A Hansen Solubility Parameter Study on the Suitability of EU Food Simulants for Migration Testing*

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Abstract

A major issue of food packaging materials is the migration into food. In the regulation of European Commission regarding polymeric materials intended to be in contact with foodstuff, some food simulants to test migration from plastic materials are proposed and although not clearly stated, the concept is actually based on the old rule of Chemistry that "*similia similibus solvuntur*" (like dissolves like). The Hansen Solubility Parameters (HSP) are based on the same principle for predicting the thermodynamic affinity/solubility between substances. Here, the reliability of the food simulants (vegetable oil and various aqueous mixtures with ethanol or acetic acid) of the EU regulation was examined based on HSP. A simple strategy was developed and the apparent HSP of 15 different foods, 3 for each of the 5 simulants, was estimated from the nutritional value statement and by treating foods as mixtures. The HSP of the simulants were also calculated. From around 900 potential migrants (permissible monomers and additives mentioned in the regulation), we were able to retrieve the HSP of 294 representative migrants. Thousands of calculations were performed and the Relative Energy Difference (RED) of food-simulant, food-migrant and simulant-migrant were calculated for a range of values of interaction radius (R_o). Experimental confirmation of selected predictions was also provided, through the determination of the apparent HSP values of a complex food (mayonnaise). Similar conclusions were obtained from both the theoretical and experimental approaches. Overall, two of the five showed limited suitability for several of the complex foods examined in this study and may lead to underestimation of migration risk under specific conditions.

Keywords: food simulants; migration; Hansen Solubility Parameters; food contact materials; food safety assessment; European Regulation

1. Introduction

Food and water contamination (Al-Mansoori, Stephenson et al. 2025, Katsara, Viskadourakis et al. 2025) arising from migration from polymeric packaging materials/articles is a major source of the microplastics that enter and/or accumulate in human organism (Siddiqui, Bahmid et al. 2023). Although there is a large interest for development of novel packaging materials (Perera, Jaiswal et al. 2023, Alghuthaymi 2025, Parra A, Clavijo et al. 2025, Rico-Rodríguez, López-Padilla et al. 2025), migration into food is less studied (Zimmermann, Geueke et al. 2025). In addition, in 2004 it was pointed out, that from novel materials may rise novel concerns and migration risks/hazards and have led to a tendency for stricter EU regulation which includes food simulants for testing packaging materials and a list of hazardous potential migrants including monomers and oligomers as well as various additives that are used in polymer manufacturing and processing (Arvanitoyannis and Bosnea 2004).

In 2011, the Commission regulation EU 10/2011 "on plastic materials and articles intended to come into contact with food" was published (EU 2011). It includes 885 substances (some of them are groups of substances) that are potential migrants due to their use as monomers or additives in plastic articles. Is also includes 6 food simulants: a) simulant A (ethanol 10 %v/v), b) simulant B (acetic acid 3%w/v), c) simulant C (ethanol 20 %v/v), d) simulant D1 (ethanol 50 %v/v), e) simulant D2 (vegetable oil) and f) simulant E (poly(2,6-diphenyl-p-phenylene oxide), particle size 60-80 mesh, pore size 200 nm) (EU 2011). In appendix III of the EU regulation (EU 2011), it is mentioned that: "*…Food simulants A, B and C are assigned for foods that have a hydrophilic character and are able to extract hydrophilic substances. Food simulant B shall be used for those foods which have a pH below 4.5. Food simulant C shall be used for alcoholic foods with an alcohol content of up to 20 % and those foods which contain a relevant amount of organic ingredients that render the food more lipophilic. Food simulants D1 and D2 are assigned for foods that have a lipophilic character and are able to extract lipophilic substances… Food simulant E is assigned for testing specific migration into dry foods…*". Clearly, the concept behind the selection of the food simulants is the old rule of Chemistry "*similia similibus solvuntur*" (like dissolves like).

Hansen solubility parameters (HSP) (Hansen 2007, Hansen Solubility Webpage 2025) are based on the exact same concept. In the webpage of HSP, it is mentioned that S could mean "similarity" instead of "solubility" (Hansen Solubility Webpage 2025). Although, HSP have received criticism for their thermodynamic background (Stefanis and Panayiotou 2008, Stefanis and Panayiotou 2012), and despite the fact that are not always successful, they exhibit a remarkable predictive ability and in addition they are very simple and easy to apply, in contrast to other more accurate and sophisticated thermodynamic models. Most likely, the reliability of HSP arises from the fact that most HSP values have been estimated from actual experimental data. Thus, HSP are widely used in academia and industry for numerous applications including selective extraction of lipids (Tsioptsias, Mitis et al. 2025), solvent screening of non-toxic solvents (Nakamura, Hirano et al. 2017), nanomaterials (Hansen 2007, Hansen Solubility Webpage 2025), glove safety (Hansen Solubility Webpage 2025), finding green solvents (Sánchez-Camargo, Bueno et al. 2019), flavor scalping (Hansen Solubility Webpage 2025), polymer adhesion (Hansen 2007, Hansen Solubility Webpage 2025), polymer and paints solubility (Hansen 2007) and recently for predicting migration into food (Tsioptsias, Goulas et al. 2025). Thus, HSP seem to be ideal in order to study the interactions/compatibility/affinity of migrants with foods and food simulants.

Beyond regulatory compliance, the accurate assessment of chemical migration from food contact materials is also highly relevant to food safety management systems. ISO 22000 is based on the identification, evaluation, and control of food safety hazards across the food chain, including chemical hazards (22000:2018; 2018), while Global Food Safety Initiative (GFSI) recognized certification schemes (BRCGS 2022, FSSC 2023, GmbH 2023) place increasing emphasis on hazard analysis, contamination prevention, and the suitability of packaging materials for their intended use. In this context, migration testing is not merely a formal legislative requirement but a critical component of chemical hazard characterization. If the selected food simulant does not adequately represent the actual food matrix, the resulting migration estimate may lead to either underestimation or overestimation of risk, thereby weakening the scientific basis for food safety decisions and compliance validation (Karageorgou and Tzikas 2025, Karageorgou, Ntereka et al. 2026).

Several studies have examined migration into food. However, it has been pointed out that the role of plastics in food packaging materials and articles has not received proper attention, despite being a well-known source of concern for both health and the environment [8]. Despite being in the right direction, this may be the case also for the EU regulation. In Table 2 of Appendix III of the EU regulation (EU 2011) there is the assignment of the food simulants to various foods. It can be seen that the simulant A (ethanol 10% v/v) is assigned to pastes from dry seeds (nuts), to fresh vegetables, to animal products and eggs, fried potatoes, mustard and other (EU 2011) (in some cases two simulants are assigned to the same food). All these are quite different foods and have quite different compositions. In addition, most of the foods are complex heterogeneous mixtures whereas one of the simulants is a vegetable oil and the other simulants are simple binary mixtures of water with ethanol or acetic acid.

However, it remains unclear whether the currently used food simulants are equally suitable for all food categories to which they are assigned. In particular, there may be cases in which the selected simulants do not adequately reflect the physicochemical characteristics of the actual food matrix and may therefore lead to underestimation of migration risk. The scope of the present study was to provide insight into this issue. For this purpose, a simple methodology based on HSP was developed. In total, 15 foods, 5 simulants, and 294 potential migrants (monomers and additives used in polymer manufacturing and processing) were examined. Experimental determination of HSP was also performed to support the theoretical predictions.

2. Theoretical methodology

From the 885 permissible substances (potential migrants) specified in the original EU regulation (EU 2011) we retrieved the HSP of 294 substances from the literature (Hansen 2007, Hansen Solubility Webpage 2025). These substances are quite representative since, quite a few of the other substances are inorganic and their HSP are not typically measurable. Such substances are expected to migrate in hydrophilic foods with high water content. The name and the CAS number of 294 substances are presented in Table S1 of the Supplementary material. The HSP of the simulants and foods were calculated as the HSP of mixtures from the following equations (Hansen Solubility Webpage 2025):

$$\delta_{d,mixture} = \sum_{i}^{n} x_{v,i} \times \delta_{d,i} \quad (1)$$

$$\delta_{p,mixture} = \sum_{i}^{n} x_{v,i} \times \delta_{p,i} \quad (2)$$

$$\delta_{hb,mixture} = \sum_{i}^{n} x_{v,i} \times \delta_{hb,i} \quad (3)$$

where,

$\delta_{d,mixture}$: is the dispersion HSP of the mixture

$\delta_{p,mixture}$: is the polar HSP of the mixture

$\delta_{hb,mixture}$: is the hydrogen bonding HSP of the mixture

$\delta_{d,i}$: is the dispersion HSP of the ith component of the mixture

$\delta_{p,i}$: is the polar HSP of the ith component of the mixture

$\delta_{hb,i}$: is the hydrogen bonding HSP of the ith component of the mixture

n: the total number of the components of the mixture

$x_{v,i}$: the volume fraction of the ith component of the mixture

For the simulants, the volume fractions were calculated from the % v/v concentrations that are given in the regulation. For food simulant B the density of acetic acid was taken into account to convert the regulation concentration from w/v to v/v. For food simulant D2 the HSP of olive oil were used (Hansen 2007). For foods, the volume fractions were calculated from the nutritional statement in packaging material and the densities. In essence, the HSP of foods were simulated by more complex mixtures (not binary) and by taking into account their content in carbohydrates, proteins, fats and lipids and water (and ethanol for alcoholic beverages). For carbohydrates, the average values of HSP of 5 sugars (Hansen 2007, Hansen Solubility Webpage 2025) were used (see Table S2 in Supplementary Material). For fats and lipids the average values of HSP of 11 glycerides and fatty acids (Hansen 2007, Hansen Solubility Webpage 2025) was used (see Table S3 in Supplementary Material). For proteins, the HSP of water-insoluble zein (Hansen 2007) or water-soluble Bovine Serum Albumin (AlQasas and Johnson 2023) were used respectively for lipophilic and hydrophilic foods. For water, the HSP values of 18.1, 17.1 and 16.9 MPa$^{1/2}$ were used (Hansen 2007). In Tables 1 and 2, respectively the HSP values of the simulants and the examined foods respectively are presented.

Table 1. Composition and calculated HSP of the food simulants.

Simulant	**Composition**	**δ_d, MPa$^{1/2}$**	**δ_p, MPa$^{1/2}$**	**δ_{hb}, MPa$^{1/2}$**
A	ethanol 10% v/v	17.9	16.3	17.2
B	acetic acid 3% w/v	18.0	16.8	16.8
C	ethanol 20% v/v	17.6	15.4	17.4

D1	ethanol 50% v/v	17.0	13.0	18.2
D2	olive oil	15.9	1.2	5.4

Table 2. Calculated apparent HSP of the examined foods and assigned simulants.

Food	**Simulant**	**δ_d, MPa$^{1/2}$**	**δ_p, MPa$^{1/2}$**	**δ_{hb}, MPa$^{1/2}$**
Honey	A	17.3	15.3	21.5
Almond butter	A	17.1	9.4	11.9
Mayonnaise	A	16.9	8.4	10.8
Vinegar	B	18.0	16.4	16.4
Pesto sauce	B	17.2	10.1	12.9
Yogurt	B	18.1	16.8	16.9
Aperitif 11%	C	17.8	16.1	17.2
Orange juice	C	18.0	16.9	17.4
Apricot marmalade	C	17.6	15.9	19.9
Whiskey	D1	17.2	13.8	17.9
Milk	D1	18.1	16.3	16.8
Cottage cheese	D1	18.0	16.5	16.7
Caesar dressing	D2	17.3	11.4	13.0
Tahini	D2	17.7	6.8	11.8
Mayonnaise	D2	16.9	8.4	10.8

For every food-simulant pair as well as, for food-migrant and simulant-migrant pairs, the R_a distance in Hansen Space was calculated from equation 4.

$$R_a = \sqrt{4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{hb1} - \delta_{hb2})^2} \qquad (4)$$

where subscripts 1 and 2 refer respectively to substance 1 and 2. The R_a offers a measure of the similarity of two substances (Hansen 2007, Hansen Solubility Webpage 2025). Low values of R_a suggest miscibility/compatibility of the two substances while non-compatible substances exhibit high values. How low or high should be the value of R_a has no universal answer. However, typical values are in the range 7-12 $MPa^{1/2}$ and the value of 8 $MPa^{1/2}$ is considered to be a reference value (Hansen Solubility Webpage 2025). The concept of Relative Energy Difference (RED) is also useful, which is defined form the following equation:

$$\mathrm{RED} = \frac{\mathrm{R_a}}{\mathrm{R_o}} \quad (5)$$

where,

Ro: the interaction radius of Hansen sphere

Values of RED >1 suggest immiscibility and values of RED <1 suggest miscibility (Hansen 2007, Hansen Solubility Webpage 2025). Again, the value of R_o is different for each substance and has no universal value. Based on the above a value of R_o=8 is reasonable for many cases (Hansen 2007, Hansen Solubility Webpage 2025). For each pair of food-simulant, food-migrant and simulant-migrant the RED was calculated for values of R_o equal to 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15. This was done since for every pair, the value of R_o was not known, and it was considered more representative to estimate the value of RED for a range of values of R_o instead of using a single value. Then, the average value and standard deviation of the 11 values of RED were calculated.

In order to estimate the percentages of underestimation and overestimation of migration risk the following criteria were used. Precisely, the criterion expressed in equation 6 below, provides insights regarding the risk of underestimation, in cases that the criterion is satisfied, the migrant has no compatibility with the simulant (thus low tendency for migration is expected in the simulant) but has better compatibility with the food (and thus higher migration is expected to occur in the food).

$$\mathrm{R_{a,simulant-migrant}} > \mathrm{R_o} \text{ and } \mathrm{R_{a,food-migrant}} < \mathrm{R_o} \quad (6)$$

For the case that the test of migration in the simulant may lead for some substances to overestimation of migration, the criterion inequation 7 was used. This is the reverse case of equation 6, and the migrant has good compatibility with the simulant but poor compatibility with the food.

$$\mathrm{R_{a,simulant-migrant}} < \mathrm{R_o} \text{ and } \mathrm{R_{a,food-migrant}} > \mathrm{R_o} \tag{7}$$

Substances that are chemically related to food, are the most dangerous for migration and thus, are of particular interest. Migrants that are chemically related to food were considered to be the migrants that satisfy the following equation:

$$\mathrm{R_{a,food-migrant}} < \mathrm{R_o} \tag{8}$$

Based on the number of substances that satisfy the criteria in equations 6-8, three percentages were calculated from equation 9-11. These percentages were calculated for the 11 different values of R_o, and thus for each case the average value and the standard deviation of the 11 values was calculated.

$$\%\text{ total underestimated substances} = \frac{\text{number of migrants satisfying equation 6}}{\text{number of total migrants}} \tag{9}$$

$$\%\text{ chemically related underestimated substances} = \frac{\text{number of migrants satisfying equation 6}}{\text{number of migrants satisfying equation 8}} \tag{10}$$

$$\%\text{ total overestimated susbtances} = \frac{\text{number of migrants satisfying equation 7}}{\text{number of total migrants}} \tag{11}$$

3. Materials and Methods

Olive oil, eggs, vinegar, edible salt, and mayonnaise were purchased from a local market. Ethyl acetate (Pancreac, 99.9%), methanol (Chemsolute 99.5%), ethanol (Riedel de Haen), isopropanol (Sigma-Aldrich, 99.8%), n-hexane (Carlo Erba ACS reagent), 1-pentanol (Fluka AG, 98%), di-isopropyl ether

(Pancreac, 99% stabilized with 50ppm BHT), chloroform (Fisher Chemical 99.8%), 3-methyl-1-butanol (Pancreac, 98.5%), acetonitrile (Fisher Chemical 99.8%), acetone (Chemsolute 99.8%), distilled water, acetic acid (Honeywell/Fulk, 99.8%), glycerol (Chemsolute, 99%), 1,4-dioxane (Merck, 99.8%), dibutyl phthalate (Fluka, 98%) and ethanolamine (Pancreac, 99%) were used in the experiments.

In some preliminary experiments, commercial mayonnaise was used, and about 3 g of mayonnaise were immersed in 50 mL of simulant A (10% v/v ethanol) and simulant D2 (olive oil) for 3 days at room temperature (16±1 ^{o}C), or in acetone for 2 days, to check whether any interaction/"solubility" occurred. In addition to commercial mayonnaise, homemade mayonnaise was produced in order to know its exact composition and was used for the experimental determination of its HSP.

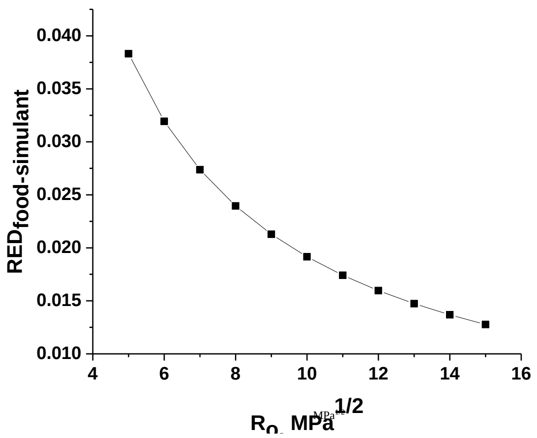
Homemade mayonnaise was prepared by mixing 1 egg (66.7 g), 171.6 g of olive oil, 10.2 g of vinegar, and 1 g of salt. Based on these amounts and considering that egg contains 13 g of protein, 10 g of lipids, 77 g of water and no carbohydrates per 100 g, and that vinegar is a mixture of 6% acetic acid and 94% water, the nutritional declaration of the homemade mayonnaise was calculated.

The apparent HSP of mayonnaise were experimentally determined using the standard procedure (Hansen 2007, Hansen Solubility Webpage 2025). Briefly, about 1 g of mayonnaise was placed in a test tube, and 7 ml of solvent was added. The mixture was left for 3 days at room temperature and then it was observed and characterized as "soluble" or "not soluble". Seventeen solvents were used, namely ethyl acetate, methanol, ethanol, isopropanol, n-hexane, 1-pentanol, di-isopropyl ether, chloroform, 3-methyl-1-butanol, acetonitrile, acetone, distilled water, acetic acid, glycerol, 1,4-dioxane, dibutyl phthalate, and ethanolamine. Python code was used to derive Ro and the HSP from these data. The code was written with the assistance of ChatGPT. To ensure that the adopted procedure, including the use of 17 solvents and the Python code, yields reliable results, the HSP of olive oil, which have been reported in the literature [11], were also determined experimentally.

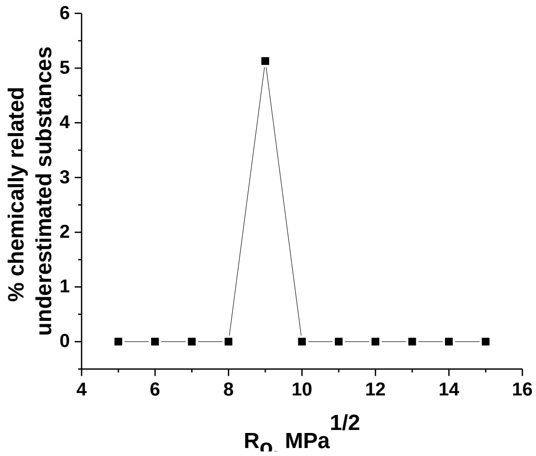
4. Results and discussion

4.1 Theoretical HSP-Based Evaluation of the Suitability of EU Food Simulants

As mentioned above, the RED values of food-simulant, food-migrant and simulant-migrant were calculated for a range of values of R_o and various percentages were calculated. Suggestively, in Figures 1 and 2, respectively are presented the pairs of food-simulant with the lowest and highest average RED value along with the percentages of chemically related underestimated substances. Precisely, in Figure 1 the results for the pair yogurt-simulant B are presented and in Figure 2 the results for Caesar dressing-simulant D2.

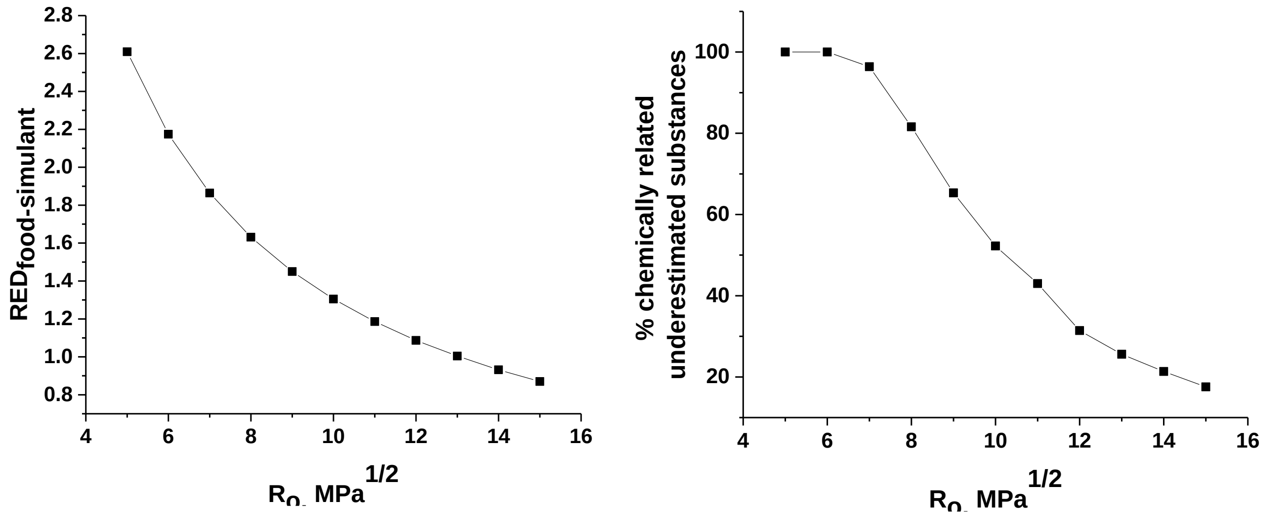


(**a**)



(**b**)

Figure 1. Results for the food-simulant pair with the lowest RED value (yogurt-simulant B): (**a**) RED as function of R_o; (**b**) % chemically related substances that are underestimated as function of R_o.



(**a**) (**b**)

Figure 2. Results for the food-simulant pair with the highest RED value (Caesar dressing-simulant D2): (**a**) RED as function of R_o; (**b**) % chemically related substances that are underestimated as function of R_o.

As can be seen in Figure 1a, the RED value of the food-simulant is very low and independent of the value of R_o. No matter what is the value of R_o the RED value if below 0.05. This is a very low value and suggests excellent compatibility between the food and the simulant. Consequently, the food (yogurt) and the simulant are of very similar hydrophilic/hydrophobic nature and thus substances of the same nature are expected to migrate in the test to the simulant and in reality, to the food. In such a case, the number of substances for which the migration risk is underestimated should be low and close to zero. Indeed, as can be seen in Figure 1b, the % number of chemically related to food substances that are underestimated for migration risk is zero for the vast majority of the values of R_o. Only for one case of R_o the % percentage is not zero but still is quite low (~5%).

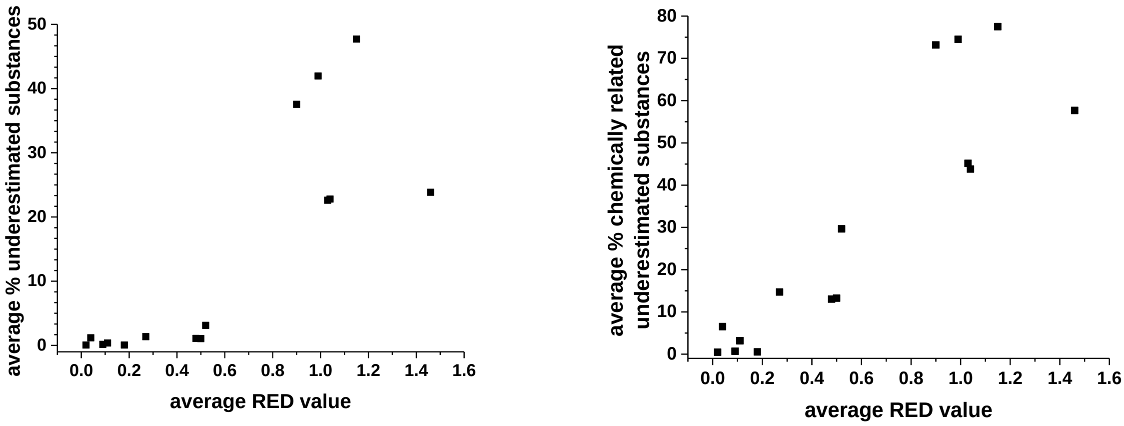
Completely different conclusions were drawn for the case of Caesar dressing-simulant D2. As can be seen in Figure 2a, the food-simulant RED value was higher than 1 for the vast majority of Ro values. This suggests reduced physicochemical affinity between the food and the simulant and indicates that the simulant may be less suitable for this particular food, since the HSP-based predictions point to substantially different polarity characteristics. This is also apparent in the percentages of chemically related underestimated substances. As can be seen in Figure 2b, this percentage was generally high

(>50%) for most Ro values, suggesting that migration risk may be underestimated for many migrants. In Table 3, the average values and standard deviations of RED values, as well as those of the three percentages, are presented for all food-simulant pairs.

Table 3. Average values and standard deviations of the food-simulant RED values and percentages of underestimation and overestimation of migration risk.

Food	**RED food-simulant**	% **total underestimated substances**	% **chemically related underestimated substances**	% **total overestimated susbtances**
Honey	0.52±0.20	3.12±2.55	29.65±32.02	7.27±5.03
Almond butter	0.99±0.38	41.96±11.60	74.49±20.72	4.79±1.63
Mayonnaise	1.15±0.97	47.71±12.48	77.49±20.26	6.15±2.40
Vinegar	0.04±0.01	1.18±0.89	6.51±6.89	0.03±0.1
Pesto sauce	0.90±0.34	37.54±11.32	73.16±20.82	3.12±0.87
Yogurt	0.02±0.01	0.06±0.21	0.47±1.55	0.28±0.37
Aperitif 11%	0.09±0.03	0.15±0.23	0.69±1.19	2.57±1.24
Orange juice	0.18±0.07	0.06±0.14	0.54±1.35	5.66±2.65
Apricot marmalade	0.27±0.1	1.36±1.10	14.71±16.05	6.86±4.16
Whiskey	0.11±0.04	0.37±0.28	3.17±5.91	1.58±1.01
Milk	0.48±0.18	1.08±0.55	13.04±16.67	9.61±2.58
Cottage cheese	0.50±0.19	1.05±0.58	13.25±16.82	9.92±2.74
Caesar dressing	1.46±0.56	23.84±7.55	57.68±32.56	25.32±13.44
Tahini	1.03±0.39	22.60±5.47	45.14±29.26	15.06±11.57
Mayonnaise	1.04±0.87	22.79±5.86	43.80±28.29	13.57±11.12

As can be seen in Table 3, in 9 out of the 15 examined foods the RED value of food-simulant is lower than 1 even if the upper standard deviation is considered (average + standard deviation). This suggests good compatibility between the food and the simulant, indicating that the corresponding simulants appear suitable for these particular foods. In the other 6 pairs the RED value is quite high and clearly shows that the foods and the corresponding simulants are of quite different polarity, thus migration of substances of different polarity is expected. These foods are Caesar dressing, tahini, mayonnaise (all these were assigned to simulant D2), almond butter and mayonnaise (assigned to simulant A) and pesto sauce (assigned to simulant B). In all these 6 cases, there is a considerable number of substances, including substances chemically related to the food matrix, for which migration risk may be underestimated due to the simultaneous poor compatibility with the simulant and good compatibility with the food. It also appears that the average RED value of the food-simulant pair is correlated with the underestimation percentages. In order to test this hypothesis, the corresponding plots were made and are presented in Figure 3. In Figure 3a, the plot of average RED value of food-simulant against the average value of % underestimated substances is presented. In Figure 3b, the respective plot for the % chemically related underestimated substances is presented. As can be seen, for the cases of food-simulant for which RED>0.9 the % percentages of underestimation are quite high, and these points are located in the upper-right part of the plot. On the contrary, pairs with RED values <0.5 are located in the lower-left part of the plot and clearly exhibit much lower percentages. Interestingly, and as can be seen in Figure 3b, even for cases for which it is true that 0.3<RED<0.5, the % percentage of chemically related underestimated substances is countable and in the range 15-35%. This suggests that, even when compatibility exists between the food and the simulant, some underestimation of migration risk is still possible.



(**a**) (**b**)

Figure 3. (**a**) Average RED values of food-simulant versus average value of % total underestimated substances; (**b**) Average RED values of food-simulant versus average value of % chemically related to food underestimated substances.

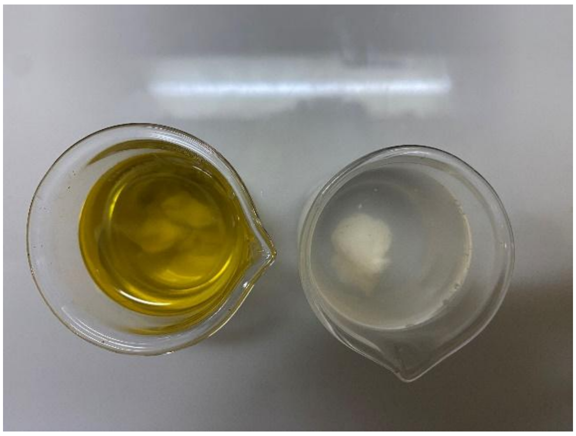
4.2 Further Discussion and Experimental Determination of the Apparent HSP of Mayonnaise

The major hypothesis in the proposed methodology is that the HSP of the foods can be approximated by treating them as mixtures and by using the information in the nutritional statement for the composition of the mixture. Clearly, this must be considered a good/acceptable approximation for foods in the form of liquid solutions such as vinegar, alcoholic beverages like whiskey and aperitif. However, many foods are multi-component dispersions, e.g. mayonnaise, Caesar dressing, etc. For such foods, this approximation may be less reliable. Consequently, the conclusion regarding the limited compatibility of these foods with the respective simulants could be questioned and attributed to possible inaccuracies in the estimation of food HSP by the proposed methodology. In order to test this hypothesis, two approaches were followed: a) preliminary experiments with mayonnaise in simulant A, simulant D2 and acetone and b) preparation of homemade mayonnaise and experimental determination of its apparent HSP.

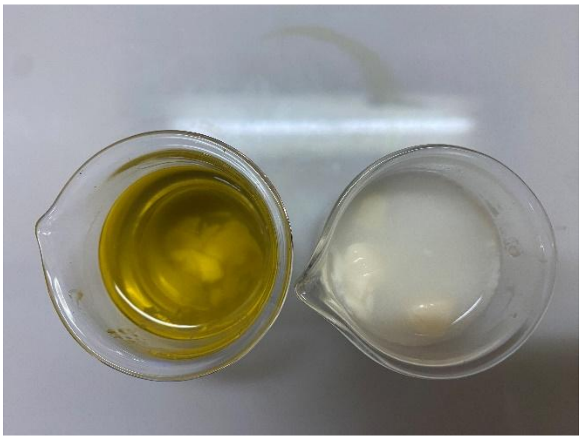
For the preliminary experiments, about 3 g of mayonnaise were immersed in 50 ml of simulant A (10% v/v ethanol) and simulant D2 (olive oil) for 3 days at room temperature (16±1 ^{o}C). Photos of the samples at day 0 and day 3 are presented respectively in Figure 4a and 4b. For the case of olive oil, the mayonnaise sample stayed at the bottom of the beaker and showed no signs of interaction e.g. swelling, loss of mechanical integrity, loss of macroscopic shape. For the case of simulant A, in order to weigh 3 g of mayonnaise, three spoons of sample were used. Due to the high oil content of mayonnaise the sample started to float. Upon floating the three pieces of the sample (from the three spoons during weighting) were separated. Some turbidity was apparent but as can be seen in Figure 4b, the samples were not swollen or lost the mechanical integrity and macroscopic shape and did not dissolve in the simulant. In the case of simulant D2 no interaction could be observed whereas in the case of simulant A only a mild interaction seems to occur. These observations appear to be consistent with the predictions of the proposed methodology, according to which mayonnaise appears to exhibit limited compatibility with both simulant A and simulant D2. In Figure 4c, a photo of mayonnaise sample after immersion for 2 days in acetone is presented. As can be seen acetone destroyed the emulsion of mayonnaise and an oil phase was formed. Acetone can dissolve both water and oils to some extent. Thus, acetone dissolved water in mayonnaise and some oil and formed one phase and the rest of the oil (with some acetone) formed another phase. The mechanical behavior was also highly affected and as can be seen in Figure 4d, the mayonnaise sample could be transferred by a spoon without being spread on the surface of the spoon, that is, it exhibited a solid-like behavior. This is attributed to the extraction of oil and water from mayonnaise which resulted in a porous protein network which behaved more like a solid than like a paste. Acetone was selected, since it was predicted that it exhibits the lowest R_a (highest interaction) with mayonnaise among various common organic solvents. Precisely, the calculated HSP of commercial mayonnaise were used to calculate the R_a with various solvents. These values are presented in Table 4. As can be seen, acetone exhibits the lowest R_a value. In the same table, is presented, the polarity index of the solvents calculated as follows:

$$\%polarity = 100 \times \frac{\delta_p + \delta_{hb}}{\delta_d + \delta_p + \delta_{hb}} \tag{12}$$

From these, it is clear that R_a distance is lower for substances of intermediate polarity.



(a)



(b)

(c) **(d)**

Figure 4. Photos of mayonnaise in inside various liquids: **(a)** in simulant A-ethanol 10% v/v (colorless) and in simulant D2-olive oil (yellow) 0 days; (**b**) in simulant A-ethanol 10% v/v (colorless) and in simulant D2-olive oil (yellow) after 3 days of immersion at room temperature (16±1 ^oC); **(c)** acetone after 2 days of immersion at room temperature (16±1 ^oC); **(d)** mayonnaise sample after two days immersion in acetone at room temperature (16±1 ^oC).

Table 4. HSP of some common organic solvents (Hansen 2007, Hansen Solubility Webpage 2025), their polarity index and their R_a distance from mayonnaise calculated using the HSP of commercial mayonnaise, the calculated HSP of homemade mayonnaise, or the experimentally determined HSP of homemade mayonnaise.

Solvent	**δ_d, $MPa^{1/2}$**	**δ_p, $MPa^{1/2}$**	**δ_{hb}, $MPa^{1/2}$**	**%polarity**	**R_a, $MPa^{1/2}$** Calculated HSP of commercial mayonnaise	**R_a, $MPa^{1/2}$** Calculated HSP of homemade mayonnaise	**R_a, $MPa^{1/2}$** Experimental HSP of homemade mayonnaise
commercial mayonnaise	16.9	8.4	10.8	53.2	0		3.6

(calculated HSP)						2.5	
homemade mayonnaise (calculated HSP)	16.6	6.9	8.8	48.6	2.5	0	5.3
homemade mayonnaise (experimental HSP)	14.3	8.9	13.2	60.7	3.6	5.3	0
hexane	14.9	0	0	0.0	13.8	11.3	15.9
simulant D2 (olive oil)	15.9	1.2	5.4	29.3	9.1	6.7	11.1
chloroform	17.8	3.1	5.7	33.1	7.4	5.0	10.1
diethylether	14.5	2.9	4.6	34.1	8.6	6.2	10.5
ethyl acetate	15.8	5.3	7.2	44.2	4.9	2.4	7.2
acetone	15.5	10.4	7	52.9	4.5	4.1	6.5
isopropanol	15.8	6.1	16.4	58.7	6.2	7.6	4.5
simulant A (10% ethanol)	17.9	16.3	17.2	65.2	10.2	12.7	9.2
methanol	14.7	12.3	22.3	70.2	12.3	14.6	9.7

According to these preliminary experimental results, the HSP values estimated for commercial mayonnaise by the proposed methodology seem to be consistent with its observed interaction with various substances. Among the examined simulants, simulant A is one of the most hydrophilic, whereas simulant D2 is the most lipophilic. According to the EU regulation, foods with both high water and lipid content, such as mayonnaise, are assigned both a hydrophilic and a lipophilic simulant. This explains why foods such as mayonnaise are tested with simulant A and simulant D2. However, the above observations (Figure 4 and Table 4), together with the HSP predictions, suggest a different physicochemical behavior.

To further investigate and support the above claims, the HSP of homemade mayonnaise were experimentally determined. The composition of the homemade mayonnaise is presented in Table 5. In addition, the HSP of olive oil were determined to ensure that the adopted procedure yields reliable results. The δ_d, δ_p and δ_{hb} of olive oil were found to be 15.5, 3.2 and 6.8 $MPa^{1/2}$, respectively, which are in reasonable agreement with the corresponding literature values of 15.9, 1.2 and 5.4 $MPa^{1/2}$ (Hansen 2007).

Table 5. Composition of the homemade mayonnaise (acetic acid was not taken into account).

Component	**wt.%**
carbohydrates	0
fats and lipids	71.6
proteins	3.5
salt	0.4
water	24.5

The experimental and calculated HSP values of the homemade mayonnaise and the calculated HSP of commercial mayonnaise are presented in Table 4. The R_a between these three sets of HSP values is also presented. As can be seen, the R_a between the various mayonnaise HSP values ranges from 2.5 to 5.3 $MPa^{1/2}$ which indicates that these sets of values are similar. The polarity index also falls within a rather narrow range (from 48.6% to 60.7%) suggesting that the mayonnaise is of medium polarity. The R_a values between mayonnaise and various solvents are consistent when either the calculated HSP values of commercial mayonnaise or the experimental HSP values of homemade mayonnaise are used. The Ra values obtained using the calculated HSP of homemade mayonnaise deviate to some extent. However, in all three cases the same basic conclusion can be drawn, that is, the maximum compatibility (minimum R_a) of mayonnaise occurs with solvents of medium polarity, such as acetone, ethyl acetate and isopropanol.

From the above it can be concluded that the proposed approach to estimate the food's HSP based on the composition of the nutritional statement appears to be reliable. In addition, it must be taken into account that mayonnaise is perhaps the most difficult food for the prediction of its HSP. Thus, if the proposed approach yields acceptable results for the case of mayonnaise, it is expected to provide acceptable estimates for less complex foods as well. The reason that mayonnaise is among the most difficult foods is the following. Mayonnaise is an oil-in-water emulsion. Typically, such emulsions, in which water is the continuous phase, contain high contents of water e.g. >50%. However, mayonnaise contains only 25% water and more than 70% oil. Thus, the high content in oil and the respective HSP will have a significant contribution to the calculated HSP. However, purely non-polar solvents such as hexane cannot interact with the outer water phase, thus interaction with mayonnaise is extremely limited (as also was experimentally verified) despite its very high oil content. In other words, theoretically the HSP values of mayonnaise tend to be lipophilic due to the high content in oil but experimentally the behavior of mayonnaise is primarily governed by the interaction with the outer aqueous phase. Thus, the experimental HSP values are more polar. Highly hydrophilic substances have some compatibility with mayonnaise and can dissolve in the outer phase but cannot dissolve in the oil phase. Highly hydrophobic substances cannot dissolve in oil since they must first dissolve in water. Thus, medium polarity substances such as acetone that can dissolve in both water and oil exhibit the highest compatibility with mayonnaise. This complex behavior seems to be adequately described by the proposed approach for estimating food HSP. Thus, the proposed approach should yield fairly acceptable estimations for less complex foods.

Finally, it is worth mentioning that, based on the HSP of foods, food-specific simulants could be identified for each food. Briefly, a suitable binary mixture, acting as a personalized simulant, could be selected so that the R_a between the food and simulant is very low e.g. <2 $MPa^{1/2}$.

5. Conclusions

A simple methodology was developed for estimating the apparent HSP of foods. This was accomplished by treating food as mixtures and by using the composition mentioned in the nutritional value statement. These calculated HSP were used along with the HSP of the food simulants proposed in EU regulation for migration from plastic materials in order to examine the compatibility and thus the reliability of the simulants. Also, 294 potential migrants were examined and their R_a distance and RED value with the foods and the simulants were calculated for a range of values of R_o.

The results showed that simulant A (10% ethanol in water) and simulant D2 (vegetable oil) were among the least suitable simulants for several of the foods that were assigned to. This may increase the likelihood of underestimation of the migration risk when using these simulants. The predicted limited compatibility between food and simulant was experimentally supported through the determination of the apparent HSP of mayonnaise. Multicomponent dispersions such as mayonnaise, despite their high lipid content, seem to exhibit behavior of intermediate polarity. Therefore, the highly hydrophilic simulant A and the highly lipophilic simulant D2 may be less suitable for certain complex foods of this type.

These findings also suggest that the current approach to migration testing may be more limited for certain complex foods than for simpler food matrices. A more realistic physicochemical similarity between foods and simulants could improve the reliability of migration testing and support more robust packaging safety evaluations. This is also relevant to food safety management systems aligned with ISO 22000 and GFSI-recognized schemes, where the reliable assessment of chemical hazards supports scientifically packaging safety decisions.

Supplementary Materials: Table S1: Names and the CAS numbers of 294 potential migrants; Table S2: HSP of carbohydrates and their average value that was used for the estimation of foods' HSP; Table S3: HSP of glycerides and fatty acids and their average value that was used for the estimation of foods' HSP.

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Supplementary material

Table S2. HSP of carbohydrates and their average value that was used for the estimation of foods' HSP.

Name	**δ_d, MPa$^{1/2}$**	**δ_p, MPa$^{1/2}$**	**δ_{hb}, MPa$^{1/2}$**
Lactose	15.6	16.9	20.4
Dextrose	17.9	13.7	23.6
Sorbitol	17.6	12.3	28.7
Sucrose	15.9	18.4	21.9
Dextro-Xylose	18.5	12.3	20.3
average	**17.1**	**14.7**	**23.0**

Table S3. HSP of glycerides and fatty acids and their average value that was used for the estimation of foods' HSP.

Name	δ_d, MPa$^{1/2}$	δ_p, MPa$^{1/2}$	δ_{hb}, MPa$^{1/2}$
Glyceryl Monostearate	16.1	4.5	9.8
Glyceryl Monooleate	16.2	4.6	9.4
Glyceryl Tributyrate	16.3	2.5	7
Glyceryl Trioleate	16.0	3.8	3.2
Glycerol Diacetate	16.4	8.9	14.2
Glycerol Triacetate	16.5	4.5	9.1
Glyceryl Tripropanoate	16.4	5.6	7.2
Stearic Acid	16.3	3.3	5.5
Hexadecanoic Acid (palmitic acid)	16.3	3.4	6.0
Oleic Acid	16.0	2.8	6.2
Linoleic Acid	16.8	3.3	6.2
average	**16.3**	**4.3**	**7.6**

NAME	CAS number
Acrylonitrile	107-13-1
Ethylenediamine	107-15-3
Ethylene Glycol	107-21-1
1,3-Butanediol	107-88-0
Butyric Acid	107-92-6
Dimethyl Ethanolamine	108-01-0
Vinyl Acetate	108-05-4
Acetic Anhydride	108-24-7
Succinic Anhydride	108-30-5
Maleic Anhydride	108-31-6
m-Cresol	108-39-4
m-Phenylenediamine	108-45-2
1,3-Benzenediol	108-46-3
Glutaric Anhydride	108-55-4
Melamine	108-78-1
Cyclohexylamine	108-91-8
Phenol	108-95-2
Dibutyl Sebacate	109-43-3
Vinyl Isobutyl Ether	109-53-5