the rate of migration (for further information see in Chapter 2 of Supp. Inf.). Correlation of the obtained slope values with the TBAC content of plastics was used to investigate the effect of plasticizer on migration rate.

2.6. Statistical analysis

The calculations were performed in the R program (R Core Team, 2021), *car*, *gstat*, *onewaytests*, *rstatix*, *sp*, and *stats* packages were used.

2.6.1. Calculation of empirical semivariograms

Semivariogram is a general tool of geostatistics to analyze the spatial or temporal autocorrelation of the data (Hatvani, Leuenberger, Kohán, & Kern, 2017). It was successfully applied in the field of hydrology (Hatvani et al., 2018; Trásy et al., 2018), hydrogeology (Garamhegyi, Hatvani, Szalai, & Kovács, 2020; Hatvani, Magyar, Zessner, Kovács, & Blaschke, 2014) and geochemistry (Hatvani et al., 2021). The detailed description of the method can be found in the work of Kovács, Korponai, Székely Kovács, & Hatvani (2012).

In this study variography was used similarly to the work of Bodai et al. (2015) and Kirchkeszner et al. (2022), to determine the necessary contact time to reach the steady-state by obtaining the range beyond which the observations are uncorrelated. More than one range can be determined if the increasing part followed by a variation around a constant is repeated, which results a nested type semivariogram. It means that, more than one process affects the variance of the data. The constant at which the empirical semivariogram points fluctuates after the initial rise is called sill (Hatvani, Erdélyi, Vreča, & Kern, 2020).

2.6.2. Analysis of variance (ANOVA)

The significant differences in the concentration levels of the additives and ASD% of investigated plastics on the plateaus were analyzed using ANOVA. Shapiro-Wilk test (Shapiro & Wilk, 1965) was applied to test the assumption of normality. Depending on the result of Bartlett's test (Bartlett, 1937) or Levene's test (Levene, 1960) were used to assess the homogeneity of variance. Since this assumption was not fulfilled, Welch's ANOVA (Welch, 1951) was used followed by Games Howell *post-hoc* test.

2.6.3. Cluster analysis

The migration and swelling kinetic curves were grouped based on the similarities (or differences) in their pattern using hierarchical cluster analysis (HCA), with Ward's method (Ward, 1963). Data on PLA and PP samples were handled separately from each other. Prior the analysis, the data points of the curves were standardized, in order to put both variables (migrated concentration and adjusted swelling degree) on the same scale (Magyar et al., 2013). This transformation ensures that, cluster formation is not influenced by the unit of measure. Therefore, the result of clustering shows (within a cluster) the similarities of migration and swelling kinetic mechanism.

3. Results and discussion

3.1. Thermal and mechanical properties of tested PLA and PP products

The main mechanical and thermal properties – melt flow rate (MFR), glass transition temperature (T_g), melting temperature (T_m), enthalpy of fusion (ΔH_m), cold-crystallization temperature (T_{cc}), cold-crystallization enthalpy (ΔH_{cc}) and crystallinity degree ($X\%$) – of tested plastics are summarized in Supp. Inf. Table 4. MFR, which is an essential rheologic

parameter for the characterization of thermoplastics, gives the rate of extruded plastic going through an orifice in 10 min, at defined temperature and load. *MFR* is in close relationship with the polymer's molecular weight, when it contains no added substance that would change the viscosity of the molten polymer. In case of both PLA and PP, the increasing plasticizer content results higher *MFR* values, because of the chain mobilizing effect of TBAC. The addition of only 2.5 w% TBAC causes only moderate change. However, considerable increase in *MFR* can be seen at 5 w% TBAC content (*L5* and *P5*) samples: 66% and 17% growth compared to the values of 2.5 w% TBAC content in PLA and PP, respectively. The change from 5 w% to 10 w% resulted 41% (PLA) and 28% (PP) further growth.

DSC thermograms of PLA (Fig. 1) clearly show a decrease in the glass transition, cold-crystallization and melting temperatures as the plasticizer content increases. The same pattern is not visible in case of PP. On the contrary, crystallinity degree increases along with increasing plasticizer content, however, the extent of this increase is different for the two polymers. Again, PLA changes more: comparison of *L0* and *L10* samples shows 45% increase in X_c ; while the difference between *P0* and *P10* samples is only 15%.

Since the *L0* and *P0* samples contained BHT, Irgafos 168, Uvinul 3039 and Tinuvin 900 but no TBAC, comparison of their values to that of the reference samples (*LR* and *PR*) give a good opportunity to observe the overall effect of ca. 4 w% stabilizer type additives without the presence of the dedicated plasticizer. The increase of the *MFR* clearly shows a modest plasticization effect. We observed almost 5 °C decrease in the T_{cc} and no significant change in the T_g and T_m values, which is in good agreement with the results of Jamshidian et al. (2012b), as they reported slight decrease or no change in T_g and T_m and 7–12 °C decrease in T_{cc} upon the addition of 1 w% of various synthetic antioxidants to PLA. Also, upon addition of 2–10 w% antioxidants, Gonçalves et al. (2013) measured 2–9 °C decrease in T_m for all tested additives. However, T_g slightly, but significantly increased for small amount of BHT and TBHQ, while it decreased for AT and bigger amounts of the previously mentioned additives.

3.2. The effect of plasticizer content on the migration of stabilizer-type polymer additives

3.2.1. Migrated concentration and steady-states

To reveal the effect of plasticizer content on different plastic additives' migration kinetics, 13 days long kinetic curves were recorded. Kinetic curves of the additives are in Supp. Inf. Fig. 4–7 for PLA and Supp. Inf. Fig. 8–11 for PP. As characteristic representatives, the results of Uvinul 3039 (from PLA to ethanol 95 v/v%) and BHT (from PP to isoctane) are presented in Fig. 2 and Fig. 3, respectively. In general, it

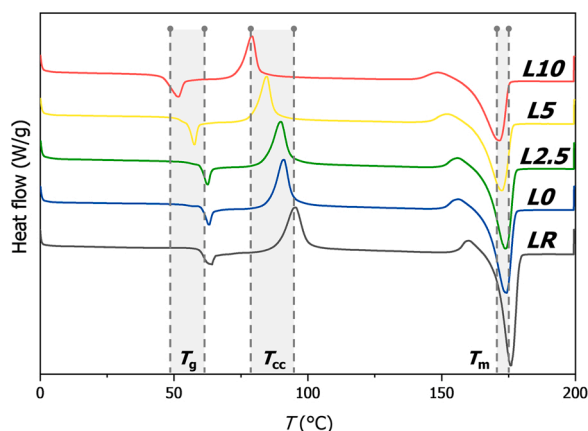


Fig. 1. DSC thermograms of PLA samples with different TBAC contents (T_g : glass transition temperature, T_{cc} : cold-crystallization temperature, T_m : melting temperature).

can be concluded that the increasing TBAC level promotes the migration of the stabilizer additives more and more. The explanation of this phenomenon is that plasticizers have a polymer chain mobilizing effect, which highly depends on the amount of plasticizer in the plastic. Because of the increased chain mobility, the diffusion of small molecules – i.e., plastic additives – is better facilitated.

The increase of the c_{max} values of Uvinul 3039 along with the TBAC content of PLA is a clear indication. When the plastic contained no plasticizer, the concentration of Uvinul 3039 was 17.54 ± 1.39 mg/dm², but at 10 w% TBAC content, this value increased to 61.66 ± 9.86 mg/dm². At low plasticizer content the difference is rather small: the kinetic curves of *L0* and *L2.5* samples run together, and eventually reach similar, though significantly different ($\alpha = 0.05$) c_{max} values (17.54 ± 1.39 mg/dm² and 20.37 ± 2.68 mg/dm², respectively). At higher plasticizer contents (5 w% and 10 w%), the differences between the curves become more evident.

Plateau formation in the kinetic curves was previously reported by e.g., Iñiguez-Franco et al. (2012), Kirckeszner et al. (2022) and Manzanarez-López et al. (2011). Both Iñiguez-Franco et al. (2012) and Manzanarez-López et al. (2011) connected this phenomenon to penetration of ethanol into PLA. Kirckeszner et al. (2022) demonstrated how variography can be used to determine the starting points of short halts in the increase of the migrated concentration, as well as the beginning of long steady states. They interpreted the observed multiple halt formation with the layered solvent uptake mechanism of PLA and PP. In Fig. 2.B–E the empirical semivariograms of PLA–Uvinul 3039 samples can be seen at different TBAC concentrations. The variograms of the PLA containing no plasticizer shows only two halts, whereas three of them were detected in the presence of TBAC. The accelerating effect of the plasticizer enabled the detection of the third one within the 13 days long experiment. However, in the case of BHT and Irgafos 168 only two halts were detected at 10 w% TBAC (Table 1). This may indicate that due to the acceleration, halts were merged or the early ones were shortened so much that they became undetectable with the applied sampling frequency.

In Fig. 3 the kinetic curves and empirical semivariograms of PP–BHT samples can be seen. Similarly to PLA, addition of 2.5 w% plasticizer does not affect considerably the \bar{c}_{max} value. Based on the empirical semivariograms in Fig. 3.B and 3.C, also the starting points of the long-lasting steady states remain 94 h with this small amount of TBAC in the polymer. But, with 5 w% and 10 w% TBAC content the slope of the kinetic curve in the dynamic range increases, therefore it takes less time to reach the steady-state. In case of 5 w% plasticizer, the time for plateau formation dropped to approximately its third (39 h) and with 10 w% plasticizer content it took only 21 h.

Further numerical results of migration tests with PP at 40 °C can be seen in Table 1. The maximum migration concentrations were found to be independent of the plasticizer content for all the stabilizers. Nevertheless, in the starting points of the long-lasting steady-states, a shift following the molecular weights of additives can be noticed at lower TBAC content. For example, the necessary time for plateau formation for Tinuvin 900 ($M_w = 447.6$ g/mol) is 109 h with no plasticizer, whereas it is 231 h for Irgafos 168 ($M_w = 646.9$ g/mol). The difference caused by the molecular weight, however, vanishes at high TBAC content: the long-lasting steady-state started at 38 and 37 h for Tinuvin 900 and Irgafos 168, respectively at 10 w% TBAC. An additional phenomenon to be noted is that every empirical-semivariogram shows a short halt in the increase of migrated concentrations at 11 h, regardless of the presence of the plasticizer. Supposedly, this halt is the result of additive migration from the surface of PP.

3.2.2. Migration rate

The final steady-state of kinetic curves and c_{max} values are representative of the possible outcomes of (mostly long-lasting) migration tests. By comparison, the interpretation of dynamic range happens rarely, however it carries information about the rate of migration. Our

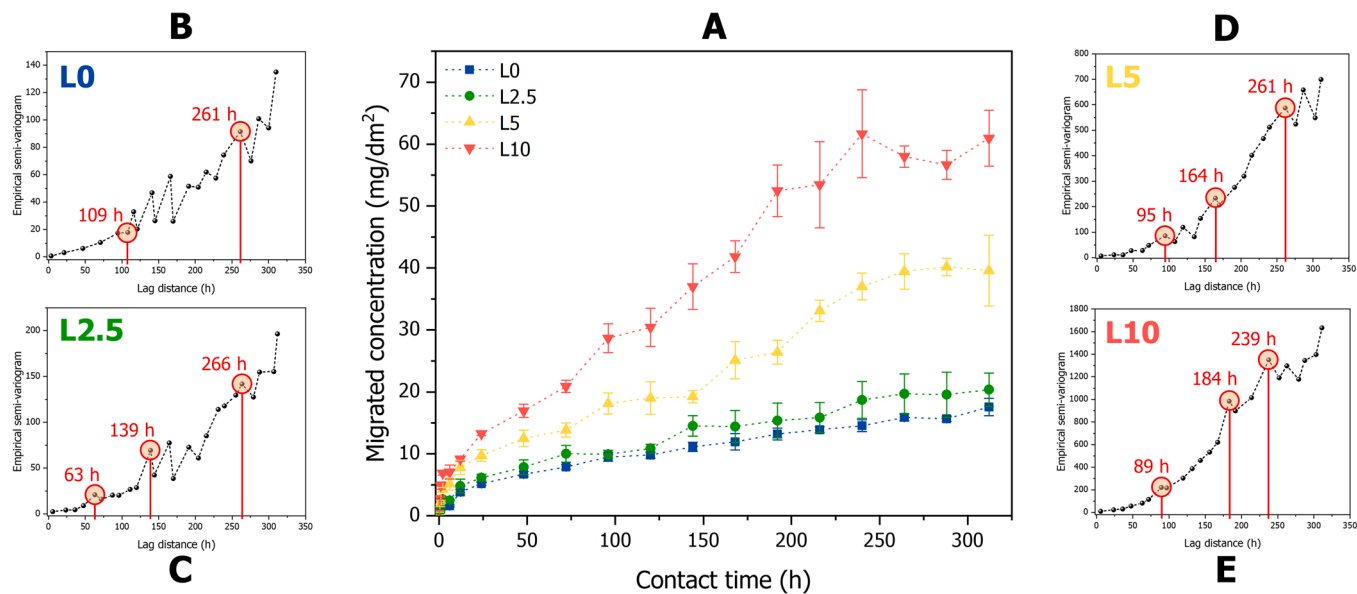


Fig. 2. Migration kinetic curves (A) and empirical semivariograms of PLA–Uvinul 3039 samples to ethanol 95 v/v% food simulant with 0 (B), 2.5 (C), 5 (D) and 10 w % (E) TBAC content at 40 °C.

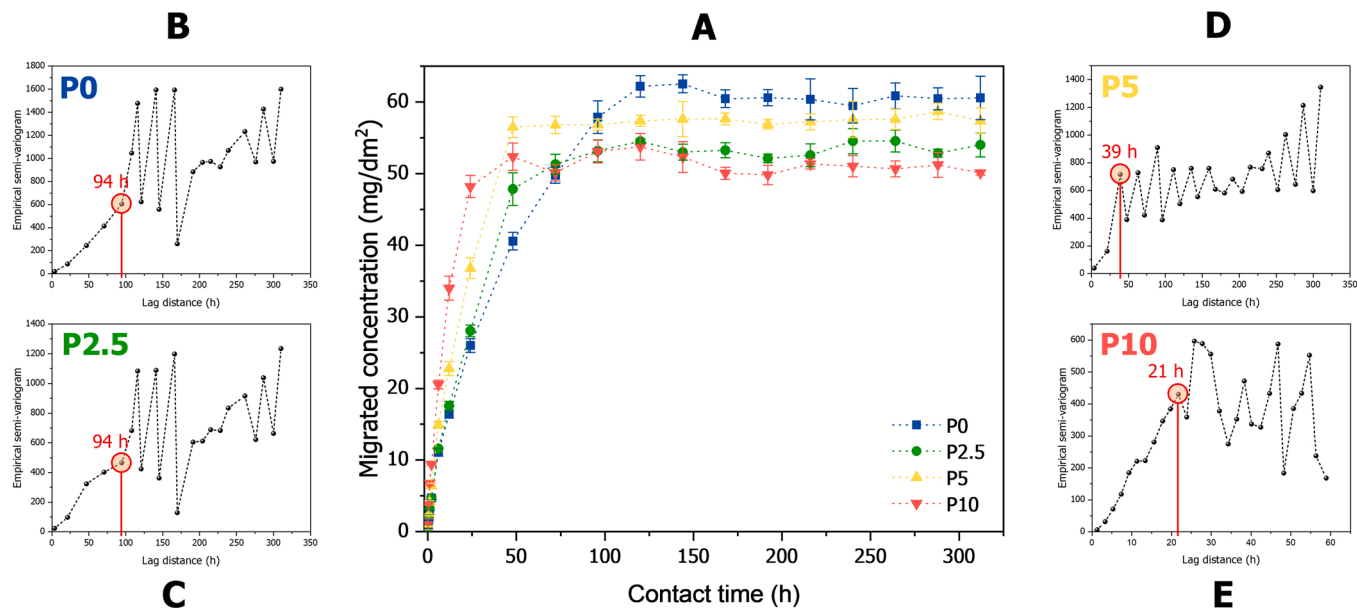


Fig. 3. Migration kinetic curves (A) and empirical semivariograms of PP–BHT samples to isooctane with 0 (B), 2.5 (C), 5 (D) and 10 w% (E) TBAC content at 40 °C.

results show that plasticizer concentration considerably affects the dynamic range of the kinetic curves: increasing TBAC content results in steeper elevation of the migrated concentration in case of both investigated polymers. After the transformation of kinetic curves, migration rate was determined (see Section 2.5.3) and confronted with the TBAC concentration, to see if linear correlation can be found between the two parameters. In case of PLA samples (Fig. 4.A), strong linear correlation was found for BHT, Uvinul 3039 and Tinuvin 900 ($PCC > 0.9500$). For Irgafos 168 this correlation weakens ($PCC = 0.6728$), the increase of TBAC concentration from 5 to 10 w% hardly affects its migration rate. Contrarily, migration rate from PP samples always increased with the increasing plasticizer concentration (Fig. 4.C). PCC values varied between 0.9579 (Uvinul 3039) and 0.9772 (BHT), which suggests strong linear correlation between the two parameters. Fickian diffusion model was applied for PP results for the confirmation of migration rate values. To honor the traditions of the field diffusion coefficients were also

calculated (Supp. Inf. Table 3), even though the process is obviously non-fickian. These results showed similar trends in the migration rate as a function of changing TBAC concentration.

In the case of PLA samples, it is also worth considering the stabilizers' maximum migrated concentration – TBAC concentration relation. (For PP samples c_{max} values were independent of the plasticizer content. See Section 3.2.1) Fig. 4.B presents strong linear correlation between c_{max} and plasticizer content for Uvinul 3039 and Tinuvin 900. Just like with migration rate, c_{max} of Irgafos 168 hardly depends on the presence of TBAC. Lastly, BHT shows a completely different pattern. 2.5 w% TBAC content has no impact on the maximum migrated concentration, compared to the plasticizer-free sample. 5 w% TBAC however significantly increases the value of c_{max} , which remains constant, when TBAC proportion is doubled again. Possibly this is the highest achievable c_{max} level under the applied circumstances.

It is worth comparing the results of L0 and P0 samples with the

Table 1

Maximum of migrated concentrations and ranges, calculated from migration kinetic curves of PLA and PP samples with different TBAC concentrations at 40 °C contact temperature. Letters next to the concentration values indicate significant differences ($\alpha = 0.05$). Data represent averages and standard deviations of five replicates.

Plasticizer content	0 w% TBAC		2.5 w% TBAC		5 w% TBAC		10 w% TBAC	
PLA								
Target compounds	c_{\max} (mg/dm ²)	Range (h)	c_{\max} (mg/dm ²)	Range (h)	c_{\max} (mg/dm ²)	Range (h)	c_{\max} (mg/dm ²)	Range (h)
BHT^a	23.84 ± 1.82 ^{b,c,d}	141; 263	22.01 ± 3.39 ^{c,d}	63; 138; 258	50.98 ± 6.96 ^{b,c,d}	119; 191; 284	48.91 ± 3.45 ^{b,c,d}	116; 261
Uvinul 3039^b	17.54 ± 1.39 ^{a,c,d}	109; 261	20.37 ± 2.68 ^{c,d}	63; 139; 266	40.18 ± 1.41 ^{a,c,d}	95; 164; 261	61.66 ± 9.86 ^{a,c,d}	89; 184; 239
Tinuvin 900^c	11.08 ± 0.72 ^{a,b,d}	109; 261	13.38 ± 0.93 ^{a,b,d}	62; 133; 262	17.36 ± 1.83 ^{a,b,d}	89; 191; 263	22.16 ± 3.29 ^{a,b,d}	88; 166; 238
Irgafos 168^d	5.41 ± 0.78 ^{a,b,c}	93; 144; 215	6.48 ± 0.66 ^{a,b,c}	63; 167; 255	7.12 ± 0.82 ^{a,b,c}	89; 230; 262	6.37 ± 0.58 ^{a,b,c}	112; 209
TBAC	–	–	67.19 ± 3.24	63; 136; 263	110.02 ± 26.75	63; 119; 238	378.40 ± 31.27	88; 159; 231
PP								
	\bar{c}_{\max} (mg/dm ²)	Range (h)	\bar{c}_{\max} (mg/dm ²)	Range (h)	\bar{c}_{\max} (mg/dm ²)	Range (h)	\bar{c}_{\max} (mg/dm ²)	Range (h)
BHT^a	60.53 ± 1.29 ^{b,c,d}	11; 94	53.45 ± 0.89 ^{c,d}	11; 94	57.33 ± 0.57 ^{b,d}	11; 39	51.08 ± 1.51 ^{b,c,d}	11; 21
Uvinul 3039^b	57.42 ± 1.32 ^{a,d}	11; 108	54.83 ± 2.44 ^d	11; 94	51.09 ± 0.78 ^{a,c,d}	11; 94	56.13 ± 2.01 ^{a,d}	11; 23; 38
Tinuvin 900^c	57.05 ± 2.83 ^{a,d}	11; 109	56.72 ± 1.61 ^{a,d}	11; 138	58.23 ± 0.81 ^{b,d}	11; 108	56.28 ± 1.17 ^{a,d}	11; 22; 38
Irgafos 168^d	44.43 ± 0.56 ^{a,b,c}	11; 109; 166; 231	41.28 ± 1.37 ^{a,b,c}	11; 86; 159; 230	43.39 ± 1.33 ^{a,b,c}	11; 108	43.25 ± 1.23 ^{a,b,c}	11; 22; 37
TBAC	–	–	128.06 ± 4.40	11; 94	229.21 ± 4.71	11; 63	475.49 ± 11.30	11; 43

previously published data on the migration of BHT. Kirckeszner et al. (2022) used the same circumstances for their migration tests, but each tested plastics contained only one stabilizer (or plasticizer). When PLA was spiked with BHT only, its maximum migrated concentration was 14.2 ± 1.06 mg/dm². Using the L0 sample – containing 3 other stabilizer additives, but no plasticizer – the same experiment resulted 23.8 ± 1.82 mg/dm² migrated concentration. The results from PP were 48.2 ± 1.82 mg/dm² (BHT only) and 60.5 ± 1.29 mg/dm² (BHT from P0). These results indicate that even when the plastic does not contain any dedicated plasticizer, the presence of other additives increases the achievable maximum of migrated concentration. This synergistic effect occurred with both PLA and PP and can be explained with the stabilizers' plasticizing effect.

3.3. Migration kinetic curves of stabilizer-type polymer additives at different temperatures

The effect of contact temperature on migration process was investigated at 20 °C and 40 °C for PLA, since typical applications of semi-crystalline PLA include cold and room temperature food, usually for limited time range. However, PP is often used for long-term storage, therefore 60 °C migration tests were also performed. Detailed results can be seen in Supp. Inf. Table 5, Supp. Inf. Fig. 12–14 for PLA and Supp. Inf. Fig. 15–17 for PP. The results of 40 °C migration tests were previously shown in Table 1. As an example, Uvinul 3039 for PLA (20 and 40 °C) and BHT for PP (20, 40 and 60 °C) are presented in Fig. 5. Differences in contact temperature have remarkable effect on the migration kinetic curves. As expected, higher contact temperature results increased migration. Applying 20 °C contact temperature results a monotonous increase in migrated concentration, however, this process is so slow, that neither PLA nor PP samples reach steady-state in 13 days. The 20 °C increase of contact temperature has considerably higher impact on the migration rate of samples that contain no plasticizer. Applying 40 °C contact temperature instead of 20 °C, results 26–86 times higher migration rate in case of PLA (L0) and 3–6 times higher one in case of PP (P0) (data not shown). This change reduced when 10 w% TBAC was compounded with the polymers along with the stabilizers. For L10 and P10 samples, the migration rate at 40 °C was only 4–30 and 2–2.5 times higher than at 20 °C, respectively. Furthermore, increase in migration rate intensifies with growing M_w of the stabilizers, therefore the migration of BHT is the least, while that of Irgafos 168 is the most affected.

Different migration rates result in shifts of the starting points of long-

lasting steady-states, if one can be reached at all within 13 days. This typically happens with PP samples at 40 °C and 60 °C contact temperatures. For Uvinul 3039 at 40 °C the steady state starts at 108 h, that decreases to 26 h at 60 °C. This effect is quite similar to the outcome of increasing a plasticizer content from 0 w% to 10 w% at 40 °C. The trend is the same for the other stabilizers too.

Temperature also affects the kinetic curves of adjusted swelling degree (ASD%) (Supp. Inf. Fig. 3). Values of ASD%_{max} are significantly lower at 20 °C, than at 40 °C (e. g. L0: 1.40 ± 0.04 % and 3.95 ± 0.10 %; P0: 4.29 ± 0.01 % and 9.38 ± 0.27 % at 20 °C and 40 °C, respectively). Since both temperature increase and addition of TBAC induce swelling, the ASD% curves for the L10 sample at 20 °C is very similar to that of the L2.5 sample at 40 °C. However, this similarity is not reflected in the c_{\max} values: e.g. for Uvinul 3039 7.35 ± 0.31 mg/dm² was measured in the presence of 10 w% plasticizer at 20 °C and 17.54 ± 1.39 mg/dm² at 40 °C, when the PLA contained no plasticizer. Similar ASD%_{max} values were found for PP without TBAC at 40 °C and with 10 w% at 20 °C (9.38 ± 0.27 % and 9.47 ± 0.23 %). Nonetheless, comparison of the c_{\max} values is not informative, since these test systems both reached steady-state by the end of experience.

As a summary, migration of additives from plasticizer-free PP at higher contact temperature reached steady-state in a shorter time, than the one with 10 w% TBAC, at lower contact temperature. Likewise, c_{\max} of PLA samples with low or no plasticizer content at elevated temperature can get close to those of samples containing greater amount of plasticizer at lower temperature. ASD% curves are also definitely influenced by both temperature and plasticizer content of the polymer. But coincidence of ASD%_{max} values of polymers with a high amount of plasticizer at low temperature and that of polymers with low amount of plasticizer at high temperature does not necessarily mean that a coincidence in the c_{\max} values of the same samples also exist. The reason for that is that an elevation in temperature enhances the diffusivity and solubility of additives along with polymer chain mobility, while plasticizer content only affects the latter.

3.4. Hierarchical cluster analysis (HCA)

Three types of clusters were observed on the dendrograms: groups of a certain contact temperature, groups of certain plasticizer content and mixed groups, in which objects with different TBAC concentration and contact temperature can be found. For example, in the dendrogram of PLA (Supp. Inf. Fig. 18) the cluster of L2.5 migration kinetic curves can be distinguished, these curves share the same kinetic mechanism. In

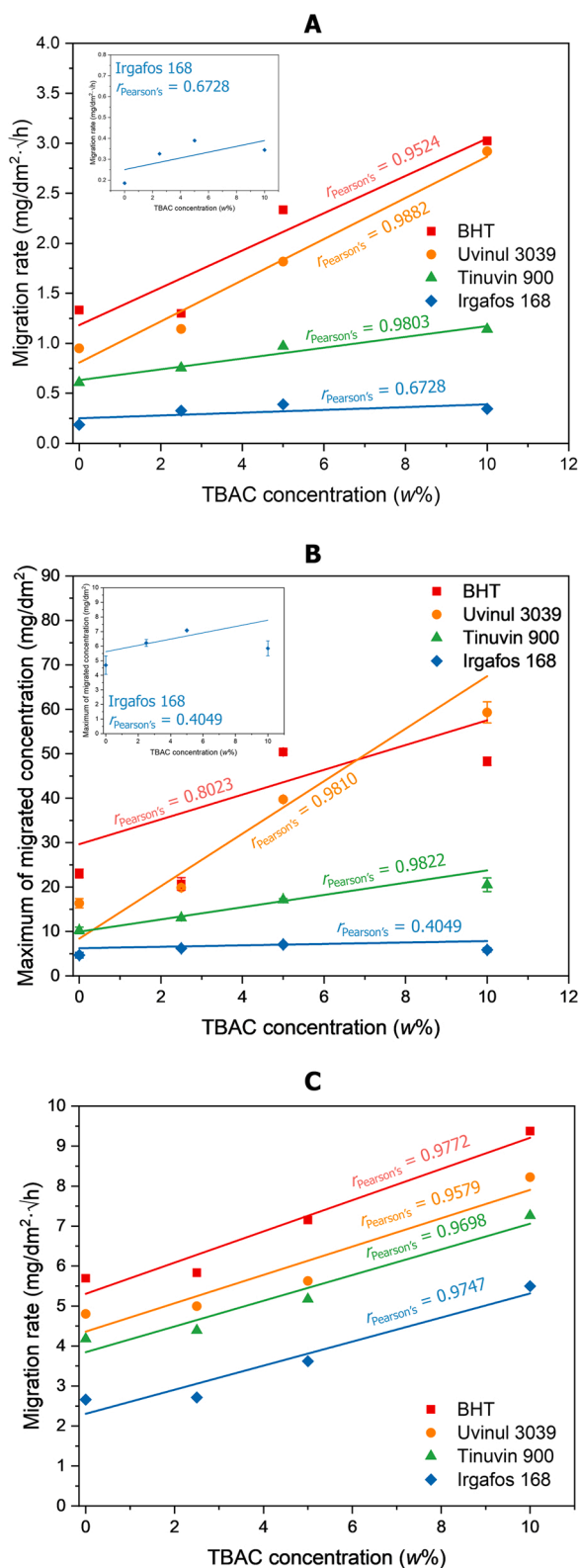


Fig. 4. Migration rate and maximum migrated concentration of stabilizers as the function of TBAC content from PLA (A, B) and PP (C) at 40 °C. Data points of each additive are connected to highlight which points belong together. Data of Irgafos 168 are repeated in the upper left corners of diagram A and B with adjusted vertical scales.

another cluster only 5 w% TBAC samples can be found, while the 10 w% and the rest of 5 w% plasticized samples share a common cluster too. In case of PP (Supp. Inf. Fig. 19) such obvious separation on the basis of plasticizer content cannot be found. However, there is a cluster in which P2.5 BHT, Uvinul 3039 and TBAC; P5 Uvinul 3039, TBAC and Tinuvin 900; and P10 Tinuvin 900 and Irgafos 168 samples are grouped. This means, that the migration kinetic mechanism of small M_w stabilizers from plastics with low plasticizer content is similar to that of the high M_w stabilizers, from plastics with high TBAC content.

Clusters belonging to certain contact temperatures were formed in case of both PLA and PP, i.e., 20 °C, non-plasticized kinetic curves were grouped together (except for PLA–Tinuvin 900). In the dendrogram of PP, at a given plasticizer content the curves of BHT and ASD% ended up in the same cluster. Likewise, PLA–BHT and PLA–Uvinul 3039 curves at a given temperature and plasticizer content were almost always grouped together (The exception is L10 sample at 40 °C). These results support the visible similarity of the above-mentioned kinetic curves.

The dendrograms of HCA analysis highlight a noteworthy phenomenon, that is observable in case of both investigated polymers. At high contact temperature (40 °C for PLA and 60 °C for PP), the migration kinetic mechanism of stabilizers from plastics with no plasticizer content is very similar to that of plastics with 10 w% TBAC at low contact temperature (20 °C for PLA and 40 °C for PP). For example, BHT shows this behavior in case of both polymers. This conclusion seemingly contradicts with the final assumption of Section 3.3. Those results, however, included quantitative information, and the extent of contact temperature's effect indeed exceeded that of the plasticizer's. In HCA analysis – due to the standardization of data – only the migration mechanisms were confronted, and apparently these are similar to each other.

4. Conclusion

The effect of contact temperature and plasticizer content of PLA and PP on the migration of commonly used stabilizers (BHT and Irgafos 168 – antioxidants and Uvinul 3039 and Tinuvin 900 – UV absorbers) were investigated in 13-days long experiments. Increasing the amount of TBAC – a phthalate alternative plasticizer – added to the polymers resulted in higher MFR, lower T_g , T_{cc} and T_m of the plastics and enhanced migration of stabilizers. The reason of this phenomenon is the polymer chain mobilizing effect of plasticizers. The addition of stabilizers (but no plasticizer) also induced increase in the MFR values, as a result of their (non-intended) plasticizing effect.

In the migration kinetic curves of PLA few days long steady-states appeared. As the result of changing TBAC content the starting points of these halts in the increase of the migrated concentrations shifted. Furthermore, for both polymers, the slope of the dynamic range in the kinetic curves got steeper with rising plasticizer amount. Strong linear correlation ($PCC > 0.9524$) was found between TBAC content and migration rate (except for PLA–Irgafos 168 samples).

As expected, higher contact temperature facilitated both the migration of additives and the solvent uptake of polymers. The changes due to the higher temperatures were often comparable with that caused by higher plasticizer content. For example, the steady-states appeared slightly sooner when PP samples with no plasticizer were stored at high temperature, compared to PP samples with 10 w% TBAC at low contact temperature. With PLA long-lasting steady states were not reached, thus similar comparison could be based on the c_{max} values. The similarity in the extent of swelling for certain plasticizer content–temperature pairs, however, did not indicate closeness in the migrated concentrations. The explanation for this phenomenon is that temperature increase not only enhances the solvent uptake of polymers (characterized with ASD%), but also rise the migration affinity of additives. Compared to that, plasticizing promotes the release of additive molecules only through influencing the polymer chain flexibility.

Alikeness of the kinetic curves (both migration and swelling) was investigated with hierarchical cluster analysis. In the dendrograms

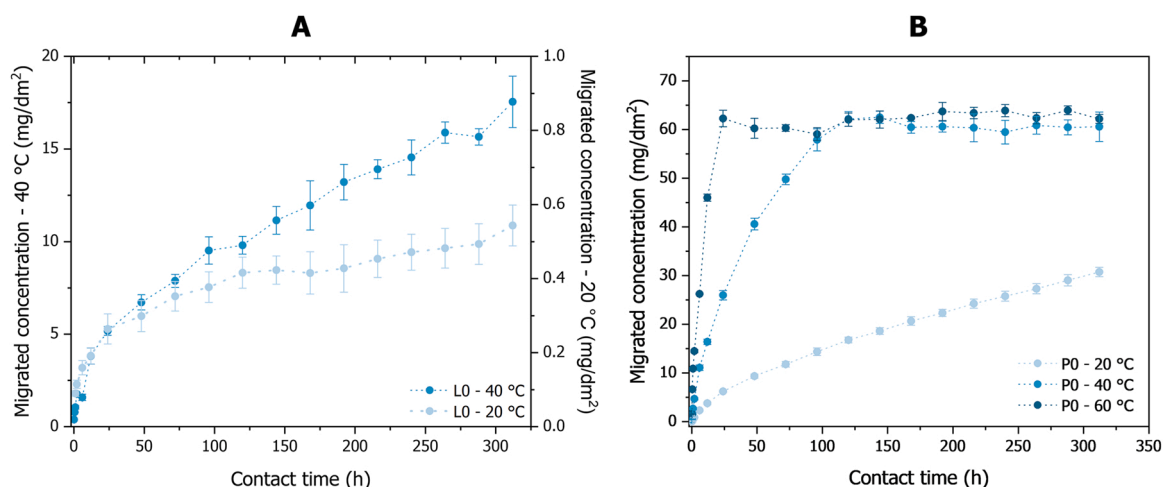


Fig. 5. Migration kinetic curves of Uvinul 3039 (A) and BHT (B) from PLA and PP, respectively, at different contact temperatures. Samples contained no plasticizer.

clusters based on contact temperature or plasticizer content, as well as mixed groups were found. The mixed clusters included the curves of certain additives in the presence of 10 w% plasticizer, measured at low contact temperature together with its non-plasticized migration curves measured at high temperatures. This means that, even though the promoting effect of higher temperature may often exceed that of the plasticizer, their effect on migration kinetic mechanism is similar.

Regarding food safety, the minimalization of additives' amount would be optimal. However, in plastic manufacturing the type and amount of additives are set to produce plastics with advantageous physical-chemical properties. Our results show that blending of multiple additives results enhanced migration, additives (both plasticizers and stabilizers) amplify each other's diffusion from the plastic to food simulants. The increase of migration due to the plasticization effect of additives (especially plasticizers) can easily be comparable – both in extent and mechanism – with the promoting effect of increased contact temperature. Taking these results into consideration, developers of new FCPs may dismiss certain directions of product development without performing costly migration tests to check for compliance with Commission Regulation (EU) No 10/2011 (2011).

CRedit authorship contribution statement

Noémi Petrovics: Conceptualization, design and conduct the experiments, data evaluation and Visualization, Formal analysis, Writing – original draft. **Csaba Kirckeszner:** Conceptualization, design and conduct the experiments, data evaluation and Visualization, Formal analysis, Writing – original draft. **Tamás Tábi:** production and analysis of plastics, data interpretation, Writing – review & editing, Funding acquisition. **Norbert Magyar:** Visualization, Formal analysis, Writing – review & editing. **Ilona Kovácsné Székely:** Visualization, Formal analysis, Writing – review & editing, Funding acquisition. **Bálint Sámuel Szabó:** Writing – review & editing, Conceptualization. **Zoltán Nyiri:** Writing – review & editing, Conceptualization. **Zsuzsanna Eke:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.fpsl.2022.100916](https://doi.org/10.1016/j.fpsl.2022.100916).

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