RESEARCH ARTICLE

Migration from acrylonitrile butadiene styrene (ABS) polymer: swelling effect of food simulants compared to real foods

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Received: 4 May 2020 / Revised: 14 September 2020 / Accepted: 12 November 2020 / Published online: 2 January 2021
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Abstract

Materials and articles made of acrylonitrile–butadiene–styrene (ABS) intended for contact with food must comply with the requirements of the European Plastic Regulation (EU) 10/2011, which lays down the food simulants and the time/temperature conditions to be applied for migration testing. Previous studies indicated that high concentrations of ethanol at temperatures above ambient may lead to swelling of ABS polymers resulting in increased migration. In this study migration kinetic data for a set of model substances at different temperatures were obtained using both food simulants stipulated in EU regulations and real food (milk, cream and olive oil). At the same time, the extent of polymer swelling was gravimetrically characterized after contact with simulants and different foods tested at several conditions to cover the majority of foreseeable applications of ABS. The obtained results confirmed that the use of high concentrations of ethanol–water, especially at high temperatures, causes the swelling of ABS polymers and results in significantly higher migration values compared to the tested foods as well as Tenax[®]. None of the real foods studied cause significant swelling of ABS. The widely used simulant 95% (v/v) aqueous ethanol proves not be suitable for compliance testing of ABS under the recommended conditions of Regulation (EU) 10/2011. Swelling of the polymer results in artificially higher diffusion coefficients or lower activation energies of diffusion. Migration prediction using polymer-specific diffusion parameters should therefore be considered to avoid over-conservative risk assessment for food contact materials and articles made of ABS.

Keywords ABS = acrylonitrile/butadiene/styrene · Food contact materials · Kitchenware articles · Food simulants · Migration testing · Migration kinetics · Polymer swelling

1 Introduction

Thermoplastic styrenic polymers have an important role in the macromolecular materials market; around 12% of global plastic production can be accredited to this category (Becari and Romano 2006). They can be produced with a wide range of properties by co-polymerisation and the incorporation of rubber impact improvers. Among these, acrylonitrile–butadiene–styrene (ABS) is a terpolymer made by polymerizing styrene and acrylonitrile in the presence of

polybutadiene. First commercialized in the 1950s, ABS is an opaque, ductile and stiff thermoplastic polymer mainly used for structural applications where heat and impact resistance, strength, and stiffness are required. Examples of ABS main applications are laboratory equipment, automotive parts, commercial cleaning equipment, toys and machine covers. ABS is also widely used for food contact applications, especially in the production of refrigerator component parts, kitchenware articles (e.g. mixing bowls, lunch boxes, measuring cups, citrus squeezers or butter dishes) and kitchen appliances (e.g. coffeemakers, mixers, blenders or food processors). ABS has also niche applications in food packaging, particularly where high tear strength is required such as in lids and tubs for margarine containers. Minor uses are for frozen desserts, prepared salads and some dairy products. The conditions of use of the ABS polymer for food contact range from low temperatures (refrigeration) for periods of days or weeks, for example packaged dairy and meat products, to elevated temperatures approaching the

Electronic supplementary material The online version contains supplementary material available at <https://doi.org/10.1007/s00003-020-01308-8>.

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boiling point of water for short periods of time, for example coffee machine.

Materials and articles made of ABS intended for contact with food must comply with the general safety requirements of the European Framework Regulation (EC) 1935/2004 (2004) and, more specifically, with the requirements of the European Plastic Regulation (EU) 10/2011, which lays down detailed rules for the conditions to be applied for migration testing. Although migration testing in the food prevails, migration is usually tested using ‘simulants’. These food simulants are representative for a food category: acetic acid 3% (w/v) is assigned for acidic foods, Tenax[®] for dry food, 10% and 20% (v/v) ethanol–water mixtures for aqueous and aqueous-alcoholic food, 50% (v/v) ethanol for dairy products and vegetable oil (e.g. olive oil) for fatty food. Substitute simulants such as 95% (v/v) ethanol and/or iso-octane can be used to replace olive oil as fatty food simulants to screen for specific migration and in case testing with olive oil is not technically feasible. According to the Regulation (EU) 10/2011, the migration testing is done under standardised time/temperature conditions, e.g. for real contact times exceeding 30 days at room temperature, the test should be performed in accelerated conditions at 60 °C for 10 days. However, when testing at accelerated test conditions the test specimen shall not undergo any physical or other changes compared to the real conditions of use [Annex V, Chapter 2, paragraph 2.1.4 of the Regulation (EU) 10/2011]. While the European food contact legislation focuses testing on the final product whenever possible, the US Food and Drug Administration (FDA) focusses testing more on the individual material. According to FDA, different approaches for different food contact material would be used. For example, FDA recommend in the Guidance for Industries (Chemistry Recommendations—Appendix I—December 2007) the use of 50% ethanol as fatty-food simulant for testing of polystyrene and rubber-modified polystyrene, since absolute or 95% ethanol has been found to be an effective fatty-food simulant for polyolefin but appears to exaggerate migration for other food-contact polymers.

Several studies are available in literature about the investigation of ABS’s suitability for food contact applications. Most of the scientific works deal with the determination of the residual levels or of the migration levels of the unreacted monomers acrylonitrile, 1,3-butadiene and styrene and other volatile substances (Yoshida et al. 1979; Tan and Okada 1981; Gilbert and Startin 1982; Startin and Gilbert 1984; Lickly et al. 1991; Ohno et al. 2002, 2008; Ohno and Kawamura 2010; Abe et al. 2013). Migration of mineral oil hydrocarbons from ABS into foods has also been studied (Castle et al. 1993). Recently, attention has been directed to the migration of styrene oligomers, which are molecules produced during polymerisation (Choi et al. 2005; Genualdi et al. 2014). Moreover, ABS has been investigated on its swelling behaviour when exposed to

organic solvents. Previous investigators (Mai 1976; Yoshida et al. 1982) indicated that high concentrations of ethanol at temperatures above ambient may plasticize the polymer and cause increased migration. By the plasticization theory, it is suggested that absorption of the liquid into the polymer will cause some plasticization which in turn lowers the glass transition temperature T_g of the polymer. Additionally, the diffusion coefficient of acrylonitrile from ABS polymer, calculated from the Fickian equation, has been reported in literature at different temperatures into the non-swelling food simulant water (Brown et al. 1978; Tatsuno et al. 1980; Lickly et al. 1991) as well as in ethanol–water mixtures (Yoshida et al. 1982). In the first case, a linear relationship was observed with the inverse of the absolute temperature of exposure. In the second case, the diffusion coefficients increased linearly with increasing the concentration of ethanol. The latter clearly indicates that strong interactions with the simulant lead to swelling of the polymer. Swelling of the polymer results in significantly higher diffusion coefficients, causing exaggerated migration, especially at high temperatures of exposure. If swelling does not occur with real foods (or in significant lower extent) migration testing with swelling simulants results in artificially high migration values and over-conservative risk assessment.

Therefore, the aim of the present study was to systematically investigate the migration behaviour from ABS through comparison of the extent of migration obtained with regulatory prescribed conditions, including food simulants and real food. At the same time, the extent of polymer swelling has been characterized gravimetrically (by weight increase) and visual changes of the specimens were recorded. Experimental migration kinetic data for a set of model spiked substances (toluene, chlorobenzene, methyl salicylate, phenyl cyclohexane, benzophenone and methyl stearate) as well as the residual monomer styrene were obtained under different time and temperature conditions using liquid food simulants, Tenax[®] and real food (UHT milk, UHT cream and olive oil). The extent of polymer swelling caused by food simulants was compared with the one obtainable with several real foodstuffs tested in order to cover the majority of foreseeable applications of ABS materials and articles. Results from these experiments inform on the suitability of recommended food simulants for compliance testing of ABS as well as for the determination of diffusion coefficients in non-swelling conditions.

2 Materials and methods

2.1 Sample materials

The ABS grade for the present study is a standard industrial material used in the European market for food contact applications. The composition and properties of the grade

are defined within the following specifications: monomer and polybutadiene rubber (PBR) fractions respectively at $62 \pm 2\%$ (styrene) and $19 \pm 2\%$ (PBR), melt flow index of $19 \text{ cm}^3/10 \text{ min}$ at $220^\circ\text{C}/10 \text{ kg}$ load, glass transition temperatures at 105°C for the SAN phase and -89°C for the PBR phase, density at 1040 kg/m^3 . All the properties are in the mid-range of the ABS performance spectrum and thus it can be regarded as representative for the industrial material used in the European market. The ABS pellets were processed using a Collin Lab & Pilot Solutions coextruder (Maitenbeth, Germany) to produce sheets with a thickness of approx. $350 \mu\text{m}$. The temperature in the extruder was approx. 210°C . Two types of sheets were obtained: reference ABS sheet without artificial contamination (by compounding neat ABS) and test sheet (by artificial contamination of the pellets with six model contaminants “surrogates” during sheet production). For the contamination, the solid model substances (approx. 100 g each) were dissolved in the liquid chemicals (approx. 100 ml each) without using an additional solvent to give a neat solution of the surrogates. This solution was pumped into the extruder directly to the extruder intake zone (approx. 6 g solution for 1 kg polymer). By use of this procedure the sheet was homogeneously contaminated. The surrogates and the spiking procedure used in the present work were chosen according to the generally accepted contamination protocols for challenge tests (determination of the cleaning efficiency of recycling process of polymers like polyethylene terephthalate). They were: toluene (CAS No. 108-88-3), chlorobenzene (CAS No. 108-90-7), methyl salicylate (CAS No. 119-36-8), phenyl cyclohexane (CAS No. 771-98-2), benzophenone (CAS No. 119-61-9) and methyl stearate (CAS No. 112-61-8). These compounds are widely used as model compounds also for migration kinetics and represent the four general categories: volatile and non-polar, volatile and polar, non-volatile and nonpolar, and non-volatile and polar. All chemicals used in the experiments were of analytical grade: toluene, styrene, methyl salicylate and benzophenone were purchased from Sigma-Aldrich (St. Louis, USA); chlorobenzene from Merck (Darmstadt, Germany); phenyl cyclohexane from Alfa Aesar (Ward Hill, USA) and methyl stearate from Fluka (Seelze, Germany).

2.2 Quantification of spiking levels of model substances and residual content of styrene

The concentrations of the test substances as well as of the monomer styrene were determined quantitatively in the ABS artificially spiked sheets by extraction with 95% ethanol (Chemsolute, Th.Geyer GmbH, Germany). 1.0 g of the ABS material was extracted with 10 ml 95% ethanol and stored at 60°C for 3 days. Three subsequent extractions were performed. The extracts were then analysed by gas chromatography with flame ionisation detection (GC-FID).

The Agilent 6890 GC/FID system (Agilent Technologies, Santa Clara, USA) was used with the following conditions: column: DB 1 (length 20 m , inner diameter 0.18 mm , film thickness $0.18 \mu\text{m}$); GC temperature program: 50°C (2 min), followed by heating at $10^\circ\text{C min}^{-1}$ to 340°C (15 min); pre-pressure: 50 kPa hydrogen; split: 10 ml min^{-1} . The injection volume was $5 \mu\text{l}$ with a split ratio of 1:20. An internal standard solution of di-(tertbutyl)-hydroxyanisol (BHA purchased from Fluka, Germany) and Tinuvin 234 (Ciba, Switzerland) was used for all GC analyses to check the stability of the retention times and the performance of the GC analysis. It was not used for quantification purposes. Quantification was achieved through calibration with respective standard substances. Table 1 lists the test substances and styrene with their molecular weight and experimentally determined concentrations in the ABS sheets.

2.3 Migration kinetics in food simulants

The migration kinetics of the artificially spiked test substances were determined into the following food simulants: Tenax[®] (modified polyphenylene oxide, MPPO purchased from Supelco, USA), 3% acetic acid, 10% ethanol, 50% ethanol, 95% ethanol and iso-octane, at temperatures of 20°C , 40°C and 60°C , monitoring several time points (from 0.5 h to 130 d , sampling times were adapted depending on the food simulant and contact condition). All solvents used in the experiments were of analytical grade and were purchased from Chemsolute, Th.Geyer GmbH, Germany. During and after migration contact, all samples were tested on appearance (decolouring, deformation). The migration solutions were also checked for turbidity or precipitation.

Migration contact with liquid food simulants was performed by placing test specimen with a surface area of 1 dm^2 (respectively 2 dm^2 of total surface contact area) in capped migration vials filled with 100 ml simulant. The vials

Table 1 Test (artificially spiked) substances and styrene with their molecular weight and experimentally determined concentrations in the ABS sheets

Substance	Molecular weight (g mol^{-1})	Average concentration ^a $\pm$ SD ($\mu\text{g g}^{-1}$)
Toluene	92	966 ± 10
Styrene	104	725 ± 9
Chlorobenzene	113	1076 ± 7
Methyl salicylate	152	1124 ± 20
Phenyl cyclohexane	160	1176 ± 18
Benzophenone	182	1098 ± 18
Methyl stearate	298	1132 ± 17

SD standard deviation

^aAverage data were obtained from duplicate analyses

were stored in thermostatic ovens at 20 °C, 40 °C and 60 °C. Each test was done in triplicate. In parallel to the samples, simulant blanks were prepared. At each kinetic time point a 0.5 ml aliquot was taken (through small and quick opening of the vial cap) for analysis. The volume taken for aliquots was not filled-up to 100 ml. Quantification of migration into simulants was obtained using gas chromatography coupled with flame ionisation detection (GC/FID) by external calibration with standard dilution series in the respective simulants. The same chromatographic conditions as for the quantification of the spiking levels were used. To check stability and possible loss by evaporation of the monomer styrene and the surrogates, control tests were performed as well. Spiked solutions for all the liquid simulants (50 µg ml⁻¹ of each substance) were stored in duplicates at 60 °C (worst case) and aliquots were taken (with the same sampling procedure as for the migration kinetic experiments) and analysed at several kinetic time points to check the recovery.

The migration tests onto Tenax[®] were carried out by placing the specimens (0.1 dm² of total surface) into headspace glass vials and completely covered with 1.5 g of Tenax[®]. The headspace glass vials were sealed and stored, as for the liquid samples, in preheated ovens at 20 °C, 40 °C and 60 °C. Each test was done in triplicates. Recovery experiments were performed as well by storing spiked amounts of Tenax[®] under the same time/temperature conditions. After cooling down to ambient temperature, the samples were removed, 0.5 g of Tenax[®] was transferred into another headspace glass vial and directly analysed by GC/FID with multiple headspace extraction (MHE). An external calibration was carried out. The Perkin Elmer AutoSystem (Perkin Elmer Industries, Shelton, USA) was used, with the following conditions: headspace auto-sampler: Perkin Elmer Turbomatrix 40, oven temperature: 200 °C, needle temperature: 205 °C, transfer line temperature: 210 °C, equilibration time: 1 h, pressurizing time: 3 min, injection time: 0.02 min, withdrawal time: 1 min; GC column: Rxi-624Sil MS (length 60 m, inner diameter 0.32 mm, film thickness 1.8 µm); GC temperature program: 40 °C (6 min), heating rate 5 °C min⁻¹ up to 90 °C and then 10 °C min⁻¹ up to 260 °C (10 min), pressure: 150 kPa helium, splitless.

2.4 Migration kinetics in real foods

UHT milk (approx. 3.5% fat content), UHT cream (approx. 30% fat content) and olive oil were chosen as real foods to be used for performing migration kinetics. They were bought from a local market in Munich, Germany. The foods were brought in contact with the spiked ABS sheet at the temperatures of 20 °C and 40 °C. Migration of the volatile model substances (toluene, chlorobenzene and styrene) was measured at the following time points: 15, 20, 30, 40, 60 and 90 days. The migration tests in real foods were performed

according to the European Standard EN 13130-1:2004 by total immersion of the specimens (ABS sheets) into each food. The used surface/volume ratio was 0.5 dm² (total surface of the specimen) per 50 g (food). Each test was carried out in triplicates. A spatula tip of sodium azide was added to avoid spoilage. After migration contact, quantification of volatile components was achieved placing the food samples into headspace vials by headspace gas chromatography with flame ionisation detection (Headspace-GC-FID). The Perkin Elmer AutoSystem XL (Perkin Elmer Industries, Shelton, USA) was used, with the following conditions: headspace auto-sampler: Perkin Elmer HS 40 XL, oven temperature: 80 °C, needle temperature: 110 °C, transfer line temperature: 120 °C, equilibration time: 1 h, pressurizing time: 3 min, injection time: 0.05 min, withdrawal time: 1 min; GC column: DB 624 (length 60 m, inner diameter 0.32 mm, film thickness 1.8 µm); GC temperature program: 40 °C (6 min), heating rate 5 °C min⁻¹ up to 90 °C and then 10 °C min⁻¹ up to 260 °C (10 min), pressure: 120 kPa helium, split: 40 ml min⁻¹. For quantification, external calibration on each food matrix was carried out individually. Standard solutions (4 levels, diluted from a stock solution prepared in ethanol) were added to each foodstuff in twice, after homogenization 5 g of each spiked food level was analysed to obtain a standard calibration curve. The matrix effect was estimated by comparing the slopes of standard curves obtained in milk, cream and olive oil with the slope of the standard curve obtained for the solvent ethanol (diluted to 10%) and was calculated as: $100 \times [1 - (\text{solvent slope})/(\text{matrix slope})]$. Control standards (known spiked amount of each food) were analysed in parallel to the samples to check for recovery.

2.5 Swelling kinetics in food simulants and real foods

The extent of the interactions between the food simulants or real foods and the ABS polymer was determined gravimetrically. In parallel to the migration kinetics, swelling kinetics were obtained by placing the ABS test specimens in capped migration vials in contact with the food simulants at the same temperature/time of exposure as for the migration experiments (20 °C, 40 °C and 60 °C, from 0.5 h to 130 days. The sampling time was adapted depending on the food simulant and contact condition). Test specimen with a surface area of 6 cm² (approx. 0.21 g) were put in capped migration vials and brought in contact with 20 ml of the food simulants 95% ethanol and iso-octane. Test specimen with a surface area of 18 cm² (approx. 0.63 g) were put in capped migration vials and brought in contact with 20 ml of the other food simulants 50% ethanol, 20% ethanol, 10% ethanol and 3% acetic acid. Swelling kinetics in UHT milk, UHT cream and olive oil were obtained at the same temperature/time of exposure as for the migration experiments (20 °C

and 40 °C, from 10 to 90 days) using the same surface/volume ratio of test specimen in contact with food. Additionally, other foods (lard, butter, fish oil, orange juice, coffee beans, coffee, noodles, oat flakes, wheat loops and water) as well as the alternative fatty food simulant Miglyol® 812 (CAS No. 73398-61-5: decanoyl- and octanoylglycerides) were tested in contact with ABS polymer to determine the extent of swelling. Several temperature/time conditions in order to cover most of the real food contact applications of ABS materials and articles were tested, such as refrigeration (5 °C) and ambient temperature (20 °C) storage for periods of 10–50 days as well as warm, hot and boiling water and brewed coffee from 10 to 30 min. The used test specimens had a surface area of 18 cm² (approx. 0.63 g) and were put in capped migration vials and completely immersed in 20 ml of each food. The vials were sealed and stored in preheated ovens. At each kinetic time point the test specimens (ABS test sheets) were taken out of the vial, surface dried (with a paper towel) and weighted. Then the specimens were put in the vial again for further storage. All investigations were performed in triplicates. The weight increase was expressed as percentage of the initial weight before contact with the simulants or foods.

2.6 WDL and LOQ in food simulants and selected foods

The Within Laboratory Detection Limit (WDL) of each substance in food simulants and selected foods (milk, cream and olive oil) was determined on a 95% confidence interval according to the calibration curve method. The sensitivity of the detection limits depends on the respective simulant and decreases from 95% ethanol to aqueous simulants. The limit of quantification (LOQ) is defined as three times the WDL. Table 2 shows the obtained WDL for each analysed substance in the respective food simulant and food (milk, cream and olive oil).

3 Results

3.1 Migration and swelling into food simulants

3.1.1 Migration and swelling kinetics in ethanol–water mixtures, iso-octane and 3% acetic acid

Migration kinetics were determined using artificial spiked sheets, since the concentrations of residual monomers and other additives in the ABS polymer were too low to determine migration kinetics. Only styrene was in a suitable concentration range to get migration values above the detection limits of the applied analytical methods. Therefore, the artificial migration of model substances, which were introduced during sheet extrusion was obtained. Due to the fact that parts of artificial contamination was removed during extrusion evaporation, the spiking levels were experimentally determined after sheet production. The spiked concentrations of the model substances as well as the residual content of styrene are given in Table 1. Low standard deviations for the average concentrations of the spiked model compounds in the sheets indicate that the concentrations of the model substances in the spiked sheets can be considered as homogeneous.

The results of the migration and swelling kinetics into 95% ethanol at 60 °C, 40 °C and 20 °C are shown in Figs. 1, 2 and 3, respectively. All experiments were carried out in triplicates and the results were averaged. Tabulated data (mean values and standard deviation of each measurement) are reported in the Annex 2 (Supplementary material). Line graphs represent the connection of the experimentally measured migration or weight increase values (dependant variable) over the same period of time (independent variable). They allow to compare the migration trend showed by the investigated substances at the different temperatures over time and to visually appreciating the slope of the resulting migration curve. No fitting of the data was done (note that the migration kinetics at 60 °C

Table 2 WDL in food simulants and foods

Substance	WDL (µg dm ⁻²)/(µg ml ⁻¹)							
	95% ethanol	50% ethanol	10% ethanol	3% acetic acid	Iso-octane	Olive oil	Cream	Milk
Toluene	30/0.6	170/3.4	710/14.2	n.d	75/1.5	50/0.5	7/0.1	22/0.2
Chlorobenzene	35/0.7	200/4.0	910/18.2	n.d	19/0.4	30/0.3	5/0.1	10/0.1
Styrene	100/2.0	184/3.7	595/11.9	n.d	95/1.9	20/0.2	13/0.1	9/0.1
Methyl salicylate	85/1.7	500/1.0	518/10.4	308/6.6	60/1.2	116/1.2	110/1.1	200/2.0
Phenyl cyclohexane	12/0.3	85/1.7	255/5.1	430/8.6	66/1.3	69/0.7	240/2.4	290/2.9
Benzophenone	85/1.7	90/1.8	143/2.9	n.d	76/1.5	n.d	n.d	n.d
Methyl stearate	105/2.1	145/2.9	932/18.6	n.d	65/1.3	n.d	n.d	n.d

n.d. not determined

is given in hours, whereas 40 °C and 20 °C are given in days). Experiments were carried out in glass vials allowing a two-sided exposure of the polymer sheets to the simulants. Surface related migration results were expressed in $\mu\text{g dm}^{-2}$ and were calculated considering the total surface of the specimens. At 60 °C, for all the substances, an initial rapid migration extent is observed. The obtained migration curves for styrene, toluene and chlorobenzene, the more volatile substances (which were also characterised by a slightly lower initial concentration in the spiked sheets compared to the other compounds) flatten off approaching plateau (equilibrium of partition between the polymer and the simulant) already after around 2 days. Also, for benzophenone and methyl stearate (the substances with the higher molecular weight of 182 and 298 Da, respectively) the observed initial migration is very fast and the curves

flatten off after around 144 h (6 days). Interestingly, the curve related to the weight increase (obtained by weighing the polymer specimens before and after contact with the simulant 95% ethanol) shows an initial rapid increase over time reaching up to 14% already after 2 days. Afterwards, the weight increase rises (but with a slower rate) till the last observed kinetic point (360 h i.e. 15 days), reaching 20%. Looking at the initial slope (only visually appreciated) of the migration curves (Fig. 1), it can be noted that all the spiked substances show the same diffusion coefficient regardless of the molecular size. This indicates that 95% ethanol at 60 °C swells ABS significantly and the substances are apparently eluted from the swollen material. This suggests that the diffusion process from the polymer is influenced by the swelling effect of 95% ethanol used as simulant. Looking at the migration curves obtained at

Fig. 1 Comparison of migration kinetic data of target substances from ABS with weight increase of ABS in 95% ethanol at 60 °C

Fig. 2 Comparison of migration kinetic data of target components from ABS with weight increase of ABS in 95% ethanol at 40 °C

Fig. 3 Comparison of migration kinetic data of target components from ABS with weight increase of ABS in 95% ethanol at 20 °C

40 °C (Fig. 2), also in this case, for all the substances considered a rapid linear increase of the migration extent until 2 days can be observed. For styrene, toluene and chlorobenzene the curves flatten off reaching equilibrium after around 6 days. In case of methyl salicylate, phenyl cyclohexane and benzophenone (intermediate molecular weight compounds) the flattening of the migration curves is approached after approx. 15 days; while migration of methyl stearate still increases till the last observed kinetic point at 40 °C (35 days). The weight increase of ABS test specimens using 95% ethanol at 40 °C rises rapidly within the first 2 days reaching 9%. Afterwards, it remains constant until 35 days. This indicates that 95% ethanol swells ABS significantly also at 40 °C. As expected, the migration rates of the surrogates were slower at 20 °C (Fig. 3). For the high molecular weight compounds methyl stearate methyl salicylate, phenyl cyclohexane and benzophenone the time dependant migration is lower compared to 40 and 60 °C. This can be explained by the physical chemical properties of these migrants (molecular size and vapour pressure), which strongly limit the diffusion at 20 °C. Regarding the swelling effect of 95% ethanol, also at 20 °C it was gravimetrically appreciable. It reaches 9% after around 30 days and remains constant until 50 days. The swelling effect of 95% ethanol as simulant in contact with ABS is significant at all the tested temperatures (20 °C, 40 °C and 60 °C). It depends on time and temperature. In fact, a maximum of 9% swelling was measured for the investigated sample material with a thickness of approx. 350 µm, at 20 °C (after 30 days of contact) and 40 °C (already after 2 days of contact); at 60 °C the weight increase measured after 2 days was 14% but was found still increasing up to 20% after 15 days. The results of the migration and swelling kinetics into 50% ethanol at 60 °C shows Fig. 4. Tabulated data are shown in Annex 2

(Supplementary material). For methyl salicylate, an analytical interferences occurred and therefore, an evaluation of the migration of this compound was not possible. The curves of styrene, toluene and chlorobenzene show an initial rapid migration extent than flatten off approaching plateau after 2 days. For phenyl cyclohexane and benzophenone, the migration increases until the last observed kinetic point after 840 h (35 days). For methyl stearate the migration process is slower as for the other substances and reaches plateau after approx. 16 days. The weight increase of the ABS test specimens increases over time reaching 10% after 38 days. Comparing the kinetic experiments carried out with 95% and 50% ethanol at 60 °C, it can be observed how approximately 6% swelling of the ABS material is reached after approx. 4 h with 95% ethanol and after about 6 days with 50% ethanol. The migration of the smaller substances toluene and chlorobenzene achieved approximately the same migration value of $900 \mu\text{g dm}^{-2}$ for the same percentage of swelling. At 40 °C the migration of surrogates into 50% ethanol is significantly lower compared to 60 °C, only migration of the low molecular weight substances (styrene, toluene and chlorobenzene) was detectable. Tabulated data are reported in the Annex 2 (Supplementary material). At 20 °C, all the migration values of surrogated into 50% ethanol are below the detection limits. Actually, the used analytical method (direct injection of the liquid simulant in GC) shows a poor performance for 50% ethanol, due to the high water content. Since a rather little aliquot for the kinetic experiments was used for the analysis, no concentration was possible; for the same reason no solvent extraction was feasible. Consequently, the rather high obtained WDL for this simulant (Table 2) did not allow the evaluations of the migration extent of the investigated substances in 50% ethanol at 40 °C and at 20 °C. As regard the swelling kinetics in 50%

Fig. 4 Comparison of migration kinetic data of target components from ABS with weight increase of ABS in 50% ethanol at 60 °C

ethanol (Fig. 5), at 40 °C, the maximal weight increase is 4.5% and is reached after approx. 15 days, afterwards remained constant until the last observed time point (50 days). At 20 °C the swelling in 50% ethanol (Fig. 5) increases linearly in the first 30 days than continues to rise with a slower rate reaching 4% after 50 days.

The control tests using spiked food simulants to check stability and possible loss by evaporation of styrene and the surrogates during the kinetics experiments showed good recovery for 95% ethanol (recovery for all substances > 93% after 56 days) 50% ethanol (recovery for all substances > 87% after 56 days) and iso-octane (recovery for all substances > 99% after 56 days). However, in case of 10% ethanol and 3% acetic acid a significant loss of the investigated substances was determined. The low recoveries for the simulants with high-water content could be explained by evaporation during the sampling or by their decomposition. Therefore, the evaluation of the migration extent of the

investigated substances with the used methodology (aliquot-experiments) in 10% ethanol and 3% acetic acid was not possible.

As regard the swelling kinetics, with the food simulant 20% ethanol, 3% weight increase is reached at 60 °C after 10 days, at 40 °C after 45 days and at 20 °C the weight difference increases slowly up to below 2% within 60 days. The weight increase of the ABS specimens after migration contact with 10% ethanol and with 3% acetic acid was determined below 2% within 60 days at all temperatures. Figure 5 reports the swelling kinetics for 50% ethanol as well as for the 20% and 10% ethanol–water mixtures and 3% acetic acid at 60 °C, 40 °C and 20 °C (Annex 2, Supplementary material).

Figure 6 shows the results of the migration and swelling kinetics in iso-octane at 60 °C (see Annex 2 in Supplementary material for tabulated data). At this temperature, for all the investigated substances, migration was not

Fig. 5 Comparison of swelling kinetics for 50% ethanol at 40 °C and 20 °C as well as for the 20% and 10% ethanol–water mixtures and 3% acetic acid at each tested temperature

detectable within 24 h, afterwards the migration extent increases rapidly over time. After around 20 days, the migration curves for methyl salicylate, styrene, toluene and chlorobenzene flatten off approaching plateau, while for phenyl cyclohexane, benzophenone and methyl stearate the curves slow down but still increase until the last observed kinetic point (50 days). The measured weight increase (swelling) of the ABS material after contact with iso-octane remains at 0.1% in the first 8 days, afterwards increases rapidly up to 5% within approx. 40 days, then flatten off and reaches 7% after 100 days. Interestingly, the migration of the substances is slow or not detectable until the measured swelling remains 0.1%. However, as the swelling of the polymer become measurable, migration increases rapidly for all the substances, regardless of their molecular weight. This finding indicates that the swelling caused by the simulant iso-octane on ABS at this temperature influences the diffusion properties of the polymer and the migration of substances is facilitated/accelerated. At 40 °C migration of chlorobenzene, toluene and styrene was not detectable within 1, 50 and 90 days, respectively. Afterwards, migration of these volatile substance increases slowly without reaching equilibrium (until 108 days). The other investigated substances were not detectable. However, the standard error of the measurements was high, probably due to analytical interferences, indicating a low accuracy of the obtained results (see tabulated data in Annex 2, Supplementary material). The weight increase in iso-octane at 40 °C is insignificant below 0.1%. At 20 °C and up to 139 days the migration of all the investigated substances is at or below the detection limit and the weight increase is, as found at 40 °C, below 0.1%.

3.1.2 Testing on appearance

During the kinetic migration tests with the liquid food simulants, changes in the appearance of the polymer were observed. Already after 6 h contact at 60 °C with 95% ethanol the test specimens appeared softer, after 2 days they were deformed and after 10 days their length were drastically reduced. At 40 °C with 95% ethanol the test specimens become rigid and curved after approx. 3 days, while no visible change was observed at 20 °C within 60 days. With 50% ethanol, changes were noted only at 60 °C after 2 days of contact. After 40 days, contact at 60 °C with 10% ethanol and 3% acetic acid the ABS test specimens changed from white to yellow discolouration and after 60 days they appeared deformed. No visible changes were observed with 10% ethanol and 3% acetic acid at 40 °C and 20 °C. At the same, no changes in the appearance of the ABS material during the storage in iso-octane and 20% ethanol at 20 °C, 40 °C and 60 °C were observed, apart from a slightly yellow discolouration. The photos of the kinetic test material taken at the different intervals are shown in Annex 1 (Supplementary material).

3.1.3 Migration kinetics onto Tenax®

The food simulants 95% ethanol, 50% ethanol and iso-octane showed a strong interaction with the ABS polymer which resulted in swelling of the polymer matrix. Therefore, also migration kinetics onto Tenax® was performed. As Tenax® is a solid simulant, no swelling (seen as uptake of liquid and consequent weight increase) of the polymer is expected. Quantification of the volatile surrogates transfer onto Tenax® was carried out by means of multiple headspace extraction (MHE). The Tenax® migrates could directly be analysed without any sample clean-up. Therefore, this

Fig. 6 Comparison of migration kinetic data of target components from ABS with weight increase of ABS in iso-octane at 60 °C

Fig. 7 Migration kinetic of toluene onto Tenax® at 60 °C, 40 °C and 20 °C

Fig. 9 Migration kinetic of styrene onto Tenax® at 60 °C, 40 °C and 20 °C

Fig. 8 Migration kinetic of chlorobenzene onto Tenax® at 60 °C, 40 °C and 20 °C

method is more sensitive than the measurement in aqueous simulants by GC using liquid injection. The control tests using spiked Tenax® to check possible loss by evaporation of the surrogates during the kinetics experiments showed good recovery (recovery for all substances > 93% after 60 days at 60 °C). The experimental results of the migration kinetics onto Tenax® at 60 °C, 40 °C and 20 °C are shown in Figs. 7, 8 and 9 for toluene, chlorobenzene and styrene. For the higher molecular weight substances methyl salicylate and phenyl cyclohexane migration onto Tenax® was below the limit of detection of $50 \mu\text{g dm}^{-2}$. Kinetic points were drawn at 3, 20, 40, and 60 days (see Annex 2 in Supplementary material for tabulated data). At 40 °C and 60 °C migration of the surrogates increased till the final kinetic point after 60 days. Significant migration values (at 60 °C after 60 days) were found for toluene to be approx. $150 \mu\text{g dm}^{-2}$, for chlorobenzene to be approx. $190 \mu\text{g dm}^{-2}$ and for styrene to be approx. $70 \mu\text{g dm}^{-2}$. Plotting the time dependant migration of toluene, chlorobenzene and styrene into Tenax® against

Table 3 Experimental determined diffusion coefficients D_p for toluene, chlorobenzene, styrene derived from the migration kinetics into Tenax® at 60 °C, 40 °C, and 20 °C

Substance	$D_p [\text{cm}^2 \text{s}^{-1}]$		
	60 °C	40 °C	20 °C
Toluene	3.2×10^{-13}	3.2×10^{-14}	5.5×10^{-15}
Chlorobenzene	4.4×10^{-13}	4.0×10^{-14}	5.3×10^{-15}
Styrene	1.1×10^{-13}	1.8×10^{-14}	2.9×10^{-15}

square root of time shows a linear dependency (Figs. 7, 8, 9). From the slope of the linear correlation, the diffusion coefficients of the surrogates were calculated (Table 3). However, mainly for styrene kinetics the linear regression is not passing through the origin, as expected from Fickian laws and diffusion theory (Crank 1975). This is an indication that the diffusion process is not the only relevant mass transport phenomenon, i.e. is “non Fickian” or the substances are not distributed homogeneously in the material investigated. On the other hand, due to the low concentrations with the associated great experimental uncertainty and only four kinetic points, passing not through the origin might be also a possible cause. The higher concentrations for toluene and chlorobenzene show nearly Fickian diffusion. Therefore, when calculating the diffusion coefficients Fickian diffusion was assumed also for styrene.

3.2 Migration into food

The migration kinetic of the lower molecular weight substances toluene, chlorobenzene, and styrene was tested using spiked ABS sheets up to a storage time of 90 days into milk, cream and olive oil at 20 °C and at 40 °C. At the same time, the occurred swelling (as % weight increase of the ABS sheet before and after contact with food) was measured.

After 90 storage days, the higher molecular weight compounds methyl salicylate and phenyl cyclohexane could not be detected at both temperatures in the tested food with a limit of detection (Table 2). For toluene, chlorobenzene and styrene external calibration on each food matrix was carried out individually. The obtained correlation coefficients were > 0.99 . The matrix effect, estimated by comparing the slopes of standard curves obtained in food matrix with the slope of standard curve obtained for the solvent ethanol (diluted to 10%), was estimated -7% for milk and -29% for cream and olive oil. The control standards (known spiked amount of each food) analysed in parallel to the samples showed good recovery ($> 90\%$).

The migration of toluene, chlorobenzene and styrene from ABS into milk, cream and olive oil was in the range of the analytical detection limits for both tested temperatures ($20\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$), the kinetics show untypical behaviour (data not shown), most probably they are overlaid by analytical artefacts. The higher migration values into milk were obtained at $40\text{ }^{\circ}\text{C}$ to be approx. $56\text{ }\mu\text{g dm}^{-2}$, $79\text{ }\mu\text{g dm}^{-2}$ and $34\text{ }\mu\text{g dm}^{-2}$ for toluene, chlorobenzene and styrene respectively. The higher migration values into cream were obtained at $40\text{ }^{\circ}\text{C}$ to be approx. $62\text{ }\mu\text{g dm}^{-2}$, $48\text{ }\mu\text{g dm}^{-2}$ and $17\text{ }\mu\text{g dm}^{-2}$ for toluene, chlorobenzene and styrene respectively. The higher migration values into olive oil were obtained at $40\text{ }^{\circ}\text{C}$ to be approx. $58\text{ }\mu\text{g dm}^{-2}$, $60\text{ }\mu\text{g dm}^{-2}$ and $46\text{ }\mu\text{g dm}^{-2}$ for toluene, chlorobenzene and styrene respectively.

The weight increase of the ABS sheets after migration contact with different foods was tested at different temperatures. The weight increase after contact with milk and cream at $20\text{ }^{\circ}\text{C}$ and at $40\text{ }^{\circ}\text{C}$ up to a storage time of 90 days is shown in Table 4. The weight increase in milk and cream was below 1% at $20\text{ }^{\circ}\text{C}$ and reached approx. 1.7% and 1.9% , respectively at $40\text{ }^{\circ}\text{C}$ after 90 days. No significant weight increase was determined in contact with olive oil both at $20\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ (below 0.3%). Due to the fact that the migration experiments into milk and cream showed a slight weight increase, but much less than the observed into food simulants, the question arose how other foodstuff interact

with ABS. Therefore, other real foods were tested using the gravimetric method. The results in Tables 5 and 6 clearly show that none of the tested foods significantly swell the ABS material. All percentages of weight increase are well below 1% . At $5\text{ }^{\circ}\text{C}$ butter shows the highest weight increase with approx. 0.8% . At $20\text{ }^{\circ}\text{C}$ clear orange juice shows a weight increase of 0.6% after 10 days that remains constant until 50 days of contact. The weight increase of all other foodstuffs at $20\text{ }^{\circ}\text{C}$ is below of 0.5% . Water was additionally investigated at hot fill conditions (at starting temperatures of 98 and $84\text{ }^{\circ}\text{C}$), it shows a weight increase of approx. 0.6% . Brewed coffee at $92\text{ }^{\circ}\text{C}$ starting temperature leads to a weight increase of ABS of 0.6% after 30 min. The weight increase for warm and hot water (at $62\text{ }^{\circ}\text{C}$ and $41\text{ }^{\circ}\text{C}$) was determined 0.3% . In all cases, changes in appearance of the ABS samples were not observed during contact with foods.

4 Discussion

In this study, experimental kinetic migration data at different temperatures for a set of model substances were obtained in the food simulants 95% ethanol, 50% ethanol, iso-octane and Tenax[®]; as well as in typical foods used in contact with ABS polymer, such as milk, cream and olive oil. Because intrinsic migrants in ABS are rare and, if available, the concentrations are low, the experimental migration kinetics were done on spiked ABS sheets. As expected, a higher temperature yields a faster migration rate for all experimental conditions. The migration extent significantly differs depending on the type of food simulant applied. Particularly, the migration process is affected by the concentration of ethanol of the food simulant. Migration into 95% ethanol and 50% ethanol (simulant for dairy products) is significantly higher than determined for the investigated foods (milk, cream and olive oil) as well as onto Tenax[®]. For example, in Fig. 10 the specific migration of the monomer styrene at $20\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ in the considered foods and onto Tenax[®] after 20 storage days is compared with the liquid food simulants after 21 storage days (tabulated data in Annex 2, Supplementary material).

Table 4 Weight increase for ABS contact with milk, cream, and olive oil at $20\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ up to storage 90 days

Food	Temperature ($^{\circ}\text{C}$)	Weight increase (%) $\pm$ SD					
		15 days	20 days	30 days	40 days	60 days	90 days
Milk	20	0.7 ± 0.1	0.5 ± 0.1	0.6 ± 0.1	0.4 ± 0.1	0.6 ± 0.1	0.8 ± 0.1
Cream		0.8 ± 0.1	0.7 ± 0.1	0.6 ± 0.1	0.6 ± 0.1	0.7 ± 0.1	1.0 ± 0.1
Olive oil		0.2 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.1
Milk	40	1.0 ± 0.1	1.0 ± 0.1	1.1 ± 0.1	1.2 ± 0.1	1.3 ± 0.1	1.7 ± 0.1
Cream		1.3 ± 0.1	1.1 ± 0.3	1.2 ± 0.1	1.5 ± 0.1	1.5 ± 0.1	1.9 ± 0.1
Olive oil		0.2 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.2 ± 0.1

SD standard deviation

Table 5 Weight increase of ABS with real food contact at 5 °C and 20 °C for up to 50 storage days

Food	Temperature (°C)	Weight increase (%) ± SD			
		10 days	20 days	30 days	50 days
Lard (100% fat)	5	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.5 ± 0.1
Butter		0.5 ± 0.1	0.8 ± 0.1	0.7 ± 0.1	0.8 ± 0.1
Fish oil ^a	20	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
Miglyol [®] 812 ^b		0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
Clear orange juice		0.6 ± 0.1	0.6 ± 0.1	0.6 ± 0.1	0.6 ± 0.1
Ground coffee beans		0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
Noodles ^c		0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
Oat flakes		0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
Wheat loops (sugared)		0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
Water		0.4 ± 0.1	0.6 ± 0.1	0.5 ± 0.1	0.5 ± 0.1

SD standard deviation

^aOmega-3 total by Norsan (contains natural fish oil, olive oil, mixed tocopheroles, cholecalciferol, natural lemon oil)

^bCAS-No. 73398-61-5: decanoyl- and octanoylglycerides

^cMade from wheat semolina with 10% egg, noodles crushed to have intimate contact

Table 6 Weight increase for ABS in hot filled aqueous foods up to 30 min storage

Food	Starting temperature (°C)	End temperature (°C)	Weight increase [%] ± SD		
			10 min	20 min	30 min
Boiling water (100 °C)	98	36	0.5 ± 0.1	0.5 ± 0.1	0.5 ± 0.1
Hot water (80 °C)	84	34	0.5 ± 0.1	0.6 ± 0.1	0.6 ± 0.1
Hot water (60 °C)	62	36	0.2 ± 0.1	0.3 ± 0.1	0.3 ± 0.1
Warm water (40 °C)	41	29	0.2 ± 0.1	0.2 ± 0.1	0.3 ± 0.1
Brewed coffee (90 °C)	92	28	0.3 ± 0.1	0.4 ± 0.1	0.6 ± 0.1

SD standard deviation

The other investigated migrants show similar behaviour. At both tested temperatures, migration of styrene in 95% ethanol is significantly higher than in real food (values found in milk and cream differ by two orders of magnitude). Also, testing with the food simulant 50% ethanol at 40 °C gives significantly higher migration values as in the foods (values differ by one order of magnitude). On the other hand, testing with Tenax[®] underestimates the migration in the considered foods. The migration values found in iso-octane at 20 and 40 °C as well as in 50% ethanol at 20 °C reflect the migration in milk and cream, however they apparently underestimate the migration into olive oil (additionally, in case of iso-octane high spiking values were obtained, indicating for low accuracy of the obtained results).

In parallel to the migration kinetics, swelling kinetics were obtained in the food simulants 95% ethanol, 50% ethanol, 20% ethanol, 10% ethanol, 3% acetic acid, iso-octane and Tenax[®] as well as into different foods tested at several conditions to cover the majority of foreseeable applications of ABS. Results obtained confirmed that the use of high

Fig. 10 Comparison of the migration of styrene for different food and food simulants at 20 °C and 40 °C (after 20 days storage in case of food and Tenax[®], after 21 days for the liquid food simulants. Tabulated data are given in the Supplementary material, Annex 2)

concentrations of ethanol–water and of iso-octane (at 60 °C) causes the swelling of the ABS polymer. None of the real foods studied cause significant swelling of ABS.

From the migration kinetic obtained for 95% ethanol at 60 °C (Fig. 1) the same initial slope of the migration curve against time is observed for all the spiked substances, regardless of their molecular weight. In other words, different substances show the same diffusion coefficient, which indicates that 95% ethanol at 60 °C considerably swells the ABS polymer and the migration follows a non-Fickian behaviour. With regard to the data for iso-octane at 60 °C (Fig. 6), for all substances a rapid release is observed between 3 and 14 days, however, the migration behaviour differs from the one observed for 95% ethanol. The migration curves obtained in 95% ethanol show an initial rapid release and flatten off for most of the compounds after around 2 days. While the migration curves obtained in iso-octane are characterised by three sequential linear regions. The initial step (to approx. 3 days) is the slow diffusion process (for all the surrogate measured migration extent is below the quantification limit). The second (from approx. 3 to 14 days) is the faster one, in which the migration extent reaches 1100–1500 mg dm⁻² (depending the surrogate considered) and it is followed by a third step, characterised by a slower migration rate, approaching plateau for methyl salicylate, styrene, toluene and chlorobenzene after approx. 65 days. For phenyl cyclohexane, benzophenone and methyl stearate the curves in the third step slow down, but still increase until the last observed kinetic point (50 days). In the case of iso-octane, the migration process is probably made up by several subsequent kinds of diffusion, firstly a slow diffusion process takes place from the non-swollen (or partially-swollen) polymer then the process becomes quickly from the largely-swollen polymer, afterwards slow again till reaching maximum degree of swelling. These considerations are consistent with the swelling curves obtained for these two simulants (Figs. 1, 6) that at a temperature of 60 °C show a similar trend over time as the migration process. Interestingly, for 95% ethanol significant swelling (approx. 10% at the end of the kinetics) was recorded also at 40 °C and 20 °C. Contrary, using iso-octane at temperatures lower than 60 °C cause no weight increase of the ABS test specimens.

Interestingly, when the weight increase of ABS in contact with the different food simulants becomes gravimetrically measurable, migration of the surrogates is facilitated and higher values are found compared to non-swelling conditions. The weight increase of ABS can be used as an indicator for the interactions between the food simulant and the polymer. High weight increase of ABS indicates strong interactions with the simulant. Strong interactions lead to a high migration due to swelling of the polymer with a non-Fickian migration behaviour of the migrants. From the results of this study, weight increase of ABS in contact with food simulants can be used as a measure of the interaction and the swelling of ABS during the migration contact of the food contact material.

The comparison of the weight increase measured at 20 °C and 40 °C for ABS in contact with different foods and Tenax® (for 20 days storage) with the other liquid food simulants (for 21 days storage) is shown in Fig. 11 (tabulated data in Annex 2, Supplementary material). The swelling effect is temperature dependant and for all the investigated foods and food simulants higher weight increase of the ABS polymer is found at 40 °C compared with 20 °C. Olive oil, Tenax® and iso-octane cause insignificant swelling (<0.2%) of the ABS at these two temperatures. The weight increase of the polymer after 20 days of contact with milk and cream is comparable to the one measured in the food simulants 10% ethanol or 3% acetic acid, whereas 20%, 50% and 95% ethanol cause significantly higher swelling.

According to the Regulation (EU) 10/2011, 95% ethanol and iso-octane can be used as alternative fatty food simulants for both overall and specific migration. Since testing using olive oil (simulant D) is time consuming and difficult to carry out, or sometimes even not feasible, the alternative simulants are often chosen to simplify analytical procedures. The EU test scheme foresees for specific migration, accelerated test conditions at elevated temperature. For example, testing for up to 10 days at 60 °C simulate contact times above 30 days at room temperature and below. The results obtained with this study show that after 10 contact days with 95% ethanol at 60 °C, the ABS polymer is significantly swollen (20% weight increase). Contrary, after 90 contact days with olive oil (real fatty food) at 20 °C or 40 °C, the swelling effect was negligible (<1% weight increase). Additionally, according to the Regulation (EU) 10/2011, 50% ethanol (simulant D1) is assigned to the food category dairy products. With this food simulant, after 10 contact days at 40 °C the ABS polymer is significantly swollen (4% weight increase). On the other hand, after 90 days contact with milk or cream at 40 °C, the swelling effect was negligible (<2% weight increase). Migration values found for toluene,

Fig. 11 Comparison of the weight increase of the ABS in contact with different foods and food simulants at 20 °C and 40 °C (after 20 days storage in case of food and Tenax®, after 21 days for the liquid food simulants)

chlorobenzene and styrene in 50% ethanol at the test condition 10 days/40 °C were in the range of 200–350 mg dm⁻² whereas for the same substances migration into milk, cream and olive oil at the same time temperature condition did not exceed 100 mg dm⁻².

5 Conclusions

Based on the experimental data obtained in this study, ethanol in concentrations > 10% in water causes swelling effects on ABS. They are further increased by the contact temperature with the effect that obtained migration values tend to overestimate the actual migration into real foodstuff unless the product itself contains higher ethanol levels. Contact conditions of 10 days at 60 °C and 40 °C with 50% or 95% ethanol are too severe for ABS compared to real food and anticipated storage conditions. These findings are in agreement with previously reported results for other polymers, such as for styrene-acrylonitrile copolymer (SAN) (Yoshida et al. 1982) and polyethylene terephthalate (PET) (Franz et al. 2016; Gehring and Welle 2018).

Determination of the weight increase of ABS in contact with foodstuff or simulants is a suitable method to measure the swelling effect, through the uptake of liquid from the polymer. Weight increase in contact with food and food simulants can be determined in nearly all laboratories without high sophisticated analytical equipment and can be used as a simple method to check the suitability of a food simulants at a particular testing temperature for each considered polymer. Due to the swelling of the polymer the migration process is facilitated. The nature and extent of food simulant interactions with the polymer depend, beyond the nature of the polymer, probably also on the geometry of the test specimen used in the experiments and on the type of contact with the simulant (i.e. total immersion or single side) can play an important role; therefore, a more in depth characterisation of the polymer swelling should be further investigated.

From the results of this study it can be concluded, that 50% and 95% ethanol cause significantly swelling of the ABS polymer, this leads to an exaggerated estimation of the migration, especially at temperatures of 40 °C and 60 °C. This over-estimative character might lead to a non-compliant of articles made from ABS in contact with food or a significant higher migration as was found in real food at the end of shelf life. In general, food simulants are useful for migration prediction of real foods. From a consumer protective point view, the migration into food simulants should be higher than the migration into real food under typical conditions of use or at the end of the shelf life. However, food simulants should be not too over-estimative, because otherwise the

tested ABS food contact article will result not in compliance with the criteria given in Regulation 10/2011.

Swelling effect of high concentrated ethanol–water mixtures and of iso-octane should be investigated also on other styrenic polymers widely used in food contact applications, such as general purpose polystyrene GPPS and high impact polystyrene HIPS. It is expected that the results of this study on ABS will assist in acquiring information about the selection of suitable migration testing conditions for styrenic polymers in consideration of the swelling effect caused by food simulants. Additionally, since swelling of the polymer results in artificially higher diffusion coefficients or lower activation energies of diffusion, migration prediction using polymer-specific diffusion parameters should be considered as well to avoid over-conservative risk assessment for food contact materials and articles made of ABS and in general for styrenic polymers.

Acknowledgements The authors gratefully acknowledge financial support by the Styrenics Steering Committee of Plastics Europe. We are grateful to Gordon Dawkins (INEOS Styrolution) and Mark Pemberton (Systox) for their helpful advice and to the Styrenics Steering Committee of Plastics Europe for providing pellet samples for the migration tests. Special thanks are due to Silvia Demiani, Veronika Hendrich, Mladen Juric, Alexandra Mauer and Sonja Smolic (Fraunhofer IVV) for technical support of this study.

Funding Open Access funding enabled and organized by Projekt DEAL. The study was financed by the Industrial consortium “Styrenic Chain” of Plastics Europe. The funding organisation did not participate in any of the following: the collection, analysis, or interpretation of data, the preparation of the article, or the decision to publish.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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