Diese Dissertation haben begutachtet

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DISSERTATION

The Influence of Food (Micro) Structure on the Migration of Contaminants

Ausgeführt zum Zwecke der Erlangung des akademischen Grades einer

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Kurzfassung

Inhalt und Zielsetzung der vorliegenden Arbeit war es, Beziehungen zwischen der Migration von zwei Modelladditiven (Benzophenon und Diphenylphthalat) aus Kunststofffolien (Polyethylen) in verschiedene Lebensmitttel und der Struktur der ausgewählten Lebensmittelgruppen zu finden und zu beschreiben.

Hierfür wurden vier verschiedene Arten von Lebensmitteln untersucht. Zum einen waren dies halbflüssige Lebensmittel, zum anderen trockene Lebensmittel. Als halbflüssige Lebensmittel wurden einerseits Ketchups untersucht, zum anderen Milchprodukte, speziell Joghurts, Sauermilch und Buttermilch. In der Gruppe der trockenen Lebensmittel wurden einerseits Weizenmehle verschiedener Typen (Ausmahlgrade) und Spezifikationen (glatt, griffig, universal) untersucht, andrerseits Zucker verschiedener Kristallgröße.

Zur Bestimmung der Migration wurden die Lebensmittel jeweils mit der Polyethylenfolie in Kontakt gebracht, und nach der Inkubationszeit extrahiert. Die Analyten wurden mittels GC/MS anlysiert und quantifiziert.

Zur Beschreibung der Lebensmittelstruktur der halbflüssigen Lebensmittel wurden rheologische Parameter herangezogen, die die innere Struktur über viskoelastische Zusammenhänge darstellen. Die Proben wurden hierzu rheologischen Messungen im Rotations- sowie im Oszillationsmodus unterzogen.

Zur Strukturbeschreibung der trockenen Lebensmittel diente die Partikelgrößenbestimmung, die mittels Laserdiffraktion durchgeführt wurde.

Die Ergebnisse der Untersuchungen zeigten, dass Struktureigenschften der Lebensmittel sehr wohl Einfluss auf die Migration zu haben scheinen. Bei den halbflüssigen Proben waren leichte Zusammenhänge zwischen Größe des Speichermoduls G’ sowie des linearen viskoelastischen Bereichs und der Migration zu erkennen. Allerdings konnten keine eindeutigen Zuordnungen getroffen werden. Dies ist vermutlich auf mehrere Aspekte zurückzuführen: die untersuchten Proben waren kommerziell erhältliche, reale Proben, deren genaue Zusammensetzung und Prozessierung nicht bekannt war. Weiters waren die Proben in ihrer Zusmmensetzung sehr unterschiedlich, insbesondere was den Gehalt an Fett, Protein und Kohlenhydrate betrifft. Deshalb konnten gemessene Strukturunterschiede nicht genau zugeordnet werden. Grenzflächeneffekte (an Folie bzw. Lebensmittel) bzw. Struktureffekte aufgrund von Temperaturänderungen konnten auch nicht ausgeschlossen werden, diese waren aber auch nicht Inhalt dieser Arbeit.

Bei den trockenen Lebensmitteln zeigte sich ein ähnliches Bild. Insbesondere Zucker als kristalliner Reinstoff zeigt eine kristallgrößenabhängige Migration, was auf Oberflächeneffekte, wie z. B. Filmbildung durch Luftfeuchtigkeit, hinweist.

Auch die Mehle weisen Migrationsunterschiede auf, die auf Struktureigenschaften zurückführbar sind, allerdings zeigten die beiden Analyten unterschiedliches Migrationsverhalten in Relation zur Pratikelgröße. Hier zeigt sich wiederum, dass es offenbar Interaktionen zwischen Lebensmitteln komplexer Zusammensetzung, den Umgebungsbedingungen und den Migranten gibt.

Ein Vergleich der praktisch erhaltenen Ergebnisse mit einer Migrationsmodellierung (Berechnung der Migration nach dem Piringer-Modell) zeigt, dass die tatsächliche Migration deutlich unter der berechneten liegt, wobei festgehalten werden muss, dass bei der Berechnung keine physikalischen Eigenschaften der Lebensmittel berücksichtigt wurden, sondern nur die Verteilungskoeffizienten der Analyten zwischen Folie und Lebensmittel variert wurden.

Summary

The aim of the present work was to detect and describe differences of food structure parameters and their influence on the migration of additives from plastic packaging films into these foods. Examined foods were semisolid foods: ketchups and dairy products (yoghurts, sour milk, and buttermilk) and dry foods: what flours of different milling grades and types as well as sugar of various crystallite sizes. Model migrants were benzophenone and diphenyl phthalate incorporated at known levels into PE films.

Migration of the model compounds was determined after particular incubation conditions (time and temperature) of the foods in contact with the PE film. Therefore the additives were extracted from the foods and analyzed by GC/MS.

Rheometry (both rotational and oscillatory) was applied to gain information about food structure parameters in the case of semisolid foods (ketchups and dairy products); in the case of dry foods (flours and sugars) particle sizing by laser diffraction was applied.

The results showed that are relationships between food structure parameters and migration; however as the food samples were real foods commercially purchased it was difficult to draw clear conclusions. It rather came up that migration into foods depends on many factors and migration conditions like time and temperature can have multiple effects on the food structure, too.

Nevertheless in the case of semisolid foods a slight relation between migration and the storage moduli G' could be observed. Particle size and surface area respectively of dry foods also have an impact on migration although surface and interfacial effects caused by ambient humidity could be the reason for these findings.

A comparison of the practically obtained migration data with simulated (modelled) data resulted in the finding that real migration is well below the computed one. In the present study a simulation applying the Piringer model was computed, which bases on the partition coefficients of the migrants between plastic film and food. Food structure properties are not part of the calculation and chemical interactions of migrant and food are not used either as the diffusion coefficient within the film is mainly estimated on temperature and the molecular weight of the migrant.

It could be demonstrated that food structure takes its part in the migration process; however it is a bundle of complex interactions of food composition, plastic film properties, ambient conditions and the migrant in question itself.

Acknowledgement

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I give all my thanks to my family who has always accompanied me through these years and to all my friends who have always encouraged me.

Looking up to a mountain from the valley it may seem insurmountable and your view will be limited but having reached the summit all the beauty and vastness of the earth develops in front of your eyes.

Content

1 Abstract

In this thesis eventual relationships between food structure and the migration of two model polymer additives (benzophenone and diphenyl phthalate) into foods were investigated. Model foods that were examined were ketchups representing semi-liquid aqueous foods containing fruit fibres, dairy products representing protein containing foods with varying fat contents dry foods represented by wheat flours of varying milling grades and sugars of different particle sizes. Determined migration was related to structure related parameters; these were visco-elastic parameters like storage and loss moduli G' and G'', linear-visco-elastic range and flow points in the case of the semi-solid samples and particle size distribution in the case of dry foods. Direct correlation of migration to rheological parameters could not be confirmed for the selected food samples. However a relation between the storage moduli of the samples and migration could be detected in the case of ketchups and dairy products. Particle size of dry foods might have an influence on migration but should be seen in a wider aspect in terms that particle size gives rise to surface related effects and interactions promoting migration. A comparison of the practical determined migration values to the computed migration applying the Piringer model revealed higher values for the simulated course.

2 Objectives

At the end of 2008 the EU project “FOODMIGROSURE - Modelling migration from plastics into foodstuffs as a novel and cost efficient tool for estimation of consumer exposure from food contact material” (Contract- No: QLK1-CT2002-2390) was only accomplished two years earlier. This project was dealing with migration of (model) additives from different plastic films into real foodstuffs in comparison to migration into food simulants that were used to control migration limits in order to comply with legal regulations (1). These food simulants are still in use for the same purposes but they have been subsequently changed in regards to their composition (2). One aim of the “FOODMIGROSURE” project was to feed a then developed modelling program with parameters to make risk assessment of migration easier.

During the project many foods were brought in contact with different plastic films containing a variety of additives; the kinetics of the migration of these additives were then determined (1).

The study produced some unexpected results. It was found that migration into the various foods did not mainly depend on the content of fat as it was believed until then. For example it was determined that migration of benzophenone was in the same range both for milk (containing 3,5% fat) and ketchup (containing fat below 1%) (3).

These findings led to the conclusion that other parameters such as (micro-)structural parameters might also influence the uptake of migrating compounds (3). This theory is also supported by JM Aguilera who has been investigating foods on their structural terms for many years. He also pointed out that food microstructure i.e. the structural composition, plays an important role in transport processes (4) (5).

These assumptions were leading to the issue that is the subject of this thesis. The aim was to investigate the influence of structural differences in selected foods on the migration rates of packaging additives.

Several foods were selected: **ketchups** representing aqueous acidic foods containing a distinct amount of fibres and plant cell fractions; **yoghurts, sour milk and buttermilk** representing dairy products (low fat and normal fat contents) with their special micellar protein network; **wheat flours** representing dry foods with a complex chemical composition and **sugar -** also a dry foodstuff but representing a material that is usually not considered for migration because of its crystalline structure.

The methods to determine structural or structure related parameters should comprise easy and cost-efficient methods. In the case of semisolid foods visco-elastic parameters were selected as structure determining characteristics to be related to migration hence rheology was chosen for this group of foodstuffs. In the case of dry foods (sugar and flour) particle size was the structure related characteristic so particle sizing was the chosen method for these foodstuffs.

3 Introduction

3.1 Plastics used as food packaging

Today plastics (synthetic polymers) are widely used for many purposes but (food) packaging is the most important application. About 40% of the 47 million tonnes of plastics produced in Europe (2011) find their application in packaging (6). In 2011 low density polyethylene (LDPE) including linear low density polyethylene (LLDPE) was the most produced plastic for packaging purposes followed by polypropylene (PP), high density polyethylene (HDPE) and poly ethylene glycol terephthalate (PET) (7). Polystyrol (PS) as well as other polyesters and polyamides are also commonly used as food packaging materials (7).

Food is packaged for many reasons. In the interest of hygiene and extended shelf life food is packaged for protection against environmental contamination, degrading radiation (visible and UV light), oxygenation or reaction with other air born gases. At the same time it has to meet consumers' requirements to get sight to the product where possible. Furthermore packaging is required to keep the specific aroma of the food. It should be light and provide certain mechanical strength. Last but not least packaging serves the distribution in defined and tradable quantities and it gives place for product related information.

Therefore all these requirements of a packaging have to be fulfilled by the packaging material. Some of the required properties are provided by the polymers themselves others have to be implemented by additives.

3.2 Additives in plastics

Additives in plastics fulfil two main tasks. Firstly they are needed as processing aids during production and compounding and secondly they are added to refine the polymer in order to gain properties to meet the required tasks in packaging materials. A number of additives are present in plastics and therefore often also in plastics used for packaging purposes.

Usually additives are compounded with the raw polymers and perform in this state. However, as this can give rise to migration there is much interest in a new approach based on derivatisation of the polymer chains (8).

The following groups of additives are common and widely used in many materials (9).

3.2.1 Antioxidants

Oxidation is a degradation process also called ageing, with oxygen attacking reactive sites in the polymer. Oxidation of polymers can occur at all stages, i.e. during production, storage or processing. Especially polymers that are unsaturated or not stabilized by mesmeric resonance are apt to oxidative onset and autoxidative reactions. Remaining catalysts from the production process and morphological properties (degree of crystallinity, orientation) also have an effect on oxidation. Oxidation or ageing has many negative effects on the optical and mechanical properties such as tensile strength or impact strength.

Oxidation is a radical reaction cascade often started via peroxide radicals, which leads to parallel reactions: start reaction, radical chain branching reactions, termination reactions.

Options to resist oxidation processes are:

1. Structural modification of the polymer by copolymerisation with stabilizing co-monomers
2. Blocking of reactive centres
3. Physical stabilization by orientation
4. Addition of antioxidants

Antioxidants are commonly used as they retard the ageing processes effectively by interfering with the radical chain reactions (start and chain branching reaction).
Primary antioxidants interfere with propagation reaction while secondary or preventive antioxidants destroy hydro-peroxide groups that are responsible for the start and chain branching reaction. (10).

3.2.2 Light stabilizers

Light stabilizers stop or delay degradation processes originated from light and oxygen that are able to change physical and mechanical properties as well as the appearance of plastic materials (11).

Light stabilizers act through different mechanisms, which are summarized below; however most compounds exhibit more than one effect:

1. UV – absorber:
   UV radiation is absorbed and transformed into thermal energy. The utilized compounds have to be light stable otherwise they dissipate in side reactions. UV absorbers need a certain thickness of the substrate to be effective, which is not the case with thin film or fibres (11).

2. Quencher:
   Degradation reactions are inhibited by transferring energy that had been absorbed by chromophores within the plastic polymer and changed into thermal energy or fluorescence or phosphorescence radiation (11).

3. Hydroxy-peroxide decomposer:
   Hydroxy-peroxides play an important role in the polymer degradation. Representative compounds are sulphur containing organo metal complexes as di-alkyl-di-thiocarbamates (11).

4. Radical scavenger:
   Aromatic compounds act as scavenger by their resonance stabilized structure.

Common used light stabilizers are:

- (Substituted) 2 - hydroxy benzophenones (UV - absorber, radical scavenger)
- 2 – hydroxy phenylbenzotriazoles (UV - absorber)
- Organo-Ni-compounds (Quencher, Radical scavenger)
- Important developments are sterically **h**indered **a**mine **l**ight **s**tabilizers (HALS) that act as very effective radical scavengers. Because of their spacious structure these compounds are non-volatile and hardly extractable and therefore less prone to migration (11).

Light stabilizers are typically added at concentrations of 0,05 – 2 % depending on the addition of other additives and the light sensitivity of the material (11).

3.2.3 Metal deactivators

Metals are always present during the production process such as catalysts or as parts of the production facilities. Metals are present in other additives and eventually in the polymers themselves, which are often used for contact with metals such as electrical wire insulating. So metals can interact with the polymers in a positive and stabilizing way and in a negative destructive way. Especially heavy metals like Fe, Co, Mn, Cu, Ce or V can transfer electrons very easily and hence promote the forming of radicals that start a process of oxidative degradation. Metal deactivators are often complex forming compounds especially chelating agents that can effectively bind present metals as they are characterized by their poly-functionality of ligands and ionogenic groups.

Important representatives of metal deactivators are diacylated hydrazines and oxalic acid dihydrazids (12).

3.2.4 Plasticizers

Plasticizers are usually small molecules that combine polar and non-polar regions. Polar groups of plasticizing chemicals interact with the dipoles of the polymer while the non-polar (aliphatic) regions separate the polymer chains. Consequently there is more space between the polymer chains leading to changes in the mechanical properties of the polymer as for instance elasticity, viscosity of the polymer melt or the glass transition temperature.

Plasticizers are often added at high concentrations up to 50%. They are mainly added to brittle thermoplastics such as PVC, PS or derivates of cellulose.

Important plasticizers are:

1. Phthalates: esters of phthalic acid
2. Adipic esters
3. Sebacic esters
4. Phosphates

Phthalates have been on the focus of research for health risk reasons as some of them have been found to act as endocrine disruptors. They are well solved in fats so in the meanwhile phthalates are not allowed to be used for the purpose of coming into contact with fatty materials or foods. Nevertheless they are ubiquitous in ground, water and air (13).

3.2.5 Lubricants

These additives are utilised to enable the processing of the polymer melt. The large polymer chains cause high viscosity of the melts, which is why they can only be processed under high pressure. The pressure provokes dissipation of mechanical energy which may promote a process of degradation. To decrease this flowing resistance in the polymer melts process aids are added influencing the rheology of the polymer melts in a requested positive way. Furthermore the use of lubricants and other process aids have a positive impact on the compounding step and the used machines and tools.

Most utilized lubricants are waxes, fatty acids and their esters (14) .

3.2.6 Slip additives

Slip additives are usually compounds that decrease the friction resistance between ready processed films. They are common with PE films (14).

3.2.7 Antistatic agents

As plastics exhibit high electric resistance they are widely used for their isolating properties. The same properties are the reason for static charging on the surface that can lead to disturbing effects both during processing and in use. That is why antistatic agents are added as interface-active compounds to all common used thermoplastics and rubbers.

Mechanisms of antistatic agents are:

1. Application of an external antistatic agent on the surface
2. Incorporation of an internal antistatic agent
3. Incorporation of electron conducting additives such as graphite, metals or organic semiconductors

Antistatic agents are applied in amounts from 0,05 to 10% depending on the used type (15).

3.2.8 Flame retardants

The addition of flame retardants is basically restricted for plastics used in the building, traffic and electrical sectors. There are different concepts of active mechanisms (physical or chemical acting) that are often combined to achieve synergistic effects.

In materials that need to be equipped with flame retardants these have to be added in quite high concentrations: up to 50% combining inorganic antimony salts and halogenated (mostly bromated) aliphatic or aromatic compounds (16).

3.2.9 Blowing agents

Blowing agents are needed to obtain so called extended plastics such as PS-E (expanded poly styrene). Chemical blowing agents are additives that are able to form gas induced by a chemical reaction. The developed gas is then used to produce foam structures in the polymers. The gas building process is often evolved by a thermal degradation process of organic or inorganic compounds. Formed gases are mainly nitrogen (N_2) and carbon dioxide (CO_2) (17).

3.2.10 Cross linking agents

Cross linking agents facilitate copolymerisation and therefore find their application to optimize the mechanical properties of the plastics. As cross linking agents peroxides are used, especially (di-) alkyl peroxides that show excellent cross linking properties but may also interact with other additives (18).

3.2.11 Fluorescent bleaching agents

Fluorescent bleaching agents are utilised to improve the colour and colouring of plastics that are sometimes slightly yellow as well as to increase the brilliance in plastics. Most thermoplastics absorb light in the blue spectral range, which leads to a yellow colour perception of the human eye. Two major concepts exist to compensate this effect. The first concept compensates the absorption in the blue spectral range while the second increases the reflexion of light. Both concepts are combined in the use of fluorescent bleaching agents (19).

3.2.12 Nucleating agents

Nucleating agents are added in order to obtain a homogenous distribution of small crystallites that are uniform in size and form, which is crucial for the mechanical and optical properties of the plastics as well as the crystallization rate. Important for the growth of crystallite nuclei is the temperature, which has to be below the melting point but above the glass transition temperature, to allow the polymer chains for the required mobility to form the ordered structure (20).

Nucleating agents are mainly used for polyamides, PP and PET in a concentration of about 0,5% (20).

Nucleating agents are (20):

1. Inorganic: Talcum, silica
2. Organic compounds
3. Polymer powders

3.3 Regulations (EU)

In 2011 the European Commission released the Regulation EU 10/2011 (on plastic materials and articles intended to come into contact with food) replacing the Commission Directive 2002/72/EC relating to plastic materials and articles intended to come into contact with foodstuffs (2) (21).

Eventually the European Commission has worked out an obligatory legislative basis on the most important group of materials to come into contact with food. Plastics are nowadays by far the most utilized material for food packaging. And the huge quantity of monomers and additives with all modifications needs to be overlooked and regulated. All other materials than plastics which are used as packaging materials or in articles for use in food contact (paper and board, wood, glass, metals, ceramics, printing inks and adhesives) are still regulated in the Framework Regulation of the European Commission 1935/2004 (22) and the Regulation EC 2023/2006 on the good manufacturing practice (23).

<u>What is regulated in the Regulation EU 10/2011:</u>

The preamble defines the framework of the regulation:

Paragraphs [8] and [9] determine that all chemicals whether they are monomers or additives are to be evaluated by risk assessment. The risk assessment is to be conducted by the European Food Safety Agency (EFSA) and has to comprise the chemical in question, but also possible contaminations,

predictable process reaction and degradation products. It has to assess possible migration in respect to the worst case scenario as well as toxicity. On base of the risk assessment restrictions of use or quantity or migration limits have to be determined in order to secure the safety of the end product.

Paragraphs [10], [11] and [16] exclude colouring agents, solvents and other production process aids (PPA) used in the polymerisation process until a later evaluation. The use and application of solvents and colouring agents has to comply with national legislation.

Paragraph [14] determines that plastics intended to be used as food contact materials may only be produced of precursors listed in the regulation (positive list of monomers and additives).

Paragraphs [18] and [20] address non-intentionally added substances (NIAS) coming from both precursors and process reaction and degradation products. They are to be risk evaluated if they are assessed to be major contaminations. It is noted that the positive list of chemicals can never contain all possible contaminations.

Paragraph [23] addresses nano particles derived from new technologies. Nano particles exhibit differing physico-chemical properties and are to be risk evaluated case by case.

Paragraphs [25] and [26] deal with migration declaring the overall migration limit (OML) of all possible substances summed up is not to exceed 10 mg/dm^2 material or 60 mg/kg food respectively. The value of 60 mg/kg derives from the assumption that 1 kg food is packed cubically, which leads to 6 dm^2 packaging material/kg food. In case of smaller packages (meaning that the relation of food surface to food volume is higher) as well as packaged baby food the overall migration limit of 60 mg/kg food has to be complied with.

Paragraphs [29] – [32] address the declaration of conformity that has to be compiled at all production and trade levels.

In articles 5 and 6 (chapter II) the scope of application of the regulation is defined.

Articles 9 - 12 define the specifications for the listed substances; these are specific migration limits (SML), overall migration limits (OML), restrictions of application.

Articles 13 and 14 refer to multi layer materials with or without functional barrier.

Article 15 constitutes the declaration of conformity at all levels of production and trade except the retail sale.

Articles 17 and 18 define the evaluation of migration values in respect to the concerned foods and the kind and size of the used packaging.

Annex I gives the positive list of the European Union of allowed substances (about 885 substances at the moment) stating eventual SML's and restrictions.

Annex III determines the food simulants to be used in migration testing and the classification of the foods in respect to the food simulants to be utilized.

These simulants are as presented in table 3.1.

Name	Description	Remark
Simulant A	10 % (v/v) Ethanol	
Simulant B	3 % (m/v) Acetic acid	
Simulant C	20 % (v/v) Ethanol	
Simulant D1	50 % (v/v) Ethanol	
Simulant D2	Vegetable oil	Distribution of fatty acids within a specified range
Simulant E	Poly(2,6-diphenyl-p-phenylene oxide), particle size: 60-80 mesh, pore size 200 nm	= Tenax®TA, PPPO

Table 3.1: Food simulants to be used in migration testing as defined in Regulation EU 10/2011

Annex V defines the migration test conditions to be complied with in respect to the declaration of conformity. It is differed between testing of food that had already been in contact with the packaging material and materials that had not been in contact with food so far.

In the first case the food has to be tested for specific substances. In the latter SML and OML are determined in food simulants.

The test conditions comprise in specific contact time and contact temperature of food contact material and food simulant whereby accelerated migration is conducted to access long time storage. Accelerated migration tests are conducted at higher temperatures as defined in chapter 2 of annex V.

A corresponding list of test conditions is given for the determination of the overall migration (chapter 3 of annex V)

In addition several amendments to the Regulation (EU) 10/2011 have been released, namely: Commission Regulations (EU) No's 284/2011, 321/2011, 1282/2011 and 1183/2012 (24) (25) (26) (27).

It can be recognized that the regulation EU 10/2011 tries to address as many probable occurrences as possible. This is also supported by the fact that the regulation EU 10/2011 is also applicable on all plastic materials intended to come into contact with food i.e. during production, transport or storage of food. Future amendments may have to address issues concerning multi layer and multi material articles in more detail especially the role of adhesives between these layers or the migration behaviour of adhesives between the single layers as well as from labels on the packaging.

3.4 Migration

As already pointed out above migration out of food contact materials is a relevant issue. Regulations, directives and risk evaluations have been published about the chemicals utilized and incorporated in the food contact materials.

Migration is generally a transport process of matter from one layer to another driven by the force of differences of the chemical potential μ and striving for a state of equilibrium (28). This process can be illustrated as in the following illustration (figure 3.1):

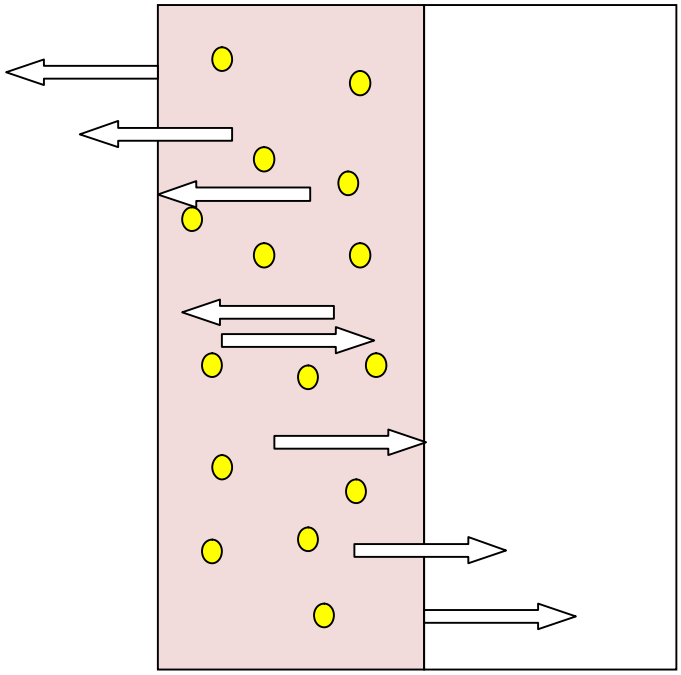

Figure 3.1: Schematic illustration of a migration process

Migration is a 3-dimensional process and of course occurring in all directions. Substances from the environment migrate into a material as well as for instance flavours or other ingredient components can migrate from the food into a packaging material which is also unwanted. In (28) this is summarized as food-packaging interaction.

Migration from plastics into food is generally accepted as being a diffusion process following the second law of Fick. However younger research on food structure led to results of migration within food that is not supported by Fick's second law. Hence another theory for the migration of oily phases has been proposed, which is the transport through capillary flow (5). This theory has been questioned because it could not be confirmed experimentally and has since been modified to allow for the influence of structural parameters, such as the particle form, which affects the diffusion process leading to differences in the migration rates (29).

It has to be remembered the fact that many additives exhibit good solubility in fat (oil) leading to high partition coefficients of the system polymer/fat phase hand hence promoting the migration of these substances into fatty materials. A concise deduction of the relationship between solubility coefficients and partition coefficient between different phases is presented in (28).

A further consideration is the interaction of the food stuff with plastic materials, which results in swelling and a change of mechanical properties of the polymer. All these factors mean that the process of migration becomes indeed a very complex matter.

Consequently the illustration of figure 3.1 has to be changed to the more complex scheme shown in the following illustration (figure 3.2).

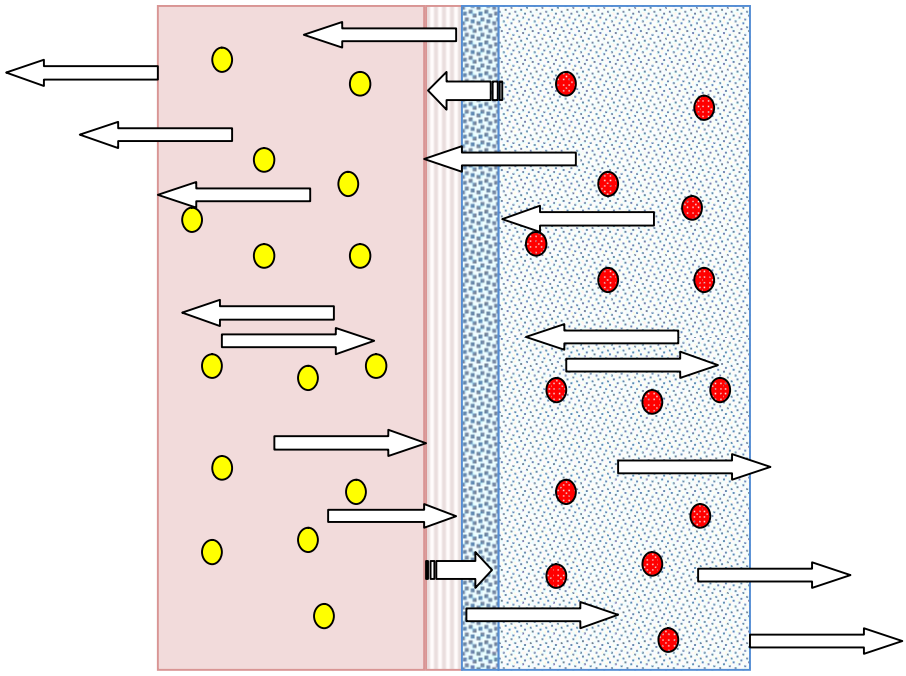

Figure 3.2: Illustration of migration processes of a food – food contact material system

The left (purple) phase represents the plastic material containing migrating additives (yellow dots) with a swelled layer at the interface to the foodstuff. The right (blue) phase represents a (liquid or semisolid) food containing migrating ingredients (red dots) and a layer where a fraction of food contents has formed an own phase at the interface to the (already swelled) plastic material. An accumulation of an ingredient fraction is for example known for fat from milk that adsorb at the polyethylene phase, which is usually non-polar.

Migration into dry foodstuffs:

Dry foods are very often packaged in plastic materials in order to protect them from moisture that would change the texture and promotes microbial deterioration by increasing the water activity in the food. Dry foods are also very multivariate. There are basic foods as flour, sugar, baby food and milk powder, breadcrumbs, rice, pasta, nuts and dried fruits, tea, coffee, cereals, also crackers, crisps, cakes and cookies and many more. Dry foods often present a high surface per mass ratio as many of them are in pieces or bulk material. Dry foods often have less direct contact with the packaging material so it could be assumed that migration from packaging does not play a big role.

In contrast many tests with dry foods resulted in different findings though. These findings finally led to the adoption of the food simulant PPPO (Tenax ®), into the regulation EC 10/201, which is to apply in migration testing of dry foodstuffs (overall migration).

3.5 Risk Assessment

Risk assessment is a highly topical expression that has developed from today's society's demand for safety assurance in all facets of life. Especially consumers have to be secured from possible risks coming from the ever growing quantity of products into their lives. Especially risks that threaten life or the health of life or the eco-system are addressed in new regulations and standards. But in trying to keep all possible risks under control we still have to be aware that authorities will always run after innovations and inventions.

Risk assessment in relationship with the present work can be regarded in at least two aspects.

1. the aspect of migration in general
2. the aspect of the migrating substances

Migration of a single substance depends on the system it is migrating from. This comprises the kind of material. For example the migration rate from a PE film will be higher compared to migration from a PS film. This is due to the degree of crystallinity, steric hindrance and mobility of the polymer chains, which influences the coefficients of diffusion (30).

Then of course migration depends strongly on the thickness of the material. The migration process is also highly temperature dependent hence the common temperature of use has to be considered. Additionally the food to be brought in contact with the material influences migration as it can interact with the material resulting in an undesirable change of properties. So when assessing the risks coming from migration in general all the named parameters have to be kept in mind.

Addressing the risk emerging von the migrating substances numerous other aspects have to be regarded.

First the concentration of a substance has to be taken into account. The higher the concentration of a substance the more will migrate into the food. Effects of molecular weight, polarity and solubility of the substances contribute to migration rate.

The main aspect is a possible toxicological effect induced by migrating compounds. These could be (smaller) acute effects like temporary irritation of skin, eyes or respiratory tract without any further effects. But some compounds can induce more hazardous or even persistent effects on human health or the environment. Human health hazards are severe acute effects, induced chronic diseases or damage on organs. Furthermore cancerogenity, mutagenity, teratogenity and endocrine disrupting effects can occur.

In order to assess the toxicological risks of substances (or groups of substances) a number of tests have been developed that can be found in the Council Regulation (EC) 440/2008 (31).

In addition to the toxicological evaluation the possible exposure has to be estimated. Combining both - toxicological risks and estimated exposure - an eventual risk is evaluated (32). If there are hazardous effects they are classified depending on the amount of a substance that leads to a negative effect.

The classes are (32)

NOAEL: **n**o **o**bserved **a**dverse **e**ffect **l**evel, meaning the highest dose without toxic effects

LOAEL: **l**owest **o**bserved **a**dverse **e**ffect **l**evel, meaning the lowest dose that lead to observable toxic effects.

3.6 Food Structure

Food structure is very much dependent on its constituents and by the way the food is processed. The variety of foods and food ingredients causes therefore countless constitutions of food structures.

The structure of food is important in terms of technical processing, but also for consumer acceptance and mouth-feel, which is often referred to as texture. Last but not least food structure has an impact on the bioavailability of nutrients and is therefore of relevance to nutrition, which is particularly relevant to designed foods.

In conclusion it can be stated that the structure of food determines its physico-chemical properties and also the way round the chemical and physicochemical properties determine structure properties.

Figure 3.3 shows an overview about the approximate scales of structural elements of foods, adapted from (33).

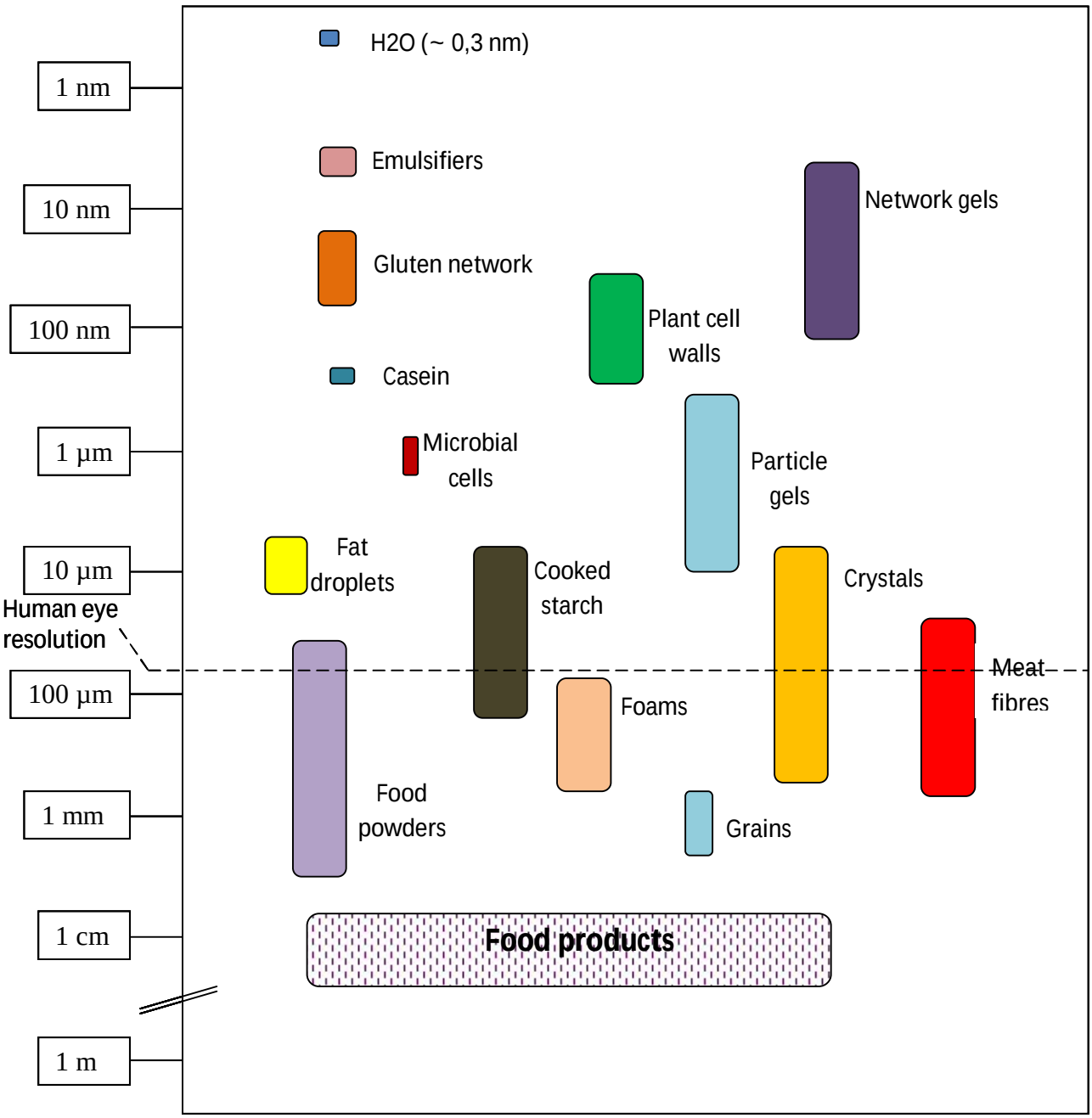

Figure 3.3: Approximate scales of structural food elements
[adapted from: Aguilera (2006), *J Sci Food Agric* 86: 1147-1155 **(33)**]

Approaches to structure characterization

As presented in figure 3.3 structural elements of foods are largely below the human eye resolution that can be indicated as about 0,5' (arc minutes, circular measure), which equates to about 80 µm at a distance of 25 to 50 cm (33) (34). In order to study structural elements they have to be made visible somehow.

Today several methods exist to characterize food structure and make it visible. All microscopic methods are to mention as well as scanning methods. Relatively new methods are the optical coherence

tomography (OCT) and photo acoustic methods (PAT and PAM). The tomographic methods allow for the option of looking 3-dimensional into a sample for instance OCT. These new methods work non-destructive but still offer poor resolution compared to scanning microscopic techniques (35).

Table 3.2 summarizes the maximum resolution of imaging (microscopic and tomographic) methods.

Method	Resolution d
Atomic force microscopy AFM	d ~ nm
Electron microscopy	500 nm > d > 0,5 nm
Scanning light microscopy	d > 50 nm
Light microscopy	d > 500 nm
Photo acoustic microscopy PAM	d > 1µm
Optical coherence tomography OCT	10 µm > d > 1 µm
Photo acoustic tomography PAT	d > 100 µm

Table 3.2: Resolution scales of microscopic methods

However the drawback of these techniques is that they only image the surface of the samples. The tomographic techniques are an exemption within the imaging methods but they are not to count to classical microscopic or scanning techniques and their resolution is poor.

Another disadvantage is the small sample section that is usually viewed unless much time and effort is invested. So the chance to get an impression of the whole sample or at least a good average is reduced.

Furthermore sample preparation can be difficult as for instance electron microscopy is operated under evacuated conditions and samples containing high water contents need to be prepared in an appropriate way. This could be coating or dry freezing of the samples, which is bound to structural changes.

Another approach to food structure is the measurement of (macroscopic) physico-chemical properties or structure relating properties: not the micro-structural elements themselves are made visible but their macroscopic effects are measured.

Visco-elastic properties are determined by the inner structure and the interaction of structural elements. These properties are usually determined using rheology and are well suited for examining semisolid food samples.

Relevant characteristics comprise viscosity η and potential yield stress τ_0, storage and loss moduli G' and G'' that reflect the distribution of energy within the food, which of course is determined by its structural composition. Furthermore the linear visco-elastic range can be determined. The linear visco-elastic range describes the robustness of visco-elastic structure and is characterised by the energy required to make the material flow. Another parameter of interest, the cohesive energy density, can be calculated from the storage modulus and the yield-deformation of the sample.

The advantage of this approach is that the sample as a whole in its 3-dimensionality is viewed. There is no special sample preparation, however careful sample handling is indispensable as the structures formed by the named structural elements are very sensitive to any energy input.

This is the approach chosen for this work as some of the studied foods were semi-solid foods with high water contents.

Dry foods and powdered foods in particular need to be approached differently. Here again microscopic techniques have to be stated.

However in the context of the studies of this thesis another approach was searched for especially in the case of the selected foods – flours and sugar.

Particle sizing, more precisely the determination of the particular particle size distribution of the selected foods was assumed to be an appropriate technique to obtain a characteristic that can be linked to migration.

4 Materials and Methods

4.1 Materials

4.1.1 Selected foods

4.1.1.1 Semisolid foods – ketchup and dairy products

4.1.1.1.1 Ketchup

Ketchup was chosen as a model food representing fruit and vegetable dispersions and spicy sauces.

Ketchup is a spicy sauce made of hot break or cold break tomato paste, pulp or juice. It can be seen as a dispersion of tomato cell fragments in an aqueous solution of salt, sugar (or sweeteners) and vinegar (36). In order to supply a stable dispersion thickeners can be added like (modified) starch or gums (xanthan, guar). Several studies have been made dealing with the rheological properties and their dependencies on varying characteristics like soluble solids, insoluble solids or varying content of different hydrocolloids (37) (38) (39) (40) (41) (42). Time and temperature dependencies have also been described (43). Migration into ketchup (one sample) was also tested in the already mentioned FOODMIGROSURE project (3).

Six different ketchups were purchased at local supermarkets. They were selected for the most distinguishing composition as could be learned by the labelled nutrition facts. Some of the purchased ketchups contained thickening agents such as (modified) starch (ketchups C, D, E, F) and in one case with xanthan gum in addition (ketchup C). Two ketchups were so called “light” products or labelled as “without addition of sugar” (D, F) but contained sucralose (ketchup D) or sucralose and Acesulfam K (ketchup F) as sweeteners. Table 4.1 informs about the used samples and their composition as labelled on the packaging.

4.1.1.1.2 Dairy products

Dairy products were chosen as model foods representing protein containing hydro-colloidal gels. The casein fraction of the milk proteins form micellar protein networks when the pH is decreased which is usually achieved by fermentation. These networks are responsible for gel structure and texture. Depending on the fat content the protein network is more or less strong with the lipid globules acting as spacer and attenuator between the protein micelles (44) (45) (46).

The products chosen out of the group of dairy products were natural stirred yoghurts containing either 1% or 3,6% fat, buttermilk containing 1% fat and sour milk containing 3,5% fat. Except for the buttermilk all products are acidified dairy products, containing live cultures of different fermentative species.

Of each kind two different products were purchased at local supermarkets representing the Austrian market. Table 4.2 informs about the used samples and their composition as labelled on the packaging.

4.1.1.2 Dry foods – wheat flour and sugar

4.1.1.2.1 Wheat flour

Wheat flour represents a highly complex food. Being a basic foodstuff in many countries it contains all nutritional relevant compounds: carbohydrates, protein, lipids, vitamins and minerals. The contents vary with the milling grade with a high milling grade reflecting whole wheat flour and a low milling grade reflecting fine white flour. Whole wheat flour shows higher contents of protein, lipids, minerals and vitamins while fine white flour shows a higher fraction of carbohydrates (44).

Eleven different wheat flours were bought at local supermarkets. Three different types (fine -“glatt”, coarse - “griffig” and all purpose - “universal”) and two different milling grades (480, 700) of flours were selected.

4.1.1.2.2 Sugar

Sugar is the term commonly used for saccharose, a disaccharide consisting of fructose and glucose (O-β-D-fru-(2→1)-α-D-glc). Saccharose occurs in many plants in varying concentrations serving as energy storage. The most important plants are sugar-beet root (*Beta vulgaris spp. Vulgaris var. altissima*) and sugar cane (*Saccharum officinarum*). The saccharose is extracted from the plants, re-crystallized and sold in different crystal sizes and refining grades (44).

Sugar was purchased in three different particle sizes: coarse crystal sugar, fine crystal sugar and powdered sugar. All of them were highly refined white sugars.
Table 4.3 gives an overview about the examined samples within the group of dry foods.

No	Description	Composition (as listed on packaging)	Nutrition facts (as listed on packaging)
A	Tomato ketchup "Bio"	Tomatoes (180 g/100 g ketchup), invert sugar syrup, spirit vinegar, salt, spices (containing celery), onion powder, garlic powder	Contents in 100 g: Energy: 536 kJ/126 kcal Protein: 1,5 g Carbohydrates: 28,9 g (thereof are sugars: 26,8 g) Fat: 0,2 g Fibres: 1,5 g Sodium: 1,2 g
B	Tomato ketchup	Tomato paste (73%), glucose-fructose syrup, spirit vinegar, salt, spice extracts	Contents in 100 ml (= 116 g): Energy: 563 kJ/133 kcal (= 485 kJ/115 kcal/100 g) Protein: 1,9 g (= 1,6 g/100 g) Carbohydrates: 29,8 (= 25,7 g/100 g) Fat: 0,2 g (= 0,17 g/100 g)
C	Tomato ketchup	Tomatoes (230 g tomatoes/100 g ketchup.), water, sugar, spirit vinegar, salt, modified corn starch, spice flavour, thickening agent: xanthan gum, preservative: sodium benzoate	Contents in 100 g: Energy: 385 kJ/91,6 kcal Protein: 1,5 g Carbohydrates: 20,4 g Fat: 0 g
D	Tomato ketchup "without sugar"	Tomato paste 53%, water, modified starch, salt, acetic acid, concentrated beet root juice, acidifier: citric acid, lactic acid, spices, spice extracts, sweetener: sucralose	Contents in 100 g: Energy: 159 kJ/38 kcal Protein: 1,5 g Carbohydrates: 7 g (thereof are sugars: 4 g) Fat: 0,1 g Fibres: 1 g Sodium: 1,2 g
E	Tomato ketchup "mild"	Tomato paste (71%), sugar, spirit vinegar, modified starch, salt, acidifier: citric acid, spice extracts, preservative: potassium sorbate	Contents in 100 g: Energy: 575 kJ/138 kcal Protein: 3,3 g Carbohydrates: 29,3 g Fat: 0,1 g
F	Tomato ketchup "light"	Tomato paste (82%), water, spirit vinegar, salt, modified starch, acidifier: citric acid, preservative: potassium sorbate, spice extracts, sweeteners: sucralose, acesulfam K)	Contents in 100 g: Energy: 298 kJ/71 kcal Protein: 3,7 g Carbohydrates: 12,6 g (thereof are sugars: 10,2 g) Fat: 0,2 g Fibres: 2,3 g Sodium: 1,2 g

Table 4.1: List of ketchups and labelled information on composition and nutrition facts

No	Description	Nutrition facts (as listed on packaging)
1	Natural stirred yoghurt 1% fat - A	Contents in 100 g: Energy: 259 kJ/61 kcal Protein: 4,9 g Carbohydrates: 7,5 g (thereof are sugars: 7,5 g) Fat: 1,0 g (thereof are saturated fatty acids: 0,6 g) Fibres: 0 g Sodium: 0,02 g
2	Natural stirred yoghurt 1% fat - B	Contents in 100 g: Energy: 192 kJ/45 kcal Protein: 4,2 g Carbohydrates: 4,3 g Fat: 1,0 g
3	Natural stirred yoghurt 3,6% fat - A	Contents in 100 g: Energy: 317 kJ/76 kcal Protein: 4,1 g Carbohydrates: 4,8 g (thereof are sugars: 4,8 g) Fat: 3,6 g (thereof are saturated fatty acids: 2,1 g) Fibres: 0 g Sodium: 0,04 g
4	Natural stirred yoghurt 3,6% fat - B	Contents in 100 g: Energy: 285 kJ/68 kcal Protein: 4,1 g Carbohydrates: 4,8 g (thereof are sugars: 4,8 g) Fat: 3,6 g (thereof are saturated fatty acids: 2,2 g) Fibres: 0 g Sodium: 0,04 g
5	Natural buttermilk 1% fat - A	Contents in 100 ml: Energy: 195 kJ/46 kcal Protein: 3,7 g Carbohydrates: 4,6 g (thereof are sugars: 4,6 g) Fat: 1 g (thereof are saturated fatty acids: 0,6 g) Fibres: 0 g Sodium: 0,05 g
6	Natural buttermilk 1% fat - B	Contents in 100 ml: Energy: 166 kJ/39 kcal Protein: 3,6 g Carbohydrates: 4,0 g Fat: 1 g
7	Sour milk 3,5% fat -A	Contents in 100 g: Energy: 263 kJ/64 kcal Protein: 4,1 g Carbohydrates: 4,1 g (thereof are sugars: 4,1 g) Fat: 3,5 g (thereof are saturated fatty acids: 2,5 g) Fibres: 0 g Sodium: 0,05 g
8	Sour milk 3,5% fat - B	Contents in 100 ml: Energy: 252 kJ/60 kcal Protein: 3,3 g Carbohydrates: 3,9 g Fat: 3,5 g

Table 4.2: List of dairy products and labelled information on composition and nutrition facts

Sample No	Food	Type	Milling grade
F1	Wheat flour brand A	coarse (griffig)	480
F2	Wheat flour brand A	fine (glatt)	480
F3	Wheat flour brand B	all purpose (universal)	480
F4	Wheat flour brand B	glatt fine (glatt)	480
F5	Wheat flour brand C	coarse (griffig)	700
F6	Wheat flour brand C	all purpose (universal)	480
F7	Wheat flour brand C	fine (glatt)	700
F8	Wheat flour brand D	coarse (griffig)	480
F9	Wheat flour brand D	all purpose (universal)	480
F10	Wheat flour brand D	fine (glatt)	700
F11	Wheat flour brand E	fine (glatt)	480
S1	Sugar	powdered	--
S2	Sugar	fine crystal	--
S3	Sugar	coarse crystal	--

Table 4.3: Overview about selected dry foods

4.1.2 Test films for the migration study

The work on the migration studies conducted for this thesis was started with a LDPE test film produced by Fraunhofer IVV, Freising, Germany which had already been tested successfully in the "FOODMIGROSURE" project. Test film A was employed for the migration study of ketchups. A second test film was produced by Gabriel Chemie GmbH, Gumpoldskirchen, Austria. This test film B was to have the same specifications as test film A but was made of LLDPE (linear low density PE). Test film B was used for the migration studies of dry foods and dairy products. Table 4.4 summarizes the specifications of both test films A and B.

SEM pictures of both films are presented in figures 4.1 and 4.2.

Test film A: LDPE used for ketchups		
Thickness (d)	164 ± 8 µm	
Mass (m)	1,5 ± 0,05 g/dm^2	
Added compounds and concentrations (c)	benzophenone (BP) diphenyl phthalate (DPP)	c(BP) = 450 mg/kg c(DPP) = 561 mg/kg
Area (A) used in migration test	A = 0,08553 dm^2 according to the diameter of the jar (d = 33 mm)	→ c(BP, A) = 57,73 µg → c(DPP, A) = 71,97 µg
Test film B: LLDPE used for dry foods and dairy products		
Thickness (d)	185 ± 7 µm	
Mass (m)	1,7 ± 0,08 g/dm^2	
Added compounds and concentrations (c)	benzophenone (BP) diphenyl phthalate (DPP)	c(BP) = 450 mg/kg c(DPP) = 561 mg/kg
Area (A) used in migration test	A = 0,08553 dm^2 according to the diameter of the jar (d = 33 mm)	→ c(BP, A) = 65,43 µg → c(DPP, A) = 81,57 µg

Table 4.4: Specifications of the test films A and B

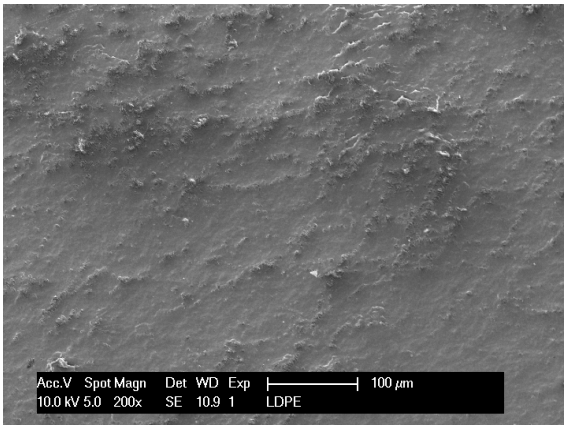

Figure 4.1: SEM picture of test film A (LDPE)

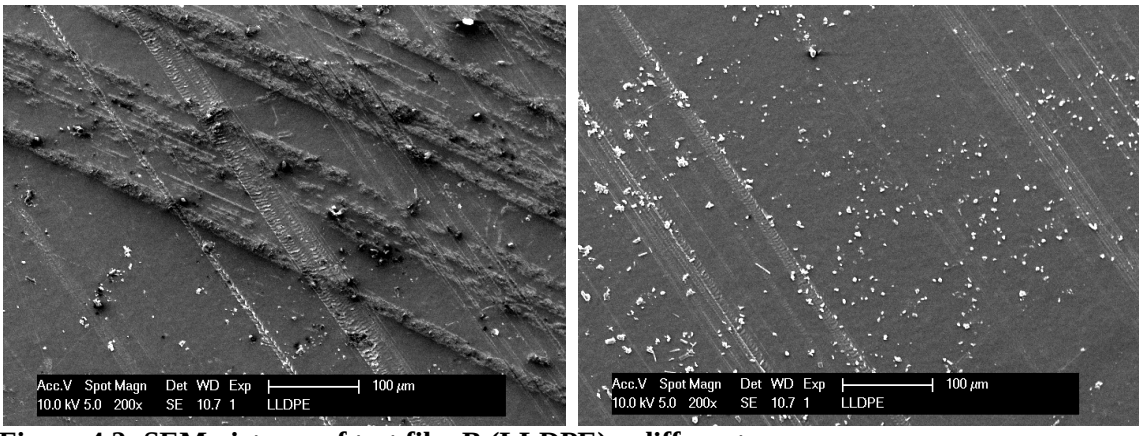

Figure 4.2: SEM pictures of test film B (LLDPE) – different areas

4.1.3 Relevance of the additives benzophenone and diphenyl phthalate

4.1.3.1 Benzophenone (BP)

Benzophenone (CAS – No: 119-61-9) is a colourless crystalline solid at room temperature with a geranium- or rose-like odour. Other nomenclature is benzene, benzoyl-; benzoylbenzene, phenyl ketone; diphenylketone; diphenyl ketone; diphenylmethanone; ketone, diphenyl; methanone, diphenyl-; α-oxodiphenylmethane; α-oxoditane (47). The chemical structure of benzophenone is presented in the following figure 4.3; characteristic physical data are summarized in table 4.5.

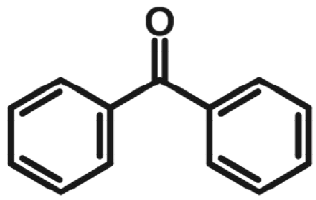

Figure 4.3: Chemical structure of benzophenone

Molecular formula	$C_{13}H_{10}O$	Solubility	0,14 g/l H_2O good in organic solvents (alcohols, acetone, ether, acetic acid, chloroform, benzene
Relative molecular mass	182,22 g/mol	Stability	decomposes on heating producing toxic gases, reactive with strong oxidants
Melting point T_m	48,5°C	Octanol-water partition coefficient log $K_{O/W}$	3,18
Boiling point T_b	305°C	Henry's law constant	$1,9 * 10^{-6}$ atm m^3/mol (25°C)
Flash point	150°C	Vapour pressure	$1,93 * 10^{-3}$ mmHg (25°C)
Density	1,111g/cm^3 (18°C)	Refractive index	1,6077 (19°C)

Table 4.5: Physical characteristics of benzophenone

Benzophenone is widely used in many applications. It is used as UV blocker and fixing agent in perfumes, soaps and cleaning agents. It is applied as an additive in plastics, coatings and adhesive formulations; it is utilized as a photo-initiator in UV cured printing inks. Exhibiting excellent wetting quality for pigments benzophenone is also applied to improve rheological properties of printing inks (47) (48).

In the latest regulation EC 10/2011 a specific migration limit (SML) of 0,6 mg/kg food is specified for benzophenone (2).

Being also a substance found naturally in grapes and other aromatic fruits (47) it is also approved to be used as food flavour without restrictions (49).

Several derivates of benzophenone are also used as UV blockers in sunscreens (47).

Benzophenone and its derivates are assessed as possibly carcinogenic to humans (group 2B) and are declared to be evidently carcinogenic in animals. Benzophenone and its derivates are also declared to exhibit endocrine activity (47). It is classified as hazardous to the aquatic environment, applying hazard statement H410 ("very toxic to aquatic life with long lasting effects") and precautionary statement P273 ("avoid release to the environment") (48).

4.1.3.2 Diphenyl phthalate (DPP)

Diphenyl phthalate (CAS - No: 84-62-8) is a white solid at room temperature; other nomenclature is phthalic acid diphenyl ester; phthalic acid, bis-phenyl ester; 1,2-benzenedicarboxylicacid, diphenylester; phenyl phthalate; diphenyl 1,2-phthalate; diphenyl benzene-1,2-dicarboxylate; diphenyl m-phthalate (50) (51)**.** The chemical structure of diphenyl phthalate is shown in figure 4.4 and some physical data are summarized in table 4.6.

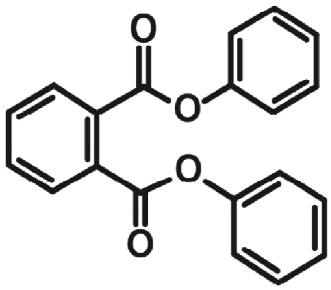

Figure 4.4: Chemical structure of diphenyl phthalate

Molecular formula	$C_{20}H_{14}O_4$	Boiling point T_b	400-405°C
Relative molecular mass	318,32 g/mol	Flash point	224°C
Melting point T_m	74-76 °C	Density	1,28 g/cm^3 (18°C)

Table 4.6: Physical characteristics of diphenyl phthalate

Diphenyl phthalate itself has no relevant functional application apart from being used as internal standard in the analysis of pesticides (52). But its parent compound bis(2-ethylhexyl) phthalate as well as several others such as butyl benzyl phthalate, di-n-hexyl phthalate, di-n-octyl phthalate, dibutyl phthalate and others are commonly used in various applications (as plasticizers in plastics, adhesives, inks and dispersion paints, cosmetics, insecticides, lubricant in pesticide solutions etc.) (53) (54). Diphenyl phthalate is not listed in the GESTIS database of hazardous chemicals.

Acute toxicity of phthalates is rather small (light irritation of mucosa of eyes, respiratory and gastro-intestinal tracts), but not many data are available. Long term toxicity comprises kidney and liver damage. Cancerogenity of phthalates was estimated possible but is now discussed controversially (55) (56).

Endocrine disrupting and teratogenic capabilities are reported for some phthalates (butyl benzyl phthalate, di-n-hexyl phthalate, dibutyl phthalate). Latest results also state a relationship with asthmatic and allergenic diseases caused by phthalates accumulated in dust from leached domestic sources as for instance vinyl flooring (55) (56).

In the latest regulation EC 10/2011 specific migration limits (SML) of some phthalates are given (varying between 0,3 and 30 mg/kg food) and a group restriction of 60 mg/kg food for all phthalates in sum is specified, too. Furthermore phthalates are only to be used as plasticisers in repeated use materials and articles containing non-fatty foods, special restrictions may be applicable for some compounds when used in single-use materials and articles (2).

4.1.4 Materials used for the migration study

4.1.4.1 Chemicals and solvents

Sodium sulphate (CAS: 7757-82-6) p.a by Merck (No 1.06649)

Standards:

Benzophenone (CAS: 119-61-9): sublimed ≥ 99% by Aldrich (No 427551)

Diphenyl phthalate (CAS: 84-62-8): 99% by Aldrich (No 105880)

Internal standards:

4-Methyl-benzophenone (CAS: 134-84-9): 99% by Sigma-Aldrich (No M2,995-9)

Benzophenone – d_{10} (CAS: 22583-75-1): 99,5 atom% D, by CDN isotopes, Canada (No D263)

Benzylbutylphthalate (CAS: 85-68-7): ≥ 97% by Merck (No 821030)

Solvents:

Acetone (CAS: 67-64-1): ≥ 99,8%, ROTIPURAN® by Roth (No 9372.2)

Dichloromethane (CAS: 75-09-2): ROTIPURAN® by Roth (No 6053.2)

Acetonitrile (CAS: 75-05-8): ≥ 99,9%, ROTISOLV® by Roth (No 7330.2)

n-Hexane (CAS: 110-54-3): ≥ 99,0%, ROTIPURAN® by Roth (No 4723.1)

Diethyl ether (CAS: 60-29-7): ≥ 99,5%, ROTIPURAN® by Roth (No 3942.4)

Petrol ether (40 – 60°C, ρ ≈0,65 kg/l): p.a., ROTIPURAN® by Roth (No T173.3)

4.1.4.2 Instruments

Wide mouthed glass jars (50 ml) with twist-off screw caps

Water bath with shaker: Grant OLS 200

Separating funnels (glass, 100 ml)

Micro syringe (glass, 100µl)

Volumetric pipettes (glass, 2 ml, 5 ml, 10 ml)

Erlenmeyer flasks (glass, 100 ml) plus glass plug

Evaporating flasks (glass, 10 ml)

Common glass and laboratory ware

Analytical balance: Sartorius A 120 S

Centrifuge: Heraeus Labofuge 400R

Nitrogen-drying station: Techne DRI-BLOCK® DB-3D

Nitrogen 4.0 (Air Liquide, A)

Filter papers (Schleicher & Schuell, Ref. No. 311644)

Rotational Evaporator: Rotavapor RE 111 and water bath 461 by Büchi, CH

Vacuum pump: Membrane pump LVS 110 Tp ecoflex by ILMVAC

Shaker: Top Mixer AT – 1 by SBS

Gas chromatograph (GC): Agilent 6890

Mass spectrometer (MS): Agilent 5973 inert

Capillary column: Optima δ-3 (30m*0,25µm*0,5µm; Macherey & Nagel No:776421,30)

Carrier gas: Helium 5.0 (Messer Austria GmbH)

4.2 Methods

4.2.1 Physico – chemical characterisation of ketchups and dairy products

In the case of ketchups and dairy products several determinations were performed to gain further information about the composition of the tested foodstuffs. These were determinations regarding the water content as well the water holding capacity of the gels. These determinations were assumed to give additional information about the structure and eventually clues to the migration behaviour. The pH of the samples was also noted.

4.2.1.1 Dry matter and water content

The dry matter and water content respectively were conducted both for ketchups and dairy products.

About 20 grams of sea sand were dried overnight at 102-105°C. 5 grams of the sample was (weighed exactly) added, thoroughly mixed with the sand and dried at 102-105°C until constancy of weight (tolerance 0,1% of the weight loss). Samples were weighed after cooling down in a desiccator for 45 min. Determinations were carried out twice for each sample in the case of ketchups and four times for each sample in the case of dairy products.

4.2.1.2 Water holding capacity (WHC)

Determination of the water holding capacity (WHC) of the ketchups was carried out by weighing about 9 – 10 g sample into a centrifugation tube and centrifuging at 15000 rpm for 20 minutes at room temperature. The WHC was then calculated as proposed by (57).

$$WHC = \left[1 - \frac{w_p}{w_i}\right] \cdot 100$$

Whereby w_p = weight of pellet after centrifugation [g], w_i= initial weight of sample [g]

The determination was carried out three times in the case of ketchups samples and six times in the case of dairy products.

4.2.1.3 Refractive index of serum

In the case of ketchups the refractive index at 20°C (n_D^{20}) of the serum obtained with the centrifugation was determined using an Erma new type Abbe's refractometer (no 16812, Erma Optical Works Ltd., Tokyo, Japan)

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4.2.1.4 pH

The pH of ketchups was determined at 20 ± 2°C with a WTW pH 720 and a WTW SenTix 41 pH electrode. The pH of dairy products was determined at 15 ± 2°C using the same instrument.

4.2.2 Migration study

In principle the migration studies consisted of three steps:

Step 1: incubation of food in contact with the test film for preset times and at defined temperatures

Step 2: extraction of migrated analytes into an appropriate solvent

Step 3: analysis of the analytes by GC-MS

The procedures of each of the three steps were mainly followed the ones already validated in the above mentioned project FOODMIGROSURE and documented by Steiner and Volansky in (58) (3):

The samples (14,25 g - corresponding a standard of 6 dm^2 packaging for 1 kg food) were weighed into glass jars. The test film (cut in corresponding circles) was placed in the lid with aluminium foil as a barrier against possible contamination from the gasket. The jar containing the sample was then closed and turned upside down to bring the samples in contact with the test film (single side contact).

4.2.2.1 Ketchup

4.2.2.1.1 Incubation parameters for ketchups

The samples were incubated at 25 °C for 1, 2, 4, 10 and 22 days and at 70 °C for 2, 4, 8, 16 and 25 hours. In addition both test series were conducted in a static way (samples were kept in a tempered oven) and in a dynamic way (samples were kept in a tempered shaking water bath at 120 rpm). These two methods were conducted to mimic two conditions of storage. The static way was to reflect the storage on the shelf whereas the dynamic method was to reflect transport processes such as in a lorry. The two temperatures were chosen to reflect migration behaviour at moderated temperatures as well as migration behaviour at higher temperatures that could well be reached for short times during transport or storage. As migration is accelerated at higher temperatures a very high temperature (70 °C) was chosen to simulate also a wider time scale. Also it was assumed that ketchup is not degraded at 70 °C.

4.2.2.1.2 Extraction of analytes

The extraction procedure was followed the one introduced by Steiner and Volansky in (58) adopting the method for aqueous liquid foods.

Preparation of the internal standard solution:

As presented in (58) following compounds were selected as internal standards (IS): 4-methylbenzophenone (4-MBP) for the quantification of benzophenone and benzylbutyl phthalate (BBP) for the quantification of diphenyl phthalate respectively. Of each compound 100 mg were weighed into a 100 ml volumetric flask that was filled to the mark with acetone.

This solution was then diluted 1:10 to obtain a final concentration of 100 µg/ml for each standard compound to be used for the analysis. Both solutions were stored refrigerated.

Extraction procedure

After incubation the film was removed from the lid and adherent sample was washed into the jar. 10 ml dichloromethane were pipetted in a 100 ml separating funnel, the sample was then transferred into the funnel with the help of a small amount of deionised water. 100 µl of the internal standard at a concentration of 100 µg/ml was added. The analytes were then extracted by shaking the funnel for 2 minutes. The dispersion was transferred into a centrifuge glass; 2 ml of dichloromethane were pipetted into the funnel to wash and were then also transferred into the centrifuge glass. Centrifugation was conducted at 4500 rpm for 10 minutes in the case of ketchups without starch. Ketchups containing (modified) starch were centrifuged for 15 minutes because the phase separation was not completed within 10 minutes.

After centrifugation the dichloromethane phase (lowest phase) was transferred back to the separation funnel (together with the upper aqueous phase). The remaining tomato fibre pellet was again thoroughly mixed with another 2 ml of dichloromethane and centrifuged under the same conditions as before. The solvent was transferred to the separation funnel and this procedure was repeated once more. The organic (dichloromethane) phase was then dried over sodium sulphate, filtered over a folded paper filter and evaporated to a volume smaller than 10 ml at about 45 °C. The residue was then transferred into a 10 ml volumetric flask and filled to the mark with dichloromethane. The extract was transferred into 2 ml GC vials. Crimp capped vials were stored refrigerated until analysis by GC/MS.

4.2.2.1.3 Analysis of benzophenone and diphenyl phthalate

GC analysis was conducted applying the method described by Volansky (3) in the laboratory of Chemcon GmbH, Vienna who supplied the instrument and help with the data evaluation.

Standard solution:

A stock solution at a concentration of 1 mg/ml of the standards - benzophenone (BP) and diphenyl phthalate (DPP) - was prepared weighing 100 mg of each compound into a 100 ml volumetric flask and filling it up to the mark with acetonitrile. Dilutions of the stock solution were prepared for calibration and recovery tests. The stock solution was stored refrigerated. New dilutions were prepared for every calibration.

GC/MS parameters:

Injection: 275°C - splitless

Temperature program: 90°C → (rate: + 30°C/min) → 330°C (held for 3 minutes)

Carrier gas: Helium at 80 kPa (flow: 25,2 ml /min)

MS: data acquisition mode: SIM (selected ion mode)

Target Ions/ Qualifier Ions: 182/105 (BP), 153/225 (DPP), 196 /119 (IS: 4-MBP), 206/149 (IS: BBP)

Retention time [min]: 6,4 (BP); 7,38 (4-MBP); 8,79 (BBP); 9,53 (DPP)

Data evaluation was carried out using the corresponding software ChemStation by Agilent.

4.2.2.2 Dairy products

4.2.2.2.1 Incubation parameters for dairy products

As dairy products are usually stored refrigerated the samples were incubated in a refrigerator at 5 ± 1°C for 1, 2, 4 and 24 hours.

4.2.2.2.2 Extraction of analytes

The procedure was followed the adopted method for milk and yoghurt drinks introduced by Steiner and Volansky in (58).

Preparation of the internal standard solution:

Instead of 4-methyl –benzophenone benzophenone-d_{10} (BP-d10) was used as internal standard for the quantification of benzophenone because difficulties occurred with the analysis of ketchups. Benzyl butyl phthalate was used for the quantification of diphenyl phthalate as before. Of each compound 100 mg were weighed into a 100 ml volumetric flask that was filled to the mark with acetonitrile.

This solution was then diluted 1:10 to obtain a final concentration of 100 µg/ml for each standard compound to be used for the analysis. Both solutions were stored refrigerated.

Extraction procedure:

After the incubation time the film was removed from the lid and adherent sample was washed into the jar. 20 ml of a 1/ 1 (v/v) mixture of diethyl ether and petrol ether were pipetted in a 100 ml separating funnel, the sample was then transferred into the funnel with the help of a small amount of deionised water. 100 µl of the internal standard [100 µg/ml] was added. The analytes were then extracted by shaking the funnel for 2 minutes. The dispersion was then transferred into a centrifuge glass; 5 ml of the ether mixture were pipetted into the funnel to wash and were then also transferred into the centrifuge glass. Centrifugation was conducted at 4500 rpm for 15 minutes.

After centrifugation 5 ml of the upper ether phase was transferred into a 10 ml flask and the solvent was evaporated at 35 °C within 15 minutes. 2 ml acetonitrile and 2 ml hexane (in order to remove extracted fat) were added and vortexed for 30 seconds. The lower phase (acetonitrile) was pipetted into 2 ml GC vials. Crimp capped vials were stored refrigerated until analysis by GC/MS.

4.2.2.2.3 Analysis of the analytes

GC analysis was conducted as with ketchups described above (3).

Standard solution:

A stock solution at a concentration of 1 mg/ml of the standards of the analytes benzophenone (BP) and diphenyl phthalate (DPP) was prepared weighing 100 mg of each compound into a 100 ml volumetric flask and filling it up to the mark with acetonitrile. Dilutions of the stock solution were prepared for calibration and recovery tests. The stock solution was stored refrigerated. New dilutions were prepared for every calibration.

GC/MS parameters:

Injection: 275°C - splitless

Temperature program: 90°C → (rate: + 30°C/min) → 330°C (held for 3 minutes)

Carrier gas: Helium at 80 kPa (flow: 25,2 ml /min)

MS: data acquisition mode: SIM (selected ion mode)

Target Ions/ Qualifier Ions: 182/105 (BP), 153/225 (DPP), 110/192 (IS: BP-d10), 206/149 (IS: BBP)

Retention time [min]: 6,38 (BP-d10); 6,4 (BP); 8,79 (BBP); 9,53 (DPP)

Data evaluation was carried out using the corresponding software ChemStation by Agilent.

4.2.2.3 Dry foods - wheat flour and sugar

4.2.2.3.1 Incubation parameters for dry food products

All dry food samples were incubated at 40 °C for 1, 4 and 10 days.

4.2.2.3.2 Extraction of analytes

Preparation of internal standard solution:

As presented in (58) following compounds were selected as internal standards (IS): 4-methylbenzophenone for the quantification of benzophenone and benzylbutyl phthalate for the quantification of diphenyl phthalate respectively. Of each compound 100 mg were weighed into a 100 ml volumetric flask that was filled to the mark with acetonitrile.

This solution was then diluted 1:10 to obtain a final concentration of 100 µg/ml for each standard compound to be used for the analysis. Both solutions were stored refrigerated.

Extraction procedure:

The procedure was followed the adopted method for flour and milk powder introduced by Steiner and Volansky (58).

After the incubation time the film was removed from the lid and the sample was transferred into a 100 ml Erlenmeyer flask. 100 µl of internal standard [100µg/ml] was added. 20 ml solvent was added. In the case

of flour n-hexane was used, in the case of sugar dichloromethane was used. The flask was plugged and shaken at 80 rpm and room temperature for one hour. The solvent was then decanted over a folded paper filter, the residue mixed with a fresh portion of 20 ml solvent, shaken and after a few minutes settling time filtered. The flask and the residue in the filter were washed with small portions of solvent. The solvent was then evaporated to less than 10 ml, transferred into a 10 ml volumetric flask and filled to the mark. 2 ml of this extract were transferred into a reagent glass, the solvent was then evaporated to dryness under a flow of nitrogen. 2 ml n-hexane and 2 ml acetonitrile were added to the residue and vortexed for 30 seconds. The lower phase (acetonitrile) was then pipetted into GC-vials. The crimp closed vials were stored refrigerated until GC/MS analysis.

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4.2.2.3.3 Analysis of the analytes

GC analysis was conducted applying the method described by Volansky (3).

Standard solution:

A stock solution at a concentration of 1 mg/ml of the standards of the analytes benzophenone (BP) and diphenyl phthalate (DPP) was prepared weighing 100 mg of each compound into a 100 ml volumetric flask and filling it up to the mark with acetonitrile. Dilutions of the stock solution were prepared for calibration and recovery tests. The stock solution was stored refrigerated. New dilutions were prepared for every calibration.

GC/MS parameters:

Injection: 275°C - splitless

Temperature program: 90°C → (rate: + 30°C/min) → 330°C (held for 3 minutes)

Carrier gas: Helium at 80 kPa (flow: 25,2 ml /min)

MS: data acquisition mode: SIM (selected ion mode)

Target Ions/ Qualifier Ions: 182/105 (BP), 153/225 (DPP), 196/119 (IS: 4-MBP), 206/149 (IS: BBP)

Retention time [min]: 6,4 (BP); 7,38 (4-MBP); 8,79 (BBP); 9,53 (DPP)

Data evaluation was carried out using the corresponding software ChemStation by Agilent.

4.2.3 Rheology

4.2.3.1 Ketchup

Rheological determinations were carried out to characterize the different ketchups regarding their visco-elastic properties. Both rotational and oscillatory rheometry was conducted. As ketchups exhibit shearthinning behaviour due to their gel like structure they were handled with care not to disturb the structure relations that should be determined. All tests were executed at least three times.

4.2.3.1.1 Apparatus

Rheometer: Physica MCR 300 by Anton Paar

Temperature device: water cooled Peltier element

Temperature for all measurements: 25°C

Measuring Geometry: plate-plate 25 mm, gap: 1 mm

4.2.3.1.2 Rotational rheometry

Rotational tests were conducted to describe the flow behaviour and the thixotropic behaviour in the controlled shear rate mode.

4.2.3.1.2.1 Shear thinning behaviour

Shear thinning behaviour was monitored during a linear shear rate ramp after pre-shearing and a settling time. The parameters for the individual measuring steps are shown in table 4.7.

Step 1 – pre-shearing, no data acquisition	
Measurement time	120 s
Shear rate	50 s^{-1}
Step 2 – settling time	
Measurement time	600 s
Shear rate	0 s^{-1}
Duration of measuring point	60 s
Step 3 – shear step	
Measurement Time	60 s
Shear rate	0...300 s^{-1} (linear)
Number of data points	100
Measurement time / data point	0,6 s

Table 4.7: Measuring profile of the flow behaviour tests of ketchups (CSR – mode)

4.2.3.1.2.2 Thixotropy

In order to describe the thixotropic behaviour (time dependent structure rebuilding after applied stress) of the ketchups a 3-interval-thixotropy-test (3ITT) was executed. Table 4.8 provides the parameters of the measuring profile set for this test.
Initial viscosity and rebuilt viscosity data 20 seconds after end of stress step were noted and evaluated.

Step 1 – sample equilibration	
Measurement time	200 s
Shear rate	0,01 s^{-1}
Number of data points	10
Measurement time / data point	20 s
Step 2 – stress step	
Measurement time	50 s
Shear rate	100 s^{-1}
Number of data points	50
Measurement time / data point	1 s
Step 3 – relaxing and structure rebuilding step	
Measurement time	400 s
Shear rate	0,01 s^{-1}
Number of data points	20
Measurement time / data point	20 s

Table 4.8: Measuring profile of the 3-interval-thixotropy-tests (3ITT) of ketchups (CSR – mode)

4.2.3.1.3 Oscillatory rheometry

Oscillatory tests were conducted to describe the visco-elastic properties of the samples in order to gain insight in the inner structure.

4.2.3.1.3.1 Amplitude sweep

The amplitude test characterizes the linear visco-elastic range (LVR). Within this range the sample deformation is fully reversible (at the given or preset frequency). The storage and loss moduli G' and G'' within the LVR provide some information about the relationship of the inner forces and potential energy distribution of the samples. This is supported by the (calculated) cohesion energy density which is a measure for the energy needed to break the structure of a material. Additionally the flow point can be evaluated at the crossover of G' and G''. This flow point is not to be equalled the yield stress τ_0 because at the crossover of G' and G'' the sample has already undergone some irreversible structure changes or destruction. But it can be evaluated as a state of the sample where the potential energies of dissipation and storage are balanced. Table 4.9 informs about the measurement profile of the amplitude sweep performed with ketchups.

Amplitude sweep - step 1 – sample equilibration	
Deformation γ	0,01%
Frequency f	1 Hz
Number of data points	20
Measurement time / data point	10 s
Amplitude sweep -step 2 - measurement	
Number of data points	999
Measurement time / data point	5 s
Deformation ramp	0,01....100 % linear
Frequency	1 Hz

Table 4.9: Measurement profile of the amplitude sweep of ketchups

4.2.3.1.3.2 Frequency sweep

The frequency sweep represents the behaviour of the samples in the high frequency range (short time scales) and the behaviour in the low frequency range (long time scales). It characterises structural changes with time. Structural stability can be described by the frequency test. The measurement profile of the frequency sweep can be learnt from table 4.10.

Frequency sweep –step1: sample equilibration	
Deformation γ	0,01%
Angular frequency ω	100/s
Number of data points	20 (not recorded)
Measurement time / data point	10 s
Frequency sweep - step 2	
Deformation	0,1%
Angular frequency ω	100...0,01/s (linear ramp)
Number of data points	90
Measurement time / data point	10 s

Table 4.10: Measurement profile of the frequency sweep of ketchups

4.2.3.2 Dairy products

Rheological determinations were carried out to characterize the different dairy products with respect to their visco-elastic properties. Both rotational and oscillatory rheometry were conducted. All tests were executed at least in three times.

4.2.3.2.1 Apparatus

Rheometer: Physica MCR 301 by Anton Paar

Temperature device: water cooled Peltier element

Measuring Geometry: plate-plate 50 mm (No: 79045); gap: 1mm

Data evaluation: Rheoplus software by Anton Paar

4.2.3.2.2 Rotational rheometry

Rotational tests were conducted to describe the flow behaviour in the controlled shear rate mode (CSR) and yield stress τ_0 in the controlled stress mode (CSS).

4.2.3.2.2.1 Controlled shear rate (CSR)

Shearthinning behaviour was monitored during a logarithmic shear rate ramp after a short settling time. The parameters for the individual measuring steps are shown in table 4.11.

Step 1 – settling time – no data acquisition	
Measurement time	60 s
Shear rate	0 s^{-1}
Step 2 – shear step	
Measurement Time	60 s
Shear rate	0,01...100 s^{-1} (logarithmic ramp)
Number of data points	41
Measurement time / data point	5.....0,05 s (logarithmic)

Table 4.11: Measurement profile of the CSR tests of dairy products

Data were evaluated by using the Herschel-Bulkley fit.

4.2.3.2.2.2 Controlled shear stress (CSS)

The controlled shear stress mode (CSS) was used to determine the yield stress data τ_0, which can be evaluated directly in the gamma-tau diagram. Yield stress τ_0 was determined applying a logarithmic shear stress ramp with a settling time before. Data acquisition was interrupted at a shear rate of 100 s^{-1}. Details of the measuring profile are presented in table 4.12.

Flow curve: step 1 – settling time – no data acquisition	
Measurement time	60 s
Shear rate	0 s^{-1}
Flow curve: step 2 – stress step	
Shear stress	0,01...100 Pa (linear ramp)
Number of data points	Max 110
Measurement time / data point	2 s

Table 4.12: Measurement profile of the CSS tests of dairy products

4.2.3.2.3 Oscillatory rheometry

Oscillatory tests were conducted to characterise the visco-elastic properties of the samples and provide an insight in the inner structure of the protein networks.

4.2.3.2.3.1 Amplitude sweep

As already described in chapter 4.2.3.1.3.1 executing an amplitude sweep leads to the visco-elastic range (LVR), the range wherein the deformation of the sample is fully reversible. The value of the LVR [%] is a measure for the elastic strength of a sample, which can also be described as the cohesion energy density in addition.
Furthermore the flow point τ_f can be ascertained at the crossover of the storage modulus G' and the loss modulus G''.

Table 4.13 gives an overview about the measuring parameters set for the amplitude sweep.

Amplitude sweep - step 1	
Temperature	5°C
Measuring gap	1 mm
Number of measuring points	2
Duration of measuring point	30 s
Amplitude sweep - step 2	
Temperature	5°C
Number of measuring points	25
Duration of measuring point	No time setting
Deformation program	0,01....100 % linear
Angular frequency	1 rad/s

Table 4.13: Measuring profile of the amplitude sweep of dairy products

4.2.3.2.3.2 Frequency sweep

Data obtained from the frequency sweep illustrate the structure as well as structure changes during short and long time observation.
Table 4.14 gives an overview about the parameters set for the frequency sweep.

Frequency sweep	
Temperature	5°C
Measuring gap	1 mm
Number of measuring points	16 (4points/ decade)
Duration of measuring point	No time setting
Deformation	0,5 %
Angular frequency	100...0,1 rad/s (log)

Table 4.14: Measuring profile of the frequency sweep of dairy products

4.2.4 Particle size distribution of dry foods

Particle size distribution was chosen as the food structure related characteristic that should be related to the migration data. Particle size distribution was determined using laser diffraction automatically evaluated applying the Mie and Fraunhofer theory in the instrument software.

4.2.4.1 Apparatus

Laser Diffractor: Mastersizer 2000 by Malvern Instruments Ltd, UK

Light sources: Red light source: He-Ne: 632,8 nm (max 4mW)

Blue light source: LED: 470 nm (max 0,3 mW)

Dispersion unit: Scirocco 2000 (dry dispersion) by Malvern Instruments Ltd, UK

4.2.4.2 Measurement

The parameters preset for the measurement of the particle size distributions are shown in table 4.15.

Preset parameters	Flour	Sugar
Particle refractive index	1,43	1,51 - 1,52
Absorption	0,1	0,1
Distribution measurement	volume	

Table 4.15: parameters set for the determinations of particle size distributions of dry foodstuffs

All measurements were carried out at least twice but mostly three times.
The data were evaluated using the MS2000 software by Malvern Instruments Ltd. using the Fraunhofer and Mie models.

4.2.5 Modelling of migration

Computational modelling of migration kinetics as for example developed during the FOODMIGROSURE project shall minimize the time-consuming migration testing with the original materials.

The migration data obtained by the practical tests and extractions were compared to the results obtained by a modelling program.

Used software:

SML Advanced version 4.02 ("Prediction of specific migration from multilayer packaging materials into food") by AKTS (Advanced Kinetics and Technology Solutions AKTS AG)

Here the (free) version for one layer packaging was used (59).

This modelling program calculates the specific migration using various approaches to determine the diffusion coefficient of a migrant at a particular temperature. These approaches are the Piringer model, the calculation via the Arrhenius activation energy, a known (determined) value of the diffusion coefficient and a customized version. The program leads through the parameters of the packaging dimensions and the material properties. Furthermore the migrant has to be defined, its concentration in the packaging material and its partition coefficient towards the foodstuff. The migration after a set time period is then calculated.

To model the migration of benzophenone and diphenyl phthalate from the two test films A and B into the different foodstuffs the following parameters were set or assumptions made:

Package geometry:

The standard package geometry was set: The package parameters are summarized in table 4.16.

Package geometry	rectangular (cubic)
Width= height=length	10 cm
Contact surface	600 cm^2 (= 6 dm^2)
Volume of foodstuff	1000 cm^3
mass of foodstuff	1000 g

Table 4.16: Parameters of package geometry

Package properties:

The properties of the package materials, the migrants and the migration conditions have to be known to obtain computed results. Migrants in the practical testing were benzophenone and diphenyl phthalate. The Piringer model was chosen to compute the diffusion coefficient and consequently the modelled migration. This model uses the molecular weight of the migrants to calculate of the diffusion coefficients at particular temperatures. This can be seen from the formula calculating the diffusion coefficients (60):

$$D = 10^4 * e^{[A_p - a*MW - b*(\frac{1}{T})]}$$

Herein is:

D.....diffusion coefficient [cm/s]

A_p.....polymer constant

a, b....correlation factors: a = 0,01 mol/g; b = 10,450 K

MW...molecular weight of migrant [g/mol]

As there were no data available for the partition coefficients of the migrants between plastic and food different values were set for them reflecting high (K = 0) or low solubility (K = 100) of the migrant in the foodstuff. Table 4.17 summarizes the package properties.

Parameter	**Test film A (LDPE)**	**Test film B (LLDPE)**
Thickness [µm]	164	185
Density [g/cm^3]	0,91	0,92
Migrants	Benzophenone: M =182,22 g/mol Diphenyl phthalate: M = 318,32 g/mol	Benzophenone: M =182,22 g/mol Diphenyl phthalate: M = 318,32 g/mol
Initial concentration of migrants [mg/kg]	Benzophenone: 450 Diphenyl phthalate: 561	Benzophenone: 450 Diphenyl phthalate: 561
Partition coefficients K	0; 1; 10; 100	0; 1; 10; 100
Temperature [°C]	25; 70	5; 40
Polymer constant A_p	11,5	11,5

Table 4.17: Package properties

The Piringer model calculates the migration as given in the following formula (60):

$$M_t = c_0 * \rho * L \left(\frac{\alpha}{1+\alpha}\right) * [1 - \sum_{n=1}^{\infty} 2\alpha(1+\alpha)(1+\alpha+\alpha^2 q_n^2) * exp\left(\frac{Dtq_n^2}{L^2}\right)]$$

Herein is:

M_t....migration at time t

c_0....concentration of migrant in polymer

ρ.... density of polymer

L....film thickness

$\alpha = V_F / K*V_P$

V_F....Volume of food

V_P....Volume of polymer

K...partition coefficient

$\tan q_n = - \alpha * q_n$

D...diffusion coefficient

t...shelf time (migration time)

5 Results

5.1 Ketchup

5.1.1 Physico – Chemical Characterisation

The results of the determinations carried out with the ketchups are summarized in table 5.1.

No	Description	Dry matter [%]	Water content [%]	WHC [%]	Water-WHC [%]	n_D^{20} of Serum	pH (21 ± 1°C)
A	Ketchup without thickening agent	32,7 ± 0,1	67,3 ± 0,1	54,9 ± 0,9	12,4	1,3897 ± 0,0005	3,70
B	Ketchup without thickening agent	30,9 ± 0,1	69,1 ± 0,1	54,7 ± 0,7	14,4	1,3859 ± 0,0003	3,88
C	Ketchup containing starch and xanthan	27,4 ± 0,0	72,6 ± 0,0	16,7 ± 0,8	55,9	1,3759 ± 0,0000	3,86
D	Ketchup containing starch and sweetener	13,6± 0,4	86,4 ± 0,4	33,9 ± 0,1	52,5	1,3508 ± 0,0001	3,76
E	Ketchup containing thickening agent	31,4± 0,1	68,6 ± 0,1	32,4 ± 1,1	36,2	1,3838 ± 0,0002	3,81
F	Ketchup containing starch and sweetener	15,1±0,5	84,9 ± 0,5	46,6 ± 0,8	38,3	1,3557 ± 0,0001	3,91

Table 5.1: Results of additional determinations of ketchups

As is evident from the listed results the ketchups can be differentiated quite well. Ketchups A and B led to very similar values for water content, dry matter and water holding capacity (WHC). Ketchups C and E were in the same range as ketchup A and B regarding water content and dry matter but differed in the values of their water holding capacity. Ketchups D and F – the samples without sugar addition – were alike in dry matter and water content respectively but differed in the values of water holding capacity. Interestingly ketchups D and E resulted in similar values for WHC though differing much in the other parameters.

However, regarding the applied calculation to obtain the values of WHC this seems to be questionable. In the calculation of Wu, Hulbert and Mount (57) the supernatant after centrifugation is equalled as the water holding capacity. Another way to see the issue is to determine the difference of water content and supernatant after centrifugation. This would be the part of moisture that can be hold by the gel itself i.e. by structures that are responsible for forming the gel, namely the particles and the hydro-colloidal carbohydrate networks. Regarding the samples this way a different picture is drawn. Ketchups A and B – not being stabilized by hydrocolloid forming carbohydrates - show little ability to fix water. Ketchups C and D exhibit the most distinct ability to immobilize water constantly to a high extent although they were characterized by clearly differing dry matter contents. Ketchups E and F were situated between these two groups. They also differed distinctly in dry matter but were interestingly produced by the same company.

The refractive indices n_D^{20} of the sera obtained by centrifugation also reflected the sugar ratio of the samples as it can be read as Brix grades (°Bx). Here again the data matched the labelled carbohydrate content (or sugar content respectively) very well, resulting in very low values for the samples without added sugar followed by ketchups C and A while ketchups B and E exhibited the highest values.

5.1.2 Migration Study

The precise data are presented on the following pages in tables 5.2 and 5.3 and in figures 5.1 – 5.4.

As will be described the obtained data reveal different pictures for the migration of benzophenone and diphenyl phthalate respectively.

25° C (dynamic)	Migration of benzophenone [mg/dm^2]				
Sample/ time	**t = 1 d**	**t = 2 d**	**t = 4 d**	**t = 10 d**	**t = 22 d**
A	0,137 ± 0,010	0,162 ± 0,009	0,209 ± 0,003	0,244 ± 0,003	0,453*
B	0,169 ± 0,031	0,254 ± 0,009	0,339 ± 0,007	0,484 ± 0,045	0,512 ± 0,046
C	0,181 ± 0,014	0,256 ± 0,006	0,350 ± 0,020	0,538 ± 0,126	0,479 ± 0,047
D	0,144 ± 0,008	0,209 ± 0,036	0,269 ± 0,037	0,355 ± 0,025	0,425 ± 0,005
E	0,168 ± 0,029	0,186 ± 0,008	0,227 ± 0,033	0,414 ± 0,108	0,586 ± 0,002
F	0,220 ± 0,010	0,283 ± 0,089	0,363 ± 0,117	0,599 ± 0,049	0,734 ± 0,023
25° C (static)					
Sample/ time	**t = 1 d**	**t = 2 d**	**t = 4 d**	**t = 10 d**	**t = 22 d**
A	0,168 ± 0,019	0,259 ± 0,022	0,356 ± 0,008	0,482 ± 0,087	0,487 ± 0,116
B	0,173 ± 0,013	0,288 ± 0,013	0,345 ± 0,032	0,460 ± 0,025	0,513 ± 0,075
C	0,195 ± 0,002	0,291 ± 0,013	0,371 ± 0,032	0,557 ± 0,068	0,529 ± 0,040
D	0,163 ± 0,009	0,241 ± 0,001	0,322 ± 0,029	0,246 ± 0,004	0,626 ± 0,070
E	0,170 ± 0,023	0,308 ± 0,002	0,377 ± 0,049	0,565 ± 0,024	0,650 ± 0,027
F	0,181 ± 0,032	0,322 ± 0,061	0,227 ± 0,008	0,505 ± 0,081	0,652 ± 0,023
70° C (dynamic)					
Sample/ time	**t = 2 h**	**t = 4 h**	**t = 8 h**	**t = 16 h**	**t = 25 h**
A	0,141 ± 0,006	0,308 ± 0,046	0,389 ± 0,004	0,425 ± 0,050	0,470 ± 0,008
B	0,190 ± 0,007	0,267 ± 0,006	0,317 ± 0,009	0,348 ± 0,075	0,372 ± 0,035
C	0,211 ± 0,003	0,385 ± 0,036	0,428 ± 0,088	0,408 ± 0,027	0,432 ± 0,025
D	0,197 ± 0,062	0,251*	0,350*	0,200 ± 0,043	0,354 ± 0,132
E	0,199 ± 0,006	0,238 ± 0,032	0,332 ± 0,046	0,192 ± 0,017	0,364 ± 0,008
F	0,218 ± 0,094	0,267 ± 0,014	0,277 ± 0,013	0,205 ± 0,005	0,393 ± 0,063
70° C (static)					
Sample/ time	**t = 2 h**	**t = 4 h**	**t = 8 h**	**t = 16 h**	**t = 25 h**
A	0,209 ± 0,038	0,357 ± 0,031	0,405 ± 0,026	0,397 ± 0,035	0,465 ± 0,001
B	0,205 ± 0,003	0,276 ± 0,003	0,322 ± 0,020	0,344 ± 0,081	0,440 ± 0,004
C	0,208 ± 0,008	0,334 ± 0,050	0,425 ± 0,005	0,412 ± 0,015	0,448 ± 0,054
D	0,138 ± 0,011	0,212 ± 0,029	0,211 ± 0,001	0,216 ± 0,083	0,290 ± 0,008
E	0,156 ± 0,0013	0,230 ± 0,028	0,253 ± 0,026	0,179 ± 0,000	0,431 ± 0,035
F	0,192 ± 0,049	0,274 ± 0,006	0,325 ± 0,042	0,185 ± 0,015	0,454 ± 0,054

Table 5.2: Migration of benzophenone (BP) into ketchups A – F *** only one data point available**

25° C (dynamic)	Migration of diphenyl phthalate[mg/dm^2]				
Ketchup/ time	**t = 1 d**	**t = 2 d**	**t = 4 d**	**t = 10 d**	**t = 22 d**
A	0,063 ± 0,004	0,074 ± 0,001	0,097 ± 0,004	0,149 ± 0,003	0,184 ± 0,004
B	0,055 ± 0,009	0,088 ± 0,024	0,094 ± 0,002	0,159 ± 0,009	0,201 ± 0,015
C	0,045 ± 0,000	0,064 ± 0,003	0,089 ± 0,002	0,161 ± 0,024	0,196 ± 0,003
D	0,067 ± 0,004	0,086 ± 0,009	0,119 ± 0,023	0,175 ± 0,012	0,252 ± 0,033
E	0,070 ± 0,006	0,098 ± 0,008	0,105 ± 0,008	0,158 ± 0,013	0,216 ± 0,013
F	0,078 ± 0,002	0,100 ± 0,004	0,132 ± 0,009	0,178 ± 0,016	0,270 ± 0,020
25° C (static)					
Sample/ time	**t = 1 d**	**t = 2 d**	**t = 4 d**	**t = 10 d**	**t = 22 d**
A	0,067 ± 0,000	0,082 ± 0,002	0,121 ± 0,031	0,160 ± 0,015	0,197 ± 0,033
B	0,057 ± 0,001	0,078 ± 0,009	0,088 ± 0,028	0,154 ± 0,012	0,216 ± 0,009
C	0,066 ± 0,012	0,081 ± 0,013	0,104 ± 0,003	0,154 ± 0,008	0,188 ± 0,004
D	0,068 ± 0,010	0,104 ± 0,005	0,118 ± 0,018	0,136 ± 0,000	0,219 ± 0,006
E	0,064 ± 0,001	0,094 ± 0,000	0,114 ± 0,008	0,178 ± 0,009	0,240 ± 0,025
F	0,071 ± 0,005	0,090 ± 0,018	0,106 ± 0,007	0,196 ± 0,009	0,279 ± 0,003
70° C (dynamic)					
Sample/ time	**t = 2 h**	**t = 4 h**	**t = 8 h**	**t = 16 h**	**t = 25 h**
A	0,106 ± 0,012	0,130 ± 0,020	0,196 ± 0,004	0,264 ± 0,004	0,291 ± 0,005
B	0,090 ± 0,001	0,123 ± 0,009	0,158 ± 0,002	0,209 ± 0,028	0,243 ± 0,015
C	0,073 ± 0,001	0.119 ± 0,005	0,156 ± 0,004	0,210 ± 0,005	0.218 ± 0,000
D	0,111 ± 0,011	0,142 ± 0,006	0,196 ± 0,007	0,253 ± 0,013	0,297 ± 0,045
E	0,113 ± 0,001	0,159 ± 0,004	0,226 ± 0,028	0,218 ± 0,003	0,285 ± 0,002
F	0,147 ± 0,005	0,177 ± 0,002	0,266 ± 0,009	0,270 ± 0,045	0,388 ± 0,002
70° C (static)					
Sample/ time	**t = 2 h**	**t = 4 h**	**t = 8 h**	**t = 16 h**	**t = 25 h**
A	0,095 ± 0,017	0,150 ± 0,011	0,205 ± 0,017	0,245 ± 0,027	0,301 ± 0,006
B	0,078 ± 0,002	0,126 ± 0,001	0,169 ± 0,014	0,209 ± 0,017	0,253 ± 0,013
C	0,071 ± 0,002	0,113 ± 0,017	0,155 ± 0,006	0,211 ± 0,018	0,226 ± 0,023
D	0,080 ± 0,006	0,122 ± 0,005	0,185 ± 0,028	0,236 ± 0,026	0,281 ± 0,003
E	0,097 ± 0,020	0,133 ± 0,002	0,163 ± 0,002	0,226 ± 0,003	0,307 ± 0,018
F	0,104 ± 0,029	0,174 ± 0,002	0,253 ± 0,001	0,250 ± 0,023	0,362 ± 0,000

Table 5.3: Migration of diphenyl phthalate (DPP) into ketchups A – F

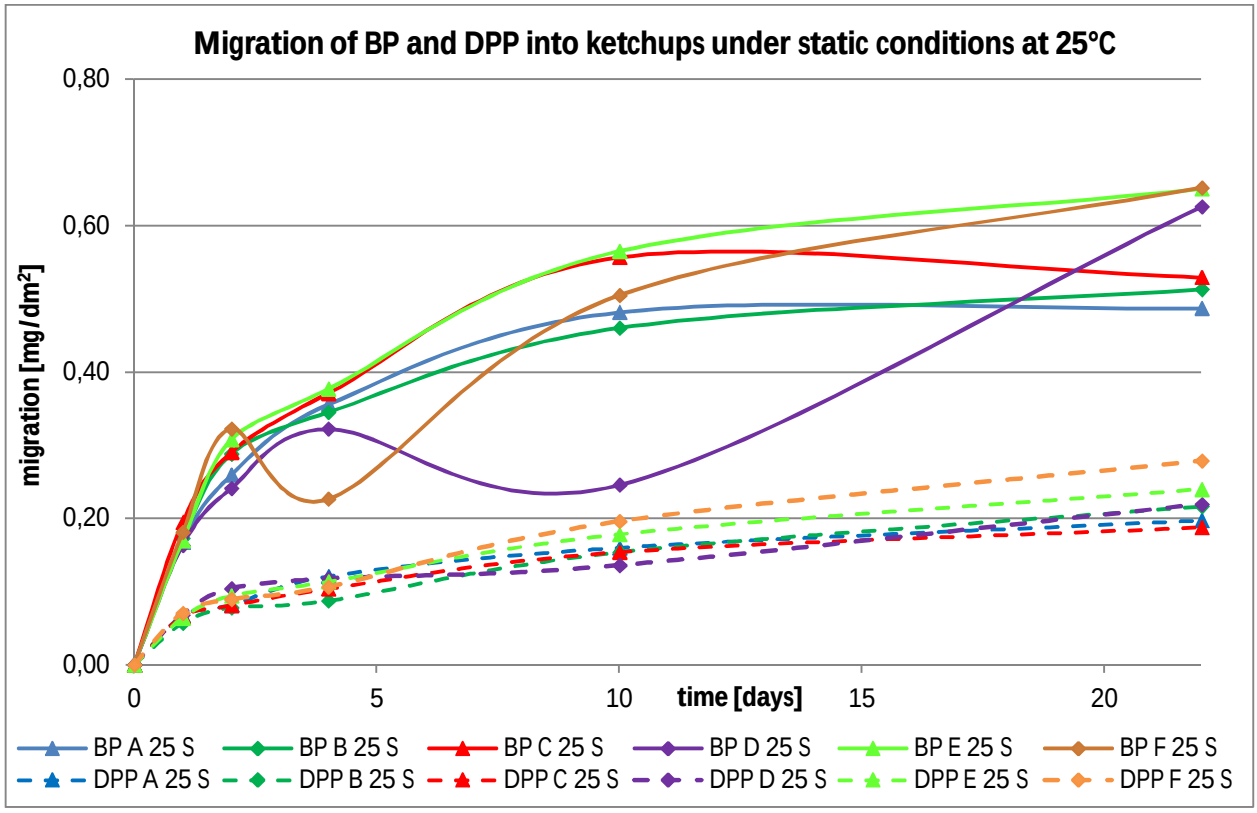

Figure 5.1: Migration of benzophenone and diphenyl phthalate into ketchups under static (S) conditions at 25°C

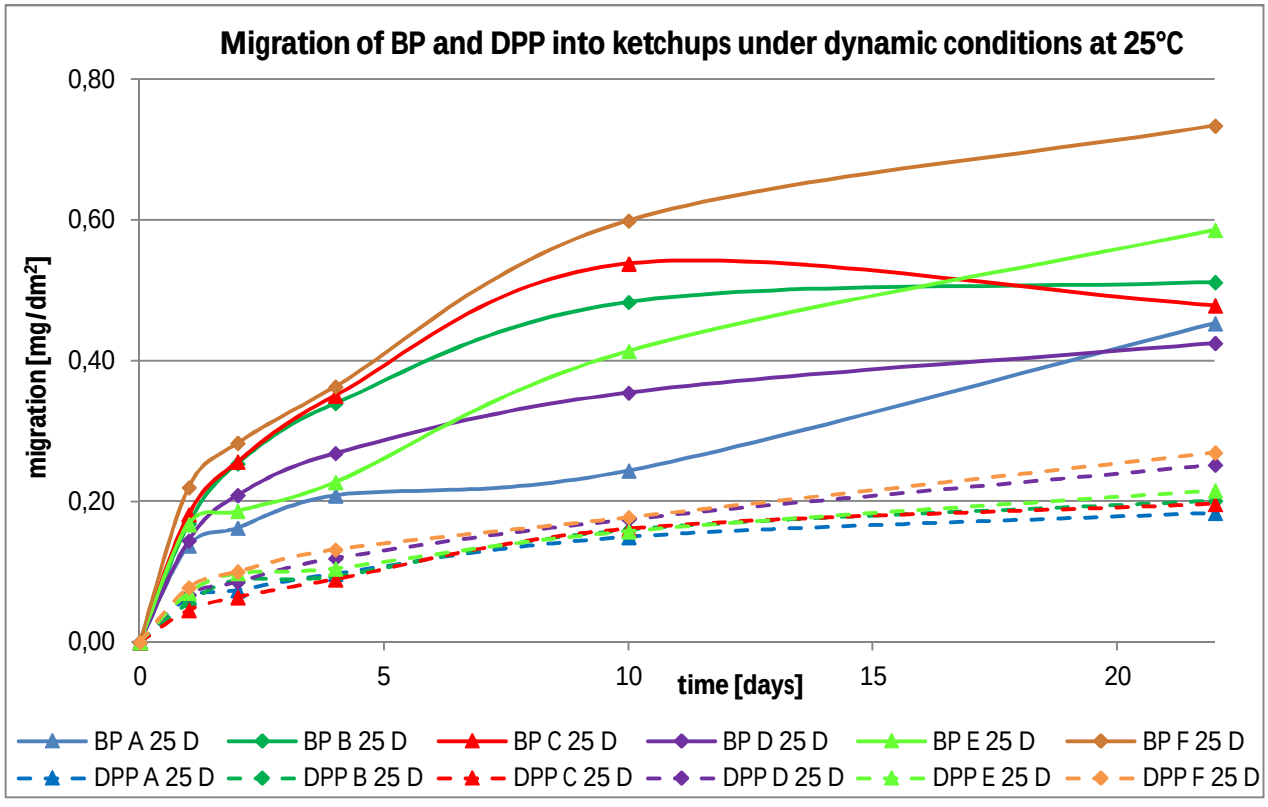

Figure 5.2: Migration of benzophenone and diphenyl phthalate into ketchups under dynamic (D) conditions at 25°C

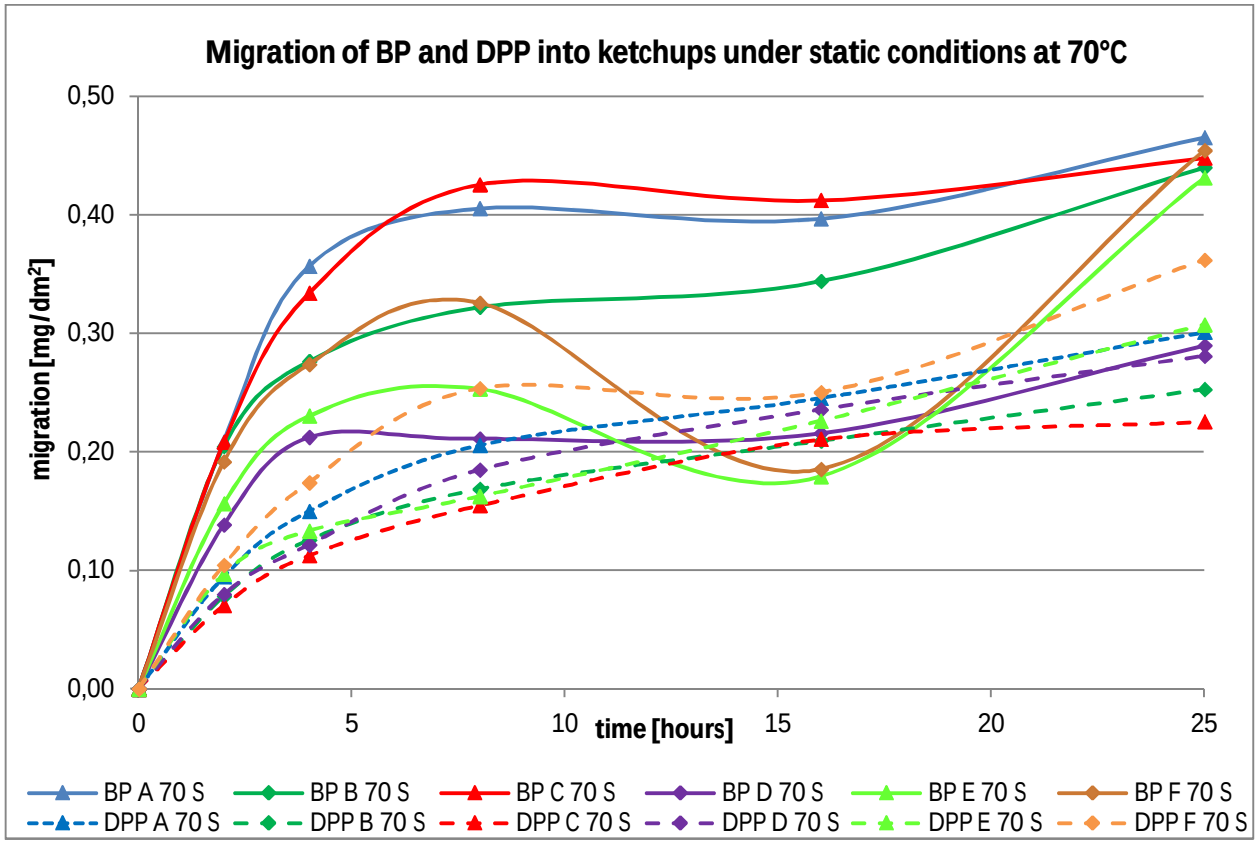

Figure 5.3: Migration of benzophenone and diphenyl phthalate into ketchups under static (S) conditions at 70°C

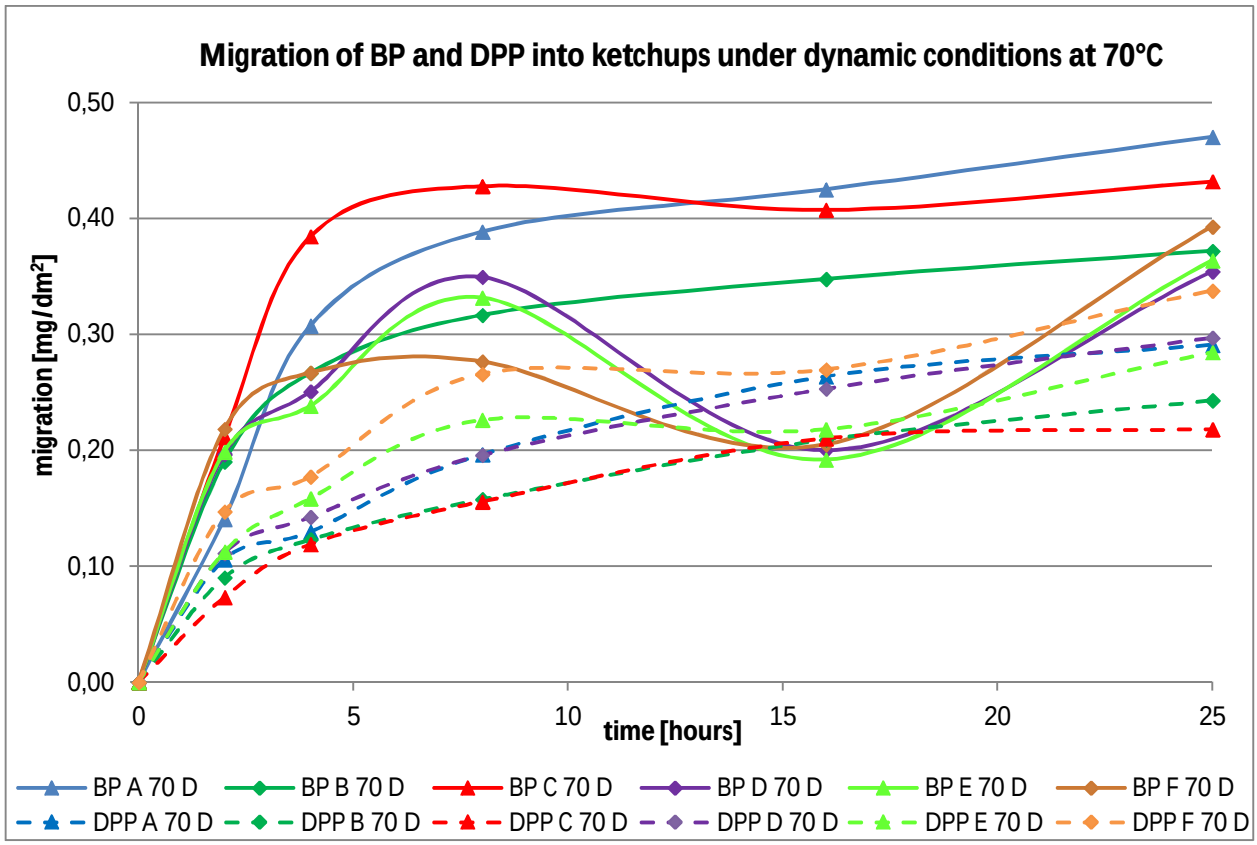

Figure 5.4: Migration of benzophenone and diphenyl phthalate into ketchups under dynamic (D) conditions at 70°C

5.1.2.1 Migration of benzophenone (BP)

Under static conditions at 25°C benzophenone migrated in a very similar range (regarding the standard deviation) within the first day. Then the migration into the different ketchups split and samples containing starch or thickening agents of any kind resulted in a higher uptake of the additive. During the following time this behaviour continued but in the case of the samples containing sweeteners instead of sugar the course was undulating. After 22 days all ketchups containing thickening agents (C, D, E, F) ended up in higher migration uptakes than the two samples (A, B) without starch.

When incubated under dynamic conditions (shaken in a water bath) at the same temperature (25°C) the courses of migration ran differently. After one day of incubation the migration values differed in a wider range than under static conditions and during the following time this behaviour did not change. After 22 days of incubation no specific trend could be recognized. In contrast to the incubation under static conditions the course of all samples was running without major undulating.

Looking at migration at 70°C a quite different picture was revealed. Under static conditions migration after 2 hours of incubation was in a similar range except for ketchups D and E that exhibited lower values. During the following course migration was high in ketchups A and C compared to the other samples. Ketchups E and F again showed an undulating course while ketchup D exhibited the lowest uptake of benzophenone. After a final incubation time of 25 hours migration into all samples except for ketchup D ended at the same level.

Under dynamic conditions the migration ran very similar to the one under static conditions. Ketchup D, E and F were undulating during the course and ketchups A and C showed the highest values of uptake. After 25 hours migration ended in a wider range compared to migration under static conditions. Final migration values of most ketchups were lower than under static conditions.

5.1.2.2 Migration of diphenyl phthalate (DPP)

At 25°C migration of diphenyl phthalate took quite a similar course both under static and under dynamic conditions. From the beginning there was a trend of ketchups D, E and F for a higher uptake of the phthalate compared to ketchups A, B and C. In both studies ketchup F revealed to be the ketchup with the highest migration rates, ketchups A and C were the ones with the lowest migration rates while ketchups B, D and E lay in between.

At 70°C again ketchup F showed the highest values of migrated DPP, both under static and under dynamic conditions. Ketchups B and C showed the lowest uptake. A change occurred to ketchup A that exhibited increased migration values of DPP at this temperature under both incubation conditions.
It has to be noted that at 70°C the course of migration was undulated in the case of ketchups E and F (as mentioned above with benzophenone)

5.1.2.3 Discussion

In the case of benzophenone a ketchup sample whose structure is determined not only by the tomato particles but also by a hydro-colloidal network as formed by (modified) starch (especially when agglutinated) seems to have a positive impact on the migration rate. However at 70°C the (re-) agglutination process is in progress and is probably disturbing the system by changing it continuously. Samples showing higher migration rates of benzophenone when incubated at 25° C resulted in more

diffuse migration values when incubated at 70° C. Another explanation for this result can be the melting point of benzophenone that is at 49°C. So the transport behaviour will differ in an uncontrollable way. This behaviour could not be noticed for DPP.

Although a higher migration rate was anticipated for the samples that were incubated under dynamic conditions this could not be recognized. The values are either in the same range as the results obtained from the static test series or even lower.

At the higher temperature the shift of the migration rates of both additives into ketchup A is remarkable. This was a very "natural" sample without any thickening or sweetening agents. Obviously some change occurred to the sample leading to this increase. Of course it has to be kept in mind that at 70°C forming of Maillard reaction products can already start but were not monitored or determined in this study. In addition the high sugar content of four of the samples could lead to syrup forming at this temperature that is also changing the structural elements of ketchups. Sticky brown lumps were detected on the rim of the jar of some samples, especially of ketchup B.

Detailed migration curves of each of the ketchups can be found in the appendix.

5.1.3 Rheology

All measurements were relative measurements, so no absolute data were ascertained.

5.1.3.1 Rotational rheometry

Rotational tests were conducted in the controlled shear rate mode to describe the flow behaviour and the thixotropic behaviour.

5.1.3.1.1 Shear thinning behaviour

The viscosity curves of the ketchups are shown in figure 5.5. The shear-thinning behaviour of all samples can be recognized and also differences between the various samples. At a shear rate of 300 s^{-1} all ketchups demonstrated viscosities below 1Pas except for ketchup E which lay slightly above this value. It can be seen that ketchups containing starch ended up at higher viscosities than the samples without starch. The samples without sugar lay between the samples with sugar and starch and the samples containing sugar but no starch. Sample B exhibits the most distinct shear-thinning behaviour.

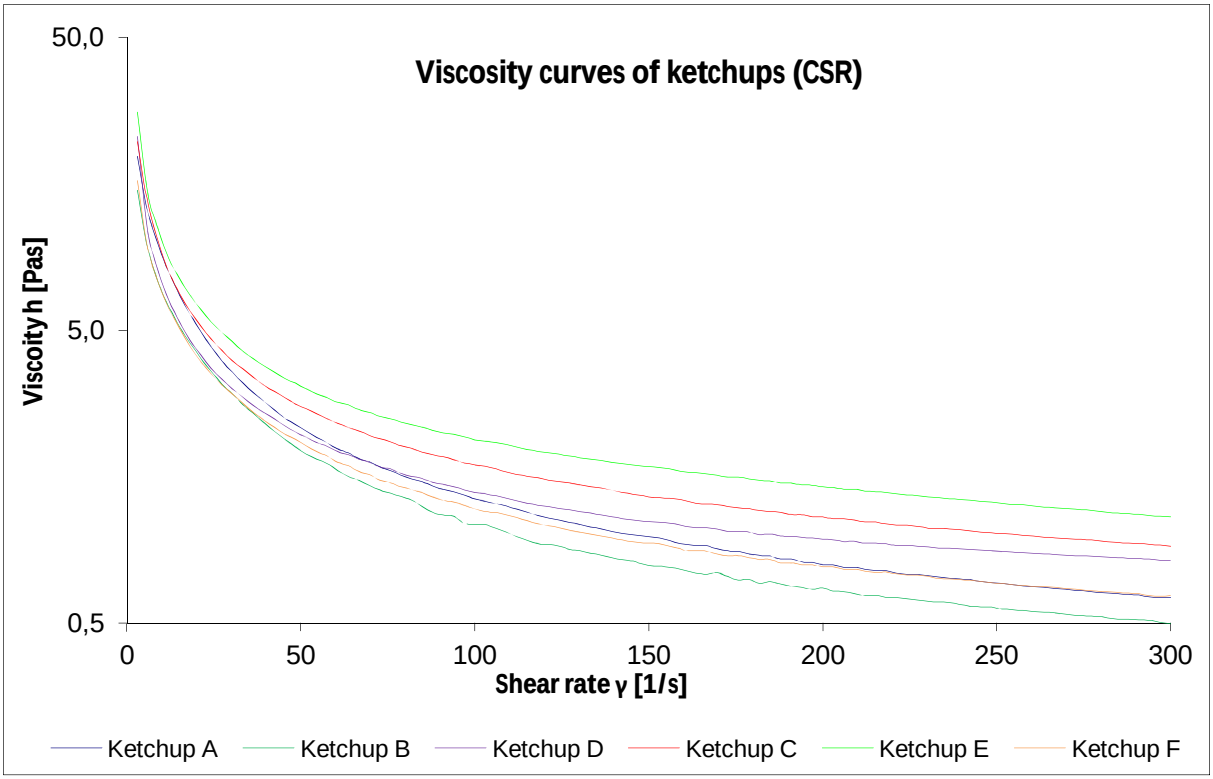

Figure 5.5: Viscosity curves of ketchups

5.1.3.1.2 Thixotropy

The data obtained from the 3-Interval-Thixotropy-Tests (3ITT) are listed in table 5.4 and in figure 5.6. Structure rebuilding was calculated using η_3.

No	Description	η_1 [Pas] (t = 200 s)	η_2 [Pas] (t = 250 s)	η_3 [Pas] (t = 270 s)	Structure rebuilding [%]
A	Ketchup without thickening agent	2360 ± 207	1,03 ± 0,03	844 ± 55	36 ± 2
B	Ketchup without thickening agent	3519 ± 200	1,45 ± 0,07	1916 ± 88	55 ± 3
C	Ketchup containing starch and xanthan	1515 ± 118	1,30 ± 0,02	652 ± 43	43 ± 1
D	Ketchup containing starch and sweetener	3512 ± 163	1,06 ± 0,01	2150 ± 86	64 ± 2
E	Ketchup containing starch	2873 ± 97	1,23 ± 0,04	1667 ± 90	58 ± 1
F	Ketchup containing starch and sweetener	2311 ± 102	0,81 ± 0,01	1345 ± 35	58 ± 1

Table 5.4: Results obtained from the 3-Interval-Thixotropy-Tests (3ITT) of ketchups

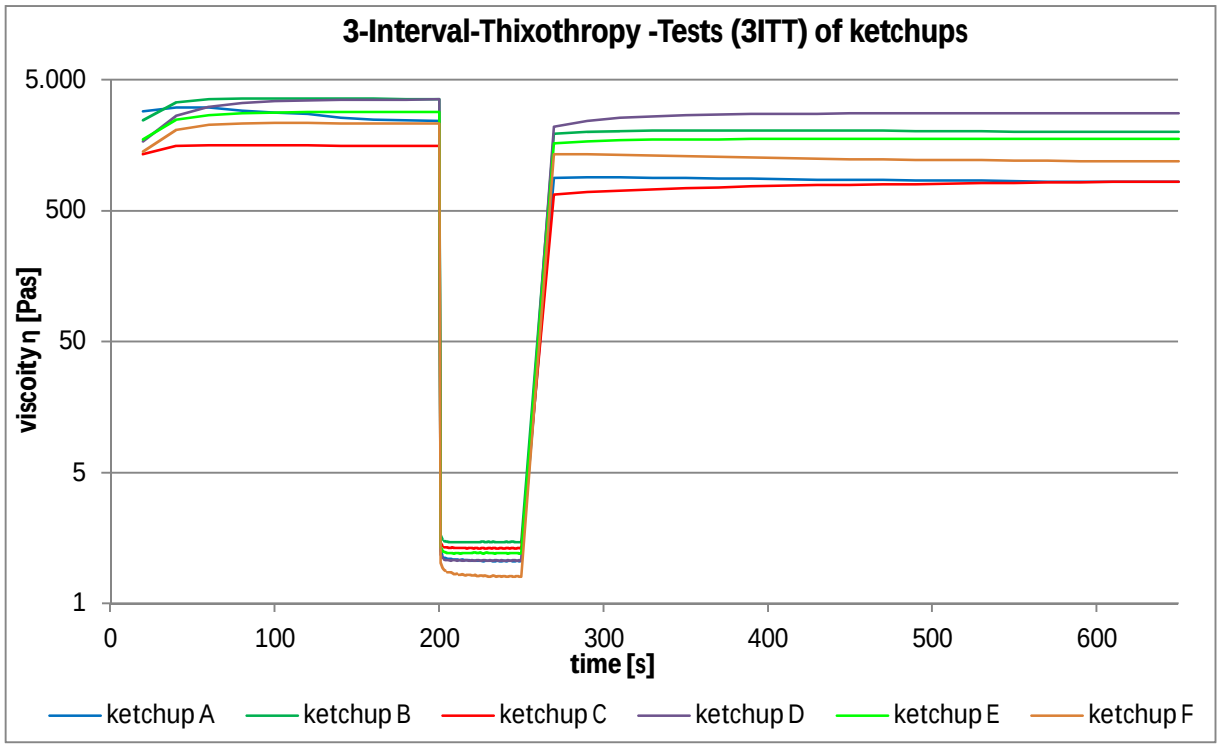

Figure 5.6: 3-Interval-Thixotropy-Tests (3ITT) of ketchups

The thixotropy test is a possibility of characterizing samples in terms of time dependent structure recovery after an applied stress. As can be seen, none of the ketchup samples recovers fully within the regarded time. It can also be recognized that the samples were influenced differently by the applied stress, which was reflected by the varying structure rebuilding rates. During the recovery rest step the ketchups also exhibited different behaviour. Ketchups A and B took a short time to build up their structures followed by a decrease of viscosity at the very low shear rate during the rest steps. This behaviour could already be observed during the first rest step. Because of macroscopic changes of the sample and reasons of comparability with the other samples the time of the first rest step was not prolonged. Ketchups C, D and E continued in the increase of viscosity within the noted time of the second rest step while ketchup F showed an immediate decrease of viscosity after the first noted data point. Because of this variety in structure recovery behaviour the first data point of the third test step (t = 270 s) was evaluated.

It is pointed out that the structure rebuilding rates showed little variance within the single measurements of each sample. It may be noted that the samples without sugar led to the highest structure rebuilding rates, which leads to the assumption that the sugar content has a strong impact on the time dependency of structure rebuilding. Regarding the two samples A and B (containing sugar but no thickening agent) there can be discovered a big difference in the structure rebuilding rates, which needs another explanation in addition. As the composition of these two samples is quite similar there must be a difference of the tomato components that could come from different processing of tomatoes. As described in literature factors like tomato processing, particle concentration or particle form influence water or syrup binding and therefore the rheological properties (38) (61).

Additionally the content of thickening agents like starch and xanthan (also carbohydrates) that act by their ability of binding water influences not only the perceived texture but also the rheological properties and parameters.

5.1.3.2 Oscillatory rheometry

5.1.3.2.1 Amplitude sweep

The results obtained from the amplitude sweeps of the ketchups are presented in table 5.5 and in figure 5.7. These are the linear visco-elastic range (LVR), the storage and loss moduli G' and G'', and obtained at the crossover of G' and G'' the flow point τ_F and the values of G' and G'' at that point. In addition the cohesion energy density (CE) can be determined. The cohesion energy is a measure for the stability of suspension structure. It reflects the amount of energy needed to break the suspension. The higher this value is the more stable is the structure. The cohesion energy is calculated as following:

$$CE = \frac{1}{2} \cdot G'(LVR) \cdot \gamma\,(LVR)^2$$

No	Description	LVR [%]	G’ (γ = 0,5%) [Pa]	G’’ (γ = 0,5%) [Pa]	τ_F (G’ = G’’) [Pa]	G’ = G’’ [Pa]	CE [J]
A	Ketchup without thickening agent	1,00±0,02	701 ± 1	173 ± 3	21,5 ± 0,7	264 ± 0	353 ± 15
B	Ketchup without thickening agent	0,53±0,01	1065 ± 7	328 ± 4	15,0 ± 0,3	435 ±12	166 ± 9
C	Ketchup containing starch and xanthan	0,92±0,07	564 ± 3	157 ± 2	28,7 ± 1,8	180 ± 3	271 ± 50
D	Ketchup containing starch and sweetener	2,9±0,21	399 ± 7	72 ± 1	54,4 ±1,5	120 ± 3	1656±309
E	Ketchup containing starch	2,05±0,06	517 ± 13	117 ± 3	51,4 ± 2,2	160 ± 4	1192±248
F	Ketchup containing starch and sweetener	1,77±0,08	428 ± 35	96 ± 7	29,2 ± 2,8	130 ±11	664 ±5

Table 5.5: Results obtained from the amplitude sweeps of ketchups

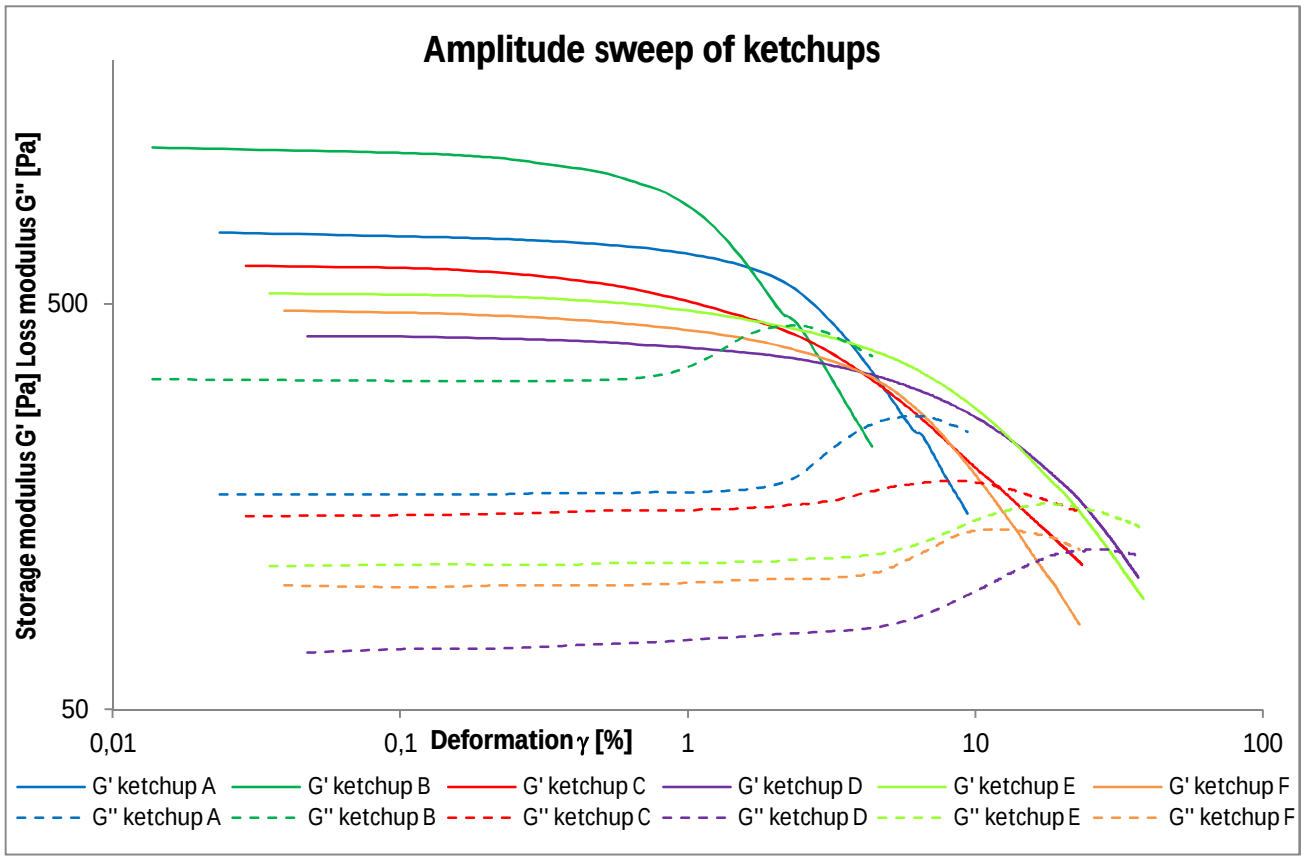

Figure 5.7: Amplitude sweeps of ketchups

From the amplitude sweeps the following issues can be described and deduced:

The storage moduli G' of all samples were higher than the loss moduli G'' as would be expected given the gel like structure of ketchups.

The two ketchup samples A and B without thickeners exhibited the highest values of G' and G'' within the linear visco-elastic range as well as the values of G' and G'' at its crossover. At the same time these ketchups were characterized by the lowest flow points τ_F and cohesion energies. Only ketchup C whose structure was based on starch and xanthan - besides the tomato particles – showed a cohesion energy lower than ketchup A but higher than ketchup B. These three samples also showed the lowest LVR's of the tested samples. From these results it can be learned that the gel like character of the ketchups is firstly based on the suspension of tomato particles that contribute to the higher rate to the elastic part of the structure. At the same time this structure is far more easily broken which can be recognized in the low flow points at deformations $\gamma < 10$ %.

Ketchups D, E and F were characterized by their relatively high values of LVR and CE compared to ketchups A, B and C meaning that more energy is needed to break the structure and let it flow. In contrast storage and loss moduli within the LVR were somewhat lower in ketchups D, E and F compared to ketchups A, B and C. But the ratio G'/G'' was higher in ketchups D, E and F, standing for stronger gels. This may be explained by the hydro-colloidal networks formed by starch and other macromolecular carbohydrates like xanthan that decrease the elastic part of the system. At the same time the viscous part – reflected by the loss modulus G'' – decreases also because water is bound in the carbohydrate network. Hence by adding thickening agents the absolute values of G' and G'' decrease, but LVR, flow point and cohesion energy density increase.

5.1.3.2.2 Frequency sweep

The results of the frequency sweeps of the ketchups are presented in table 5.6 and in figure 5.8.

No	Description	ω = 100 rad/s			ω = 0,1 rad/s		
		G' [Pa]	G'' [Pa]	tan δ	G' [Pa]	G'' [Pa]	tan δ
A	Ketchup without thickening agent	977 ± 18	552 ± 5	0,57 ± 0,00	707 ± 23	129 ± 6	0,18 ± 0,01
B	Ketchup without thickening agent	2175 ± 35	1080 ± 28	0,50 ± 0,01	1355 ± 35	225 ± 11	0,17 ± 0,01
C	Ketchup containing starch and xanthan	1230 ± 99	345 ± 7	0,28 ± 0,02	450 ± 11	93 ± 2	0,21 ± 0,00
D	Ketchup containing starch and sweetener	1130*	196 ± 11	0,18*	331 ± 2	42 ± 1	0,13 ± 0,00
E	Ketchup containing thickening agent	1070*	283 ± 13	0,27*	483 ± 6	78 ± 0	0,16 ± 0,00
F	Ketchup containing starch and sweetener	798*	237 ± 0	0,30*	356 ± 4	60 ± 4	0,17 ± 0,01

Table 5.6: Results obtained from the frequency sweeps of ketchups

*** only one data point because of instabilities of the measurement**

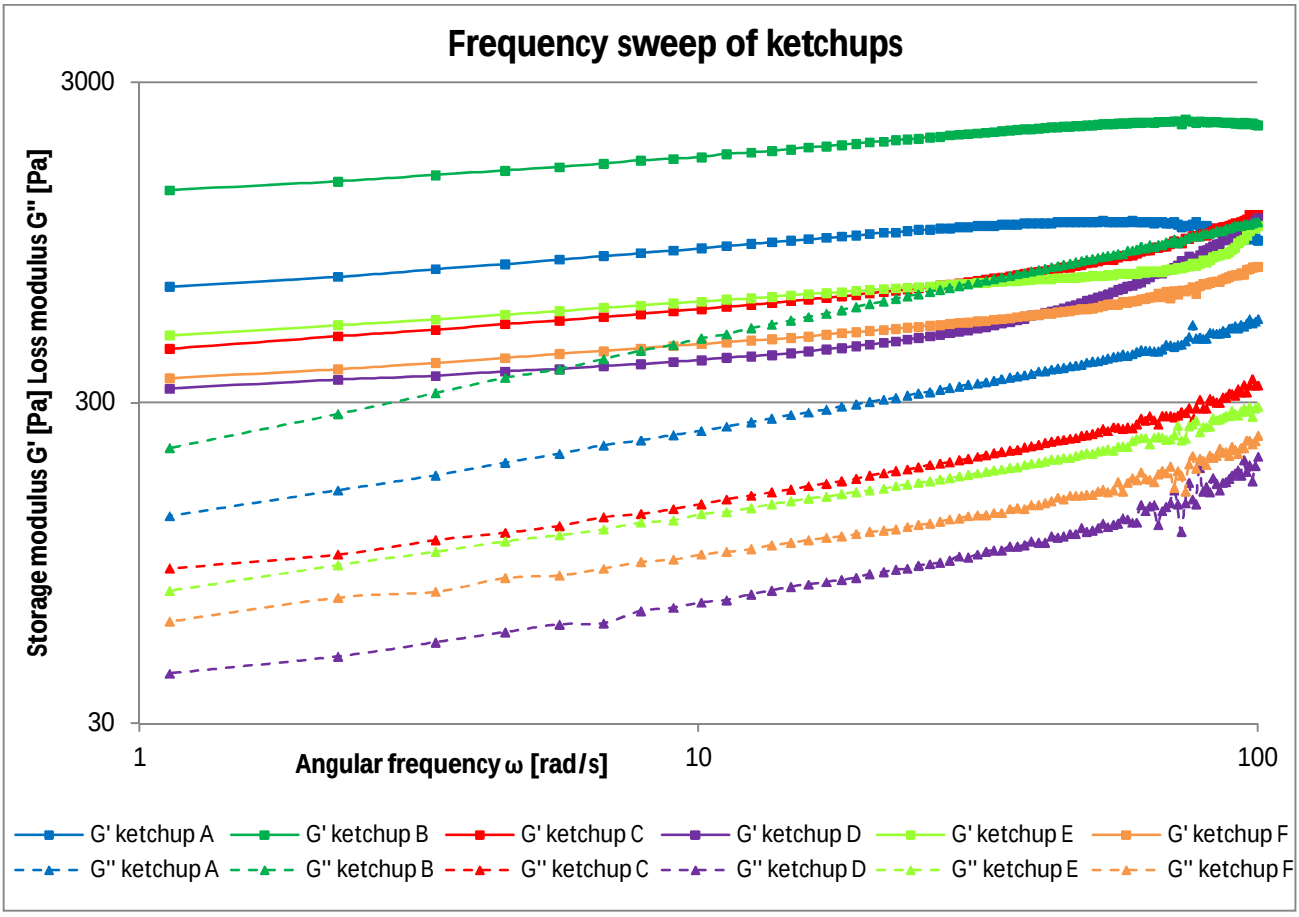

Figure 5.8: Frequency sweep of ketchups

The data obtained from the frequency sweeps show that all samples retain their gel like characteristics over a period of storage as G' exceeded G'' in all samples.

The samples exhibited varying stabilities probably due to changes of structure. The biggest changes of structure – reflected by the change of tan δ – were measured with ketchups A and B - the samples without any addition of starch or other thickening agent. The other samples exhibited little changes in their inner structure as reflected by tan δ. Samples C – F exhibited values of G' and G'' in a similar range compared to ketchups A and B at short and long time scales (at high and low frequencies respectively). Again the thickening agents seem to be responsible for a continuing stability.

5.1.4 Correlation of migration and structural properties

As the aim of these studies was to investigate the relationship between structure related properties of the food and the migration of the additives into it this will be discussed in the following. With all the considerations it has to be kept in mind that the studied additives exhibit quite different properties (cf. chapter 4.1.3).

The results show a trend of higher migration both of benzophenone and diphenyl phthalate into the samples containing thickening agents after 22 days at 25°C. This is more pronounced for DPP. The higher migration rates into these samples can be related to higher values of structure recovery after applied stress (thixotropy), larger linear visco-elastic ranges, higher values of flow points and cohesive energies. In contrast G' and G'' are low.

Migration at 70°C however showed a completely different behaviour as described above – especially in the case of BP. As rheological determinations were only carried out at 25°C a direct correlation of the migration values obtained at 70°C is difficult. The fact that the melting point of benzophenone is below 70°C might also lead to different transport processes as well as the whole system, which is already highly energized at this temperature. In the case of diphenyl phthalate whose melting point is just above 70°C (72-76°C) the migration behaviour did not vary to such a distinct extent.

General properties like the water content, the water holding capacity or the refractive index of the serum (reflecting the sugar content) did not correlate in such a distinct way although these properties also determine the viscosity. The visco-elastic properties however are determined by the complex interplay of many causes such as pH and ionic strength, size, form and concentration of the tomato particles, the amounts of added sugar, thickening agent and other ingredients, the chemical properties of the thickening agent, even the production process of the adopted tomato pastes or tomato purees as well as the effects formed by the chosen tomatoes themselves (42).

In conclusion relating the results of the migration study to the rheological results one can recognize that the migration of DPP leads to slightly higher values into ketchups with higher flow points. However this is not the case for BP although one ketchup (F) exhibits a similar trend to higher susceptibility as for DPP. An explanation for this might be that BP is a smaller molecule compared to DPP.

A correlation between the structure properties of ketchups as described by rheological characteristics and the migration of additives into them could not be shown. For the present study it has to be noticed that probably too many parameters have an impact both on the structure characterisation and the migration. To confirm some trends more samples with controlled compositions needed to be investigated.

5.2 Dry foodstuffs: wheat flour, sugar

In the case of dry foods a number of samples were analyzed for their particle size distributions firstly. After data evaluation a set of samples was chosen to be investigated in the migration study.

5.2.1 Wheat flour

Particle size distribution was determined of 11 different wheat flours of 5 different brands, 3 types (coarse - "griffig", all purpose - "universal" and fine - "glatt") and 2 different milling grades (480 and 700) to get a first overview of the samples. After evaluation of these results 5 samples were selected to be examined in the migration study.

5.2.1.1 Particle size distribution of wheat flours

The results obtained from the analysis of the particle size distributions of the flours are summarized in Table 5.7. In addition figure 5.9 gives a graphical illustration of the data obtained dependent on the examined brands.

No	Description	milling grade	particle size d (0,1) [µm]	particle size d (0,5) [µm] (median)	particle size d(0,9)[µm]	specific surface [m^2/g]
F1	Flour A griffig	480	19,0 ± 0,1	98,9 ± 0,5	199,0 ± 0,6	0,146 ± 0,001
F2	Flour A glatt	480	14,3 ± 0,1	71,9 ± 0,0	172,1 ± 0,1	0,194 ± 0,000
F3	**Flour B universal**	**480**	**29,1 ± 0,1**	**148,5 ± 0, 3**	**270,7 ± 0,3**	**0,105 ± 0,001**
F4	Flour B glatt	480	14,8 ± 0,1	83,7 ± 0,2	194,8 ± 0,1	0,183 ± 0,001
F5	**Flour C griffig**	**700**	**16,9 ± 0,1**	**90,8 ± 0,3**	**228,1 ± 0,7**	**0,158 ± 0,001**
F6	Flour C universal	480	15,6 ± 0,1	71,4 ± 0,2	155,3 ± 0,3	0,183 ± 0,000
F7	Flour C glatt	700	13,6 ± 0,1	60,8 ± 0,4	143,7 ± 0,3	0,210 ± 0,002
F8	**Flour D griffig**	**480**	**24,2 ± 0,1**	**131,6 ± 0,2**	**272,3 ± 0,6**	**0,118 ± 0,000**
F9	**Flour D universal**	**480**	**15,7 ± 0,1**	**89,6 ± 0,3**	**203,6 ± 0,5**	**0,172 ± 0,001**
F10	Flour D glatt	700	14,7 ± 0,1	64,3 ± 0,2	144,4 ± 0,3	0,195 ± 0,001
F11	**Flour E glatt**	**480**	**13,7 ± 0,1**	**66,0 ± 0,3**	**158,3 ± 0,3**	**0,203 ± 0,001**

Table 5.7: Particle size distribution of flours (bold: samples selected for following migration study)

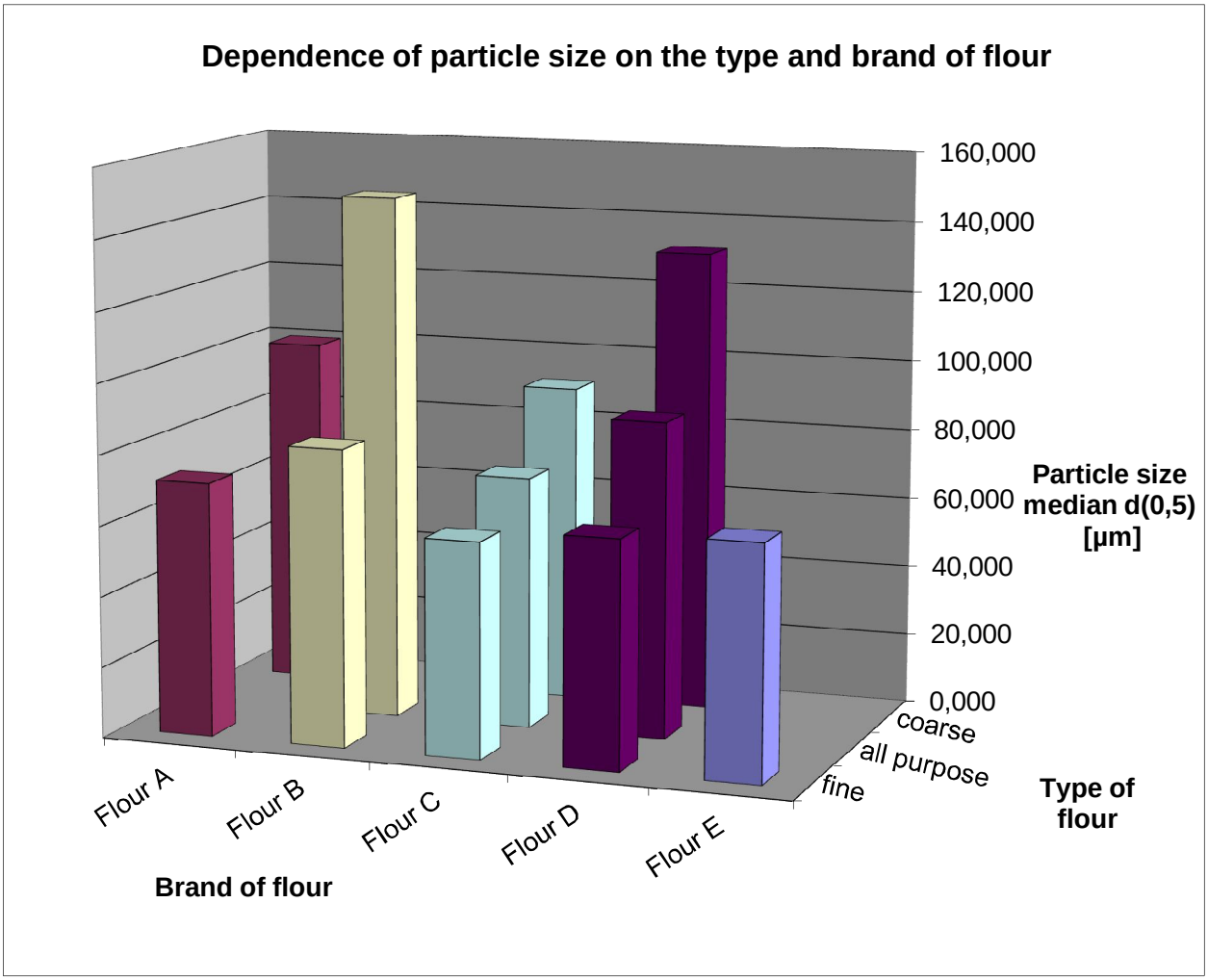

Figure 5.9: Particle size distributions of flours within brands

With respect to the different types of flours (coarse, all purpose and fine) it could be recognized that – within one brand - there is an order of particle size with the samples declared as coarse ("griffig") showing the biggest particles, as fine ("glatt") declared samples comprised of the smallest particle while the samples declared as all purpose ("universal") lay in between. This order was valid for all examined samples but the size range varied from brand to brand.

Most flours exhibited a wide monomodal distribution with a more or less distinct shoulder at smaller sizes. Only flour F3 showed a nearly bimodal distribution.

In the following the particle size distributions of the flours selected for the migration study are presented (see figure 5.10).

The selection of flours aimed to be a representative cross section over particle size (distribution), flour type (coarse, fine and all purpose) and milling grade (480 and 700 respectively). These considerations led to the selection of flours F3, F5, F8, F9 and F11 to be analysed for their migrating behaviour.

(The graphs of the particle size distributions of all flours can be found in the appendix.)

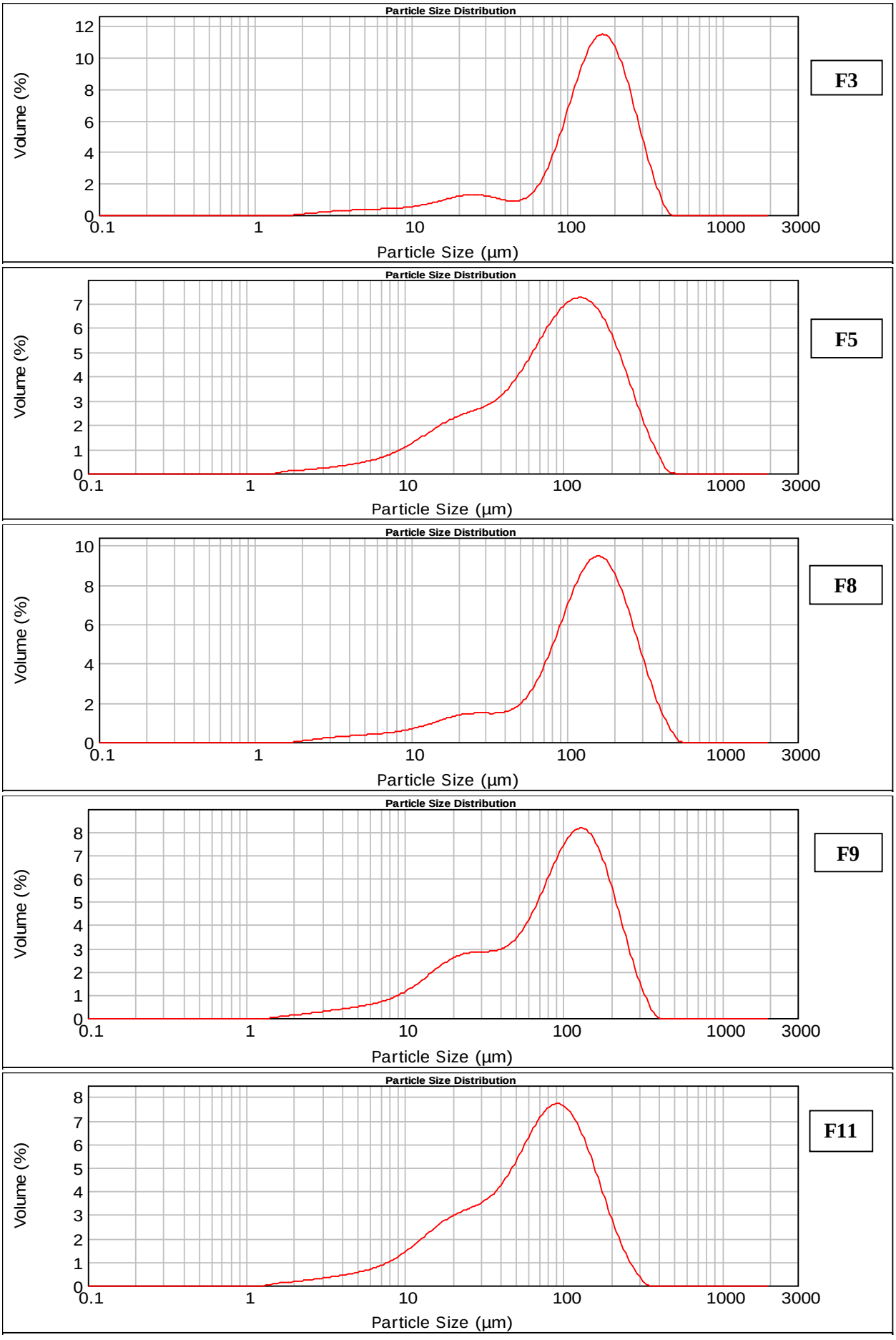

Figure 5.10: Particle size distributions of flours F3, F5, F8, F9 and F11

5.2.1.2 Migration study of wheat flours

Flours F3, F5, F8, F9 and F11 were selected for the migration study, which was conducted for 10 days at 40°C. The results of the migration study are presented in tables 5.8 and 5.9 and in figure 5.11.

No	Description	Migration of benzophenone [mg/dm^2]			
		t = 0	t = 1day	t = 4 days	t = 10 days
F3	Flour B milling grade 480 universal	0	0,161 ± 0,013	0,166 ± 0,025	0,159 ± 0,009
F5	Flour C milling grade 700 griffig	0	0,240 ± 0,008	0,216 ± 0,017	0,214 ± 0,002
F8	Flour D milling grade 480 griffig	0	0,179 ± 0,010	0,175 ± 0,011	0,174 ± 0,012
F9	Flour D milling grade 480 universal	0	0,202 ± 0,003	0,197 ± 0,028	0,195 ± 0,005
F11	Flour E milling grade 480 glatt	0	0,205 ± 0,002	0,289 ± 0,003	0,165 ± 0,013

Table 5.8: Migration of benzophenone into flours

No	Description	Migration of diphenyl phthalate [mg/dm^2]			
		t = 0	t = 1day	t = 4 days	t = 10 days
F3	Flour B milling grade 480 universal	0	0,082 ± 0,004	0,179 ± 0,009	0,258 ± 0,007
F5	Flour C milling grade 700 griffig	0	0,069 ± 0,009	0,192 ± 0,061	0,335 ± 0,038
F8	Flour D milling grade 480 griffig	0	0,091 ± 0,008	0,206 ± 0,012	0,282 ± 0,029
F9	Flour D milling grade 480 universal	0	0,047 ± 0,003	0,161 ± 0,030	0,230 ± 0,052
F11	Flour E milling grade 480 glatt	0	0,055 ± 0,012	0,164 ± 0,039	0,231 ± 0,059

Table 5.9: Migration of diphenyl phthalate into flours

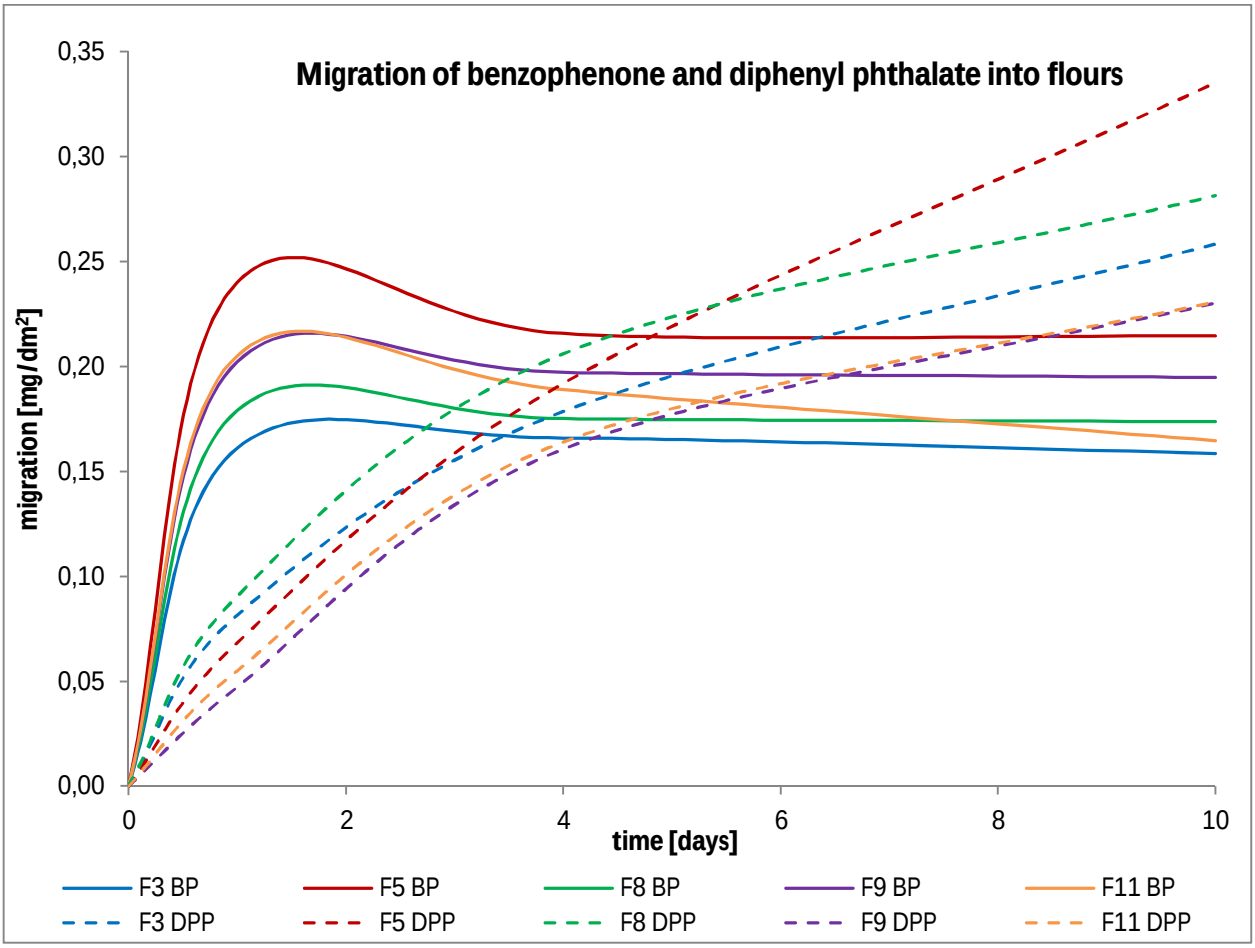

Figure 5.11: Migration of benzophenone and diphenyl phthalate into flours

It can be recognized that migration of benzophenone into flours differed distinctly to that of diphenyl phthalate. Migration of benzophenone appeared to have reached its maximum after one day. After 4 and 10 days of incubation migration values were slightly decreasing compared to the values after one day. This could be attributed to specific absorption of benzophenone by the particles, so that it could not be extracted by the solvent anymore or reacted in some way that it could not be detected anymore.

In contrast to that diphenyl phthalate migrated continuously over the entire incubation time and ended up in even higher values than benzophenone.

Both additives showed higher migration rates into the one flour with type 700 – benzophenone already after one day and the phthalate after 10 days indicating that equilibrium is reached at very differing times. Also it can be recognized that flours F9 and F11 exhibit very similar migration values – again for benzophenone already after one day and for diphenyl phthalate after 10 days respectively.

5.2.1.3 Correlation of migration and particle size (distribution) of flours

Combining the obtained data both from the particle size distribution and the migration tests there can be recognized some relations.

First of all migration of the different additives runs differently. While benzophenone - being a relative small and planar molecule - reached the equilibrium of migration after only one day (at 40 °C) the phthalate had not reached this state after 10 days at the same temperature.

In the beginning benzophenone migrated into samples with small particle size (median) or higher surface area respectively while the opposite behaviour was found for diphenyl phthalate.

The milling grade, which represents the parts of the cereal grains being ground, has a significant influence on the migration. The milling grade is defined as the outcome of flour from the input of grains in %. Consequently a higher milling grade means higher protein, fat, fibres and ash content and less carbohydrate expressed in starch. This result leads to the conclusion that the chemical composition of dry foods has a high influence on the migration but surface or surface related factors do take part in the parameters driving the migration process meaning that a characteristic such as the particle size and particle size distribution does matter.

Relating these considerations to the tested additives it can be stated that the migration behaviour can be related to size and surface area of the particles but has to be examined for each compound because particle size alone cannot be taken to assess migration. Again it is a complex interplay of chemical composition, physic-chemical properties, external conditions (like time, temperature or humidity) both of the migrating compound and the material into which it migrates.

5.2.2 Sugar

Three sugars of different crystal sizes (coarse, fine, powdered) were examined. These are the most common types of sugar available in Austria.

5.2.2.1 Particle size distribution of sugars

The particle size distributions obtained from the measurements are presented in table 5.10.

No	Description	particle size d (0,1) [µm]	particle size d (0,5) [µm] (median)	particle size d(0,9)[µm]	specific surface [m^2/g]
S1	Powdered sugar	5,3 ± 0,1	22,8 ± 0,3	186,9 ± 8,4	0,591 ± 0,008
S2	Fine crystal sugar	174,2 ± 8,6	514,7 ± 11,9	1010 ± 20	0,024 ± 0,002
S3	Coarse crystal sugar	not measured* (> 1mm)			

Table 5.10: particle size distribution of sugars *** Crystals too big for dispersion unit**

To measure the particle size distribution of coarse crystal sugar an immense amount of sample were needed to feed the dispersion unit so in this case it was not determined. In contrast powdered sugar tends to build agglomerates caused by its high hygroscopicity, which led to higher standard deviations of the volume fractions, especially for the values of d (0,9).

The particle size distributions of powdered and fine crystal sugar are shown in figure 5.12.

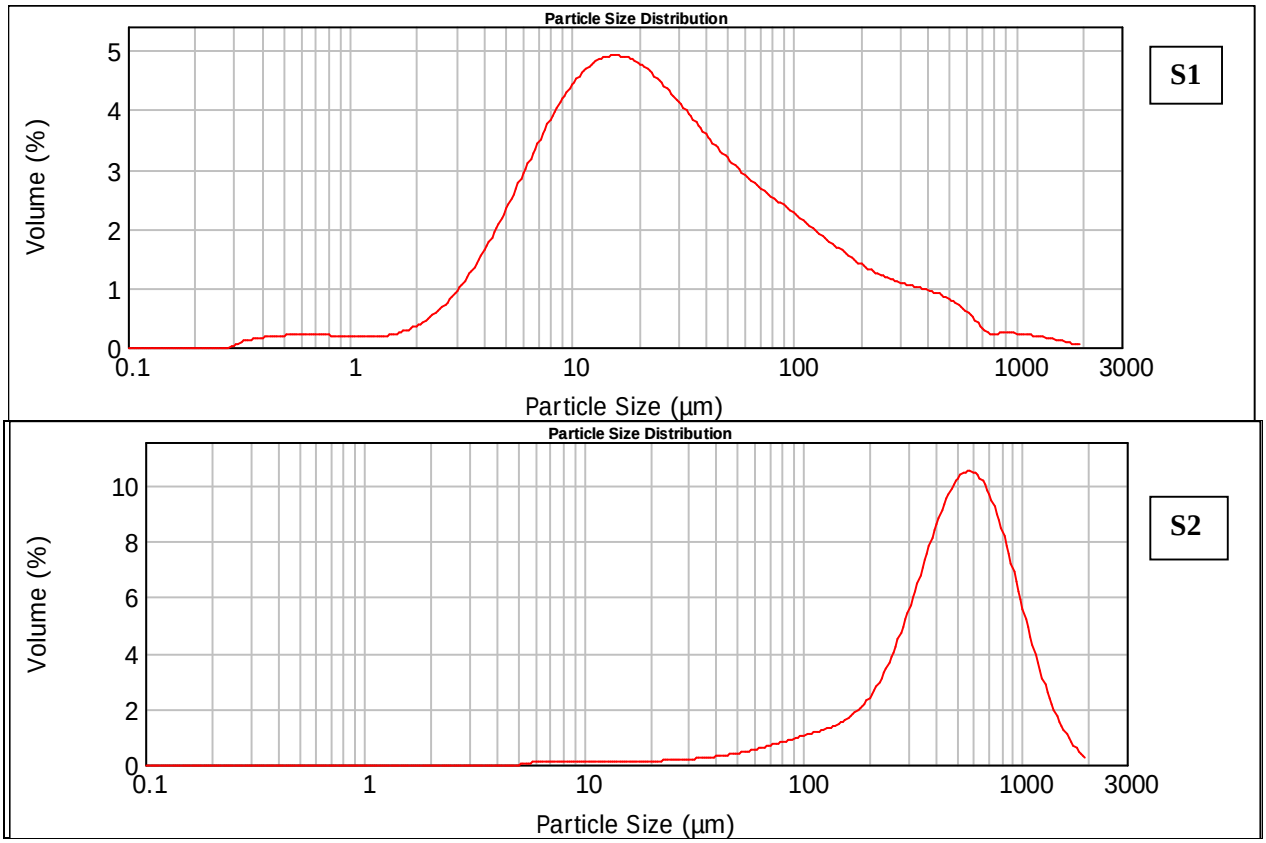

Figure 5.12: Particle size distributions of sugars S1 and S2

As can be seen in the graphs sugar showed a monomodal particle size distribution with distinct median values. Powdered sugar exhibited a wider distribution, which can be explained by its hygroscopic nature and its tendency to form agglomerates that are too sticky to be separated by the dispersion unit of the instrument.

5.2.2.2 Migration study of sugars

Sugars are generally believed to be inert against migrating components; nevertheless they were tested, too. The results of the migration tests can be learnt from tables 5.11 and 5.12 as well as from figure 5.13.

No	Description	Migration of benzophenone [mg/dm^2]			
		t = 0	t = 1day	t = 4 days	t = 10 days
S1	powdered sugar	0	0,172 ± 0,018	0,207 ± 0,047	0,222 ± 0,150
S2	fine crystal sugar	0	0,011 ± 0,002	0,012 ± 0,002	0,007 ± 0,001
S3	coarse crystal sugar	0	0,039 ± 0,007	0,037 ± 0,007	0,027 ± 0,006

Table 5.11: Migration of benzophenone into sugars

No	Description	Migration of diphenyl phthalate [mg/dm^2]			
		t = 0	t = 1day	t = 4 days	t = 10 days
S1	powdered sugar	0	0,070 ± 0,018	0,152 ± 0,006	0,154 ± 0,019
S2	fine crystal sugar	0	0	0	0
S3	coarse crystal sugar	0	0	0	0

Table 5.12: Migration of diphenyl phthalate into sugars

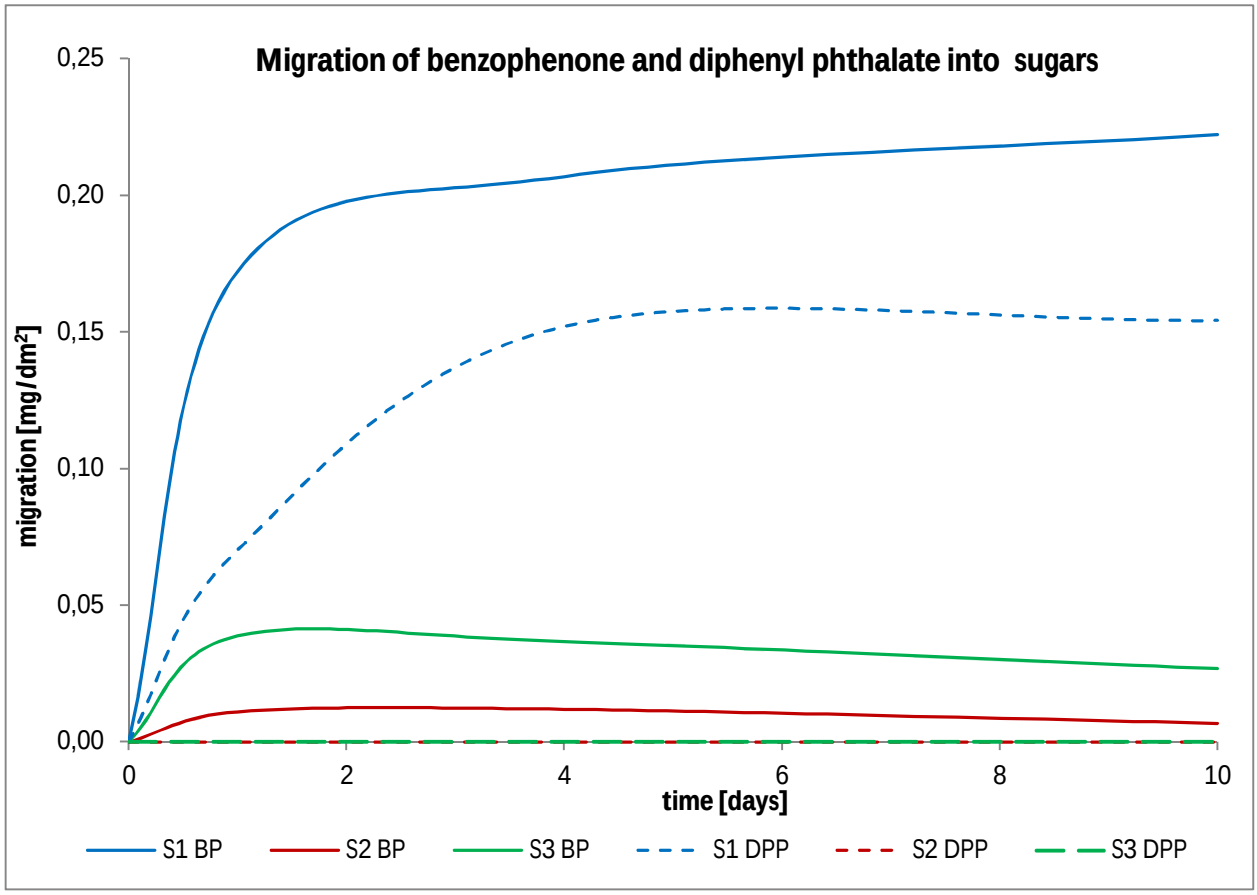

Figure 5.13: Migration of benzophenone and diphenyl phthalate into sugars

In contrast to wheat flour sugar is a completely different food stuff. As mentioned above it is generally recognized to be inert towards migration; however this could not be confirmed in this study in general.

Powdered sugar exhibited typical migration behaviour both for BP and DPP. Both compounds seem to have reached equilibrium after 4-10 days of incubation. Crystal powder in contrast showed a quite puzzling migration behaviour: There was no migration at all of the phthalate while benzophenone migrated to a higher extent into the coarse crystal sugar compared to fine crystal sugar. But migration of BP into crystal sugar was very low anyway.

So sugar is definitely not inert against migration, at least not in the case of benzophenone. Barnkob and Petersen investigated the relationship between migration of benzophenone into Tenax® and the relative humidity. They could demonstrate that the higher the relative humidity of Tenax® is the higher is the migration of benzophenone into it (62). Tenax® is used as food simulant for dry foods. Sugar of course is highly hygroscopic especially powdered sugar because of its high surface area.

5.2.2.3 Correlation of migration and particle size of sugars

Sugar itself as a material actually seems to be inert against migration and therefore migration is independent of a characteristic of particle or crystal size. However as can be deduced from the presented results migration takes place when external conditions like humidity interact with the crude material to form a complex system into which migration is promoted. How these interactions between the sugar crystals, the ambient air humidity and potent migrating compounds act was not issue of these studies and cannot explained here. However as sugar is usually a packaged food in ambient conditions this must not be neglected.

5.2.3 Discussion – Correlation of migration and particle size distribution

As could be demonstrated particle size or particle size distributions of bulk dry food stuff materials alone do not seem to be a sufficient means to asses or relate migration rates into them. Many factors interact and influence the transport process.

However it could be illustrated that there are interactions that have not been a big issue of research so far.

So humidity seems to have a bigger influence than expected and should be investigated further on. Also the combination of complex systems – material – material structure – external conditions – migrating compound (compound classes) – should be an issue of research to enlighten these complex interactions.

Particle size does influence migration rates by offering a variation of contact area both for the migrating compounds themselves and for water (from air humidity) forming a film on the surface and by this changing the state of aggregation on the surface of the food particles. In the case of flour, which represents a complex material already film forming on the particle surface by the contained fat is thinkable. So solubility of migrating compounds can vary. How far the transport process itself is affected by this film forming is still another open question. It might be possible for the diffusion to convert into capillary flow. Diffusion coefficients of a substance will change if it is solved and hence induce a changed transport process.

5.3 Dairy Products

5.3.1 Physico – chemical characterisation

The results of the determination of dry matter, the water content and water holding capacity are summarized in table 5.13.

No	Description	Dry matter [%]	Water content [%]	WHC [%]
1	Natural stirred yoghurt 1% fat - A	13,6 ± 0,1	86,4 ± 0,1	75,4 ± 0,4
2	Natural stirred yoghurt 1% fat - B	12,1 ± 0,1	87,9 ± 0,1	80,8 ± 0,2
3	Natural stirred yoghurt 3,6% fat - A	13,2± 0,2	86,8 ± 0,2	69,5 ± 0,7
4	Natural stirred yoghurt 3,6% fat - B	13,0 ± 0,1	87,0 ± 0,1	72,8 ± 0,3
5	Natural buttermilk 1% fat - A	9,5 ± 0,1	90,5 ± 0,1	84,4 ± 0,2
6	Natural buttermilk 1% fat - B	9,9 ± 0,1	90,1 ± 0,1	82,7 ± 0,6
7	Sour milk 3,5% fat - A	12,1 ± 0,1	87,9 ± 0,1	74,2 ± 0,3
8	Sour milk 3,5% fat - B	12,2 ± 0,2	87,8 ± 0,2	72,0 ± 0,3

Table 5.13: Dry matter, water content, water holding capacity of dairy products

As can be seen from the results the samples containing higher levels of fat show bigger differences between water content and water holding capacity. This means that the casein networks containing more fat are also able to hold more water, which again contributes to the higher elastic portion of these samples.

5.3.2 Migration study

Two sets of pre-tests were performed (by students) with only four samples (samples 1, 3, 6 and 8 - one of each product group) that led to differing results.

Study 1 was conducted by student 1 and study 2 by student 2 about 2 months later. The tests were repeated because of uncertainty about the blank at t = 0 hours.

In test set no. two there are some data obtained by a single determination because some of the sample vials containing the extracts broke before GC-MS analysis.

Tables 5.14 and 5.15 inform about the results of the pre-tests.

No	Description	Migration of benzophenone [mg/dm^2]			
		t < 0,5 h	t = 2 h	t = 4 h	t =24 h
1	Natural stirred yoghurt 1% fat - A	0,013 ± 0,002	0,036 ± 0,001	0,048 ± 0,002	0,140 ± 0,005
3	Natural stirred yoghurt 3,6% fat - A	0,033 ± 0,005	0,041 ± 0,004	0,055 ± 0,002	0,098 ± 0,005
6	Natural buttermilk 1% fat - B	0,015 ± 0,003	0,043 ± 0,003	0,066 ± 0,001	0,143 ± 0,003
8	Sour milk 3,5% fat - B	0,034 ± 0,004	0,063 ± 0,004	0,078 ± 0,001	0,106 ± 0,002
No	**Description**	**Migration of diphenyl phthalate [mg/dm^2]**			
		t < 0,5 h	t = 2 h	t = 4 h	t =24 h
1	Natural stirred yoghurt 1% fat - A	0,014 ± 0,002	0,022 ± 0,003	0,028 ± 0,001	0,054 ± 0,002
3	Natural stirred yoghurt 3,6% fat - A	0,020 ± 0,000	0,023 ± 0,001	0,020 ± 0,001	0,052 ± 0,005
6	Natural buttermilk 1% fat - B	0,015 ± 0,003	0,029 ± 0,002	0,036 ± 0,001	0,058 ± 0,004
8	Sour milk 3,5% fat - B	0,013 ± 0,001	0,022 ± 0,001	0,025 ± 0,001	0,034 ± 0,004

Table 5.14: Results of migration pre-test no 1 of dairy products

No	Description	Migration of benzophenone [mg/dm^2]			
		t = 0 h	t = 2 h	t = 4 h	t =24 h
1	Natural stirred yoghurt 1% fat - A	0	0,044 ± 0,003	0,056 ± 0,006	0,121 ± 0,006
3	Natural stirred yoghurt 3,6% fat - A	0	0,045*	0,060*	0,127*
6	Natural buttermilk 1% fat - B	0	0,041 ± 0,005	0,052 ± 0,004	0,105 ± 0,020
8	Sour milk 3,5% fat - B	0	0,054 ± 0,005	0,086 ± 0,003	0,120 ± 0,017
No	**Description**	**Migration of diphenyl phthalate [mg/dm^2]**			
		t = 0 h	t = 2 h	t = 4 h	t =24 h
1	Natural stirred yoghurt 1% fat - A	0	(0,098*)	0,057 ± 0,001	0,123 ± 0,001
3	Natural stirred yoghurt 3,6% fat - A	0	0,050*	0,057*	0,108*
6	Natural buttermilk 1% fat - B	0	0,051 ± 0,009	0,065 ± 0,011	0,138 ± 0,042
8	Sour milk 3,5% fat - B	0	0,061 ± 0,012	0,068 ± 0,013	0,106 ± 0,019

Table 5.15: Results of migration pre-test of dairy products no 2 *only one data point available

The results of the pre-tests varied such a lot that at first the data should be aborted. But in combination with the results obtained by the following tests conducted with all eight products they had to be kept because it was noticed that the relation of migration and also the absolute migration rates of the two analytes altered. This will be discussed later.

The results of the migration study (carried out about one month after pre-test no 2) are presented in tables 5.16 and 5.17 and in figures 5.14 – 5.19 on the following pages.

No	Description	Migration of benzophenone [mg/dm^2]				
		t = 0 h	t = 1 h	t = 2 h	t = 4 h	t =24 h
1	Natural stirred yoghurt 1% fat - A	0	0,017 ± 0,000	0,022 ± 0,000	0,025 ± 0,000	0,053 ± 0,000
2	Natural stirred yoghurt 1% fat - B	0	0,016 ± 0,000	0,020 ± 0,000	0,026 ± 0,001	0,053 ± 0,008
3	Natural stirred yoghurt 3,6% fat - A	0	0,017 ± 0,001	0,025 ± 0,001	0,032 ± 0,001	0,052 ± 0,001
4	Natural stirred yoghurt 3,6% fat - B	0	0,013 ± 0,001	0,016 ± 0,001	0,018 ± 0,002	0,050 ± 0,001
5	Natural buttermilk 1% fat - A	0	0,014 ± 0,000	0,024 ± 0,000	0,030 ± 0,001	0,057 ± 0,000
6	Natural buttermilk 1% fat - B	0	0,015 ± 0,002	0,022 ± 0,001	0,024 ± 0,001	0,040 ± 0,002
7	Sour milk 3,5% fat - A	0	0,016 ± 0,000	0,020 ± 0,002	0,026 ± 0,002	0,044 ± 0,005
8	Sour milk 3,5% fat - B	0	0,017 ± 0,000	0,023 ± 0,001	0,031 ± 0,001	0,053 ± 0,002

Table 5.16: Migration of benzophenone into dairy products

No	Description	Migration of diphenyl phthalate [mg/dm^2]				
		t = 0 h	t = 1 h	t = 2 h	t = 4 h	t =24 h
1	Natural stirred yoghurt 1% fat - A	0	0,034 ± 0,000	0,036 ± 0,001	0,055 ± 0,001	0,077 ± 0,003
2	Natural stirred yoghurt 1% fat - B	0	0,030 ± 0,001	0,036 ± 0,002	0,039 ± 0,004	0,073 ± 0,000
3	Natural stirred yoghurt 3,6% fat - A	0	0,032 ± 0,001	0,041 ± 0,003	0,046 ± 0,003	0,075 ± 0,006
4	Natural stirred yoghurt 3,6% fat - B	0	0,029 ± 0,002	0,035 ± 0,000	0,046 ± 0,004	0,079 ± 0,001
5	Natural buttermilk 1% fat - A	0	0,042 ± 0,007	0,045 ± 0,004	0,057 ± 0,001	0,088 ± 0,002
6	Natural buttermilk 1% fat - B	0	0,031 ± 0,002	0,045 ± 0,000	0,055 ± 0,005	0,084 ± 0,004
7	Sour milk 3,5% fat - A	0	0,032 ± 0,002	0,052 ± 0,002	0,056 ± 0,008	0,083 ± 0,012
8	Sour milk 3,5% fat - B	0	0,029 ± 0,001	0,034 ± 0,002	0,042 ± 0,002	0,072 ± 0,010

Table 5.17: Migration of diphenyl phthalate into dairy products

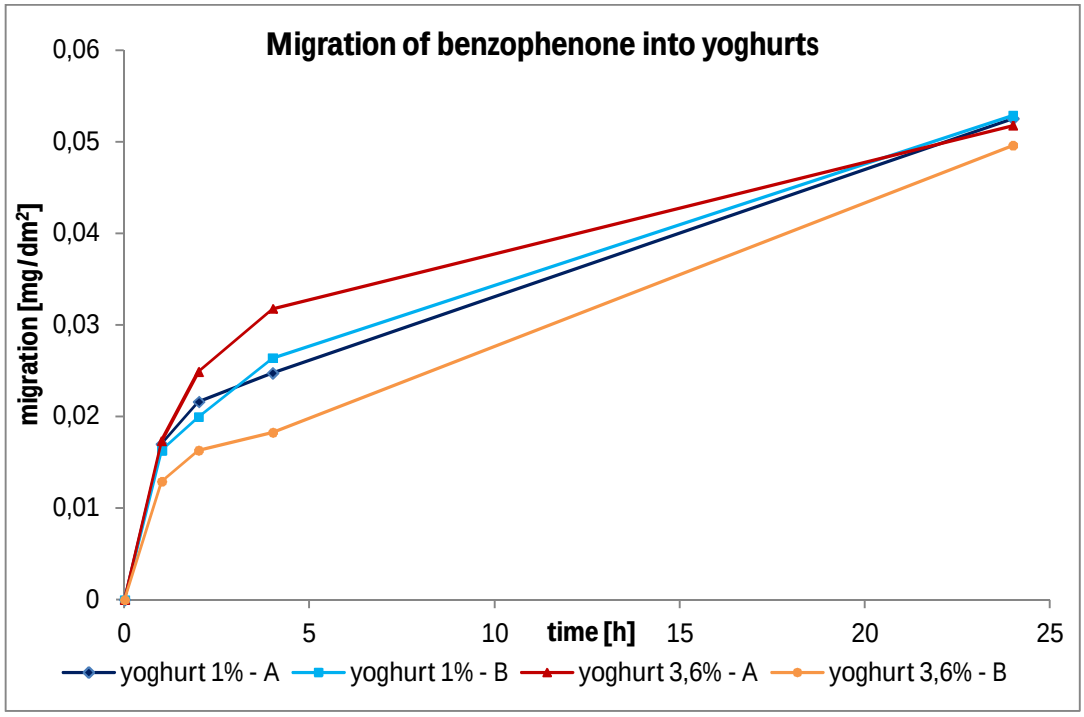

Figure 5.14: Migration of benzophenone into yoghurts (1% and 3,6% fat)

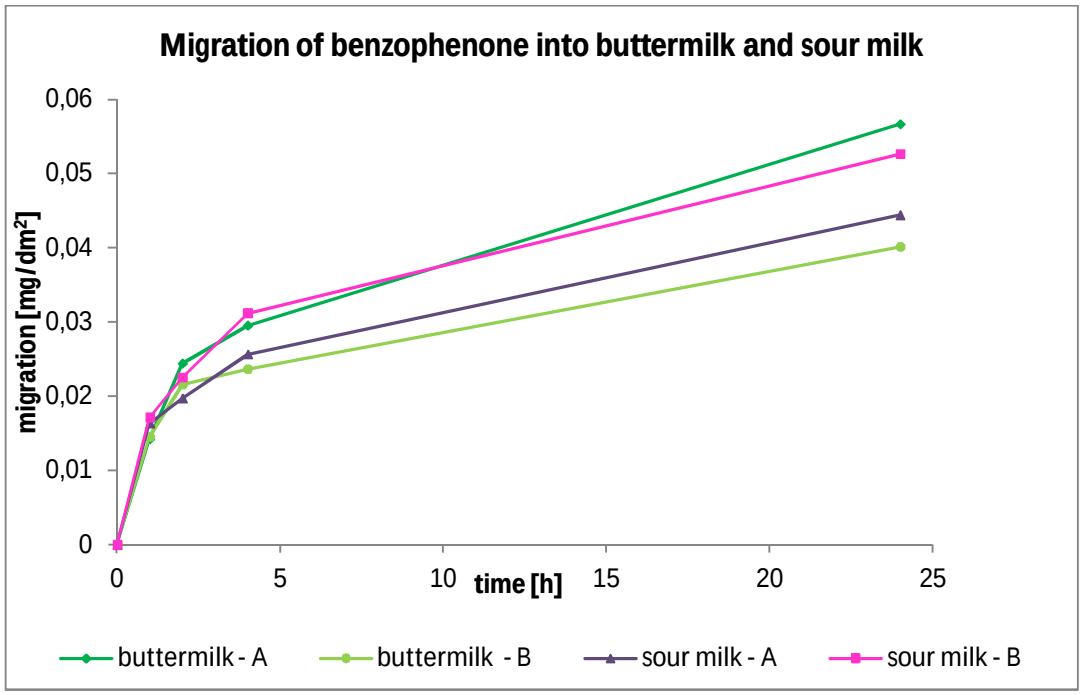

Figure 5.15: Migration of benzophenone into buttermilk (1% fat) and sour milk (3,5% fat)

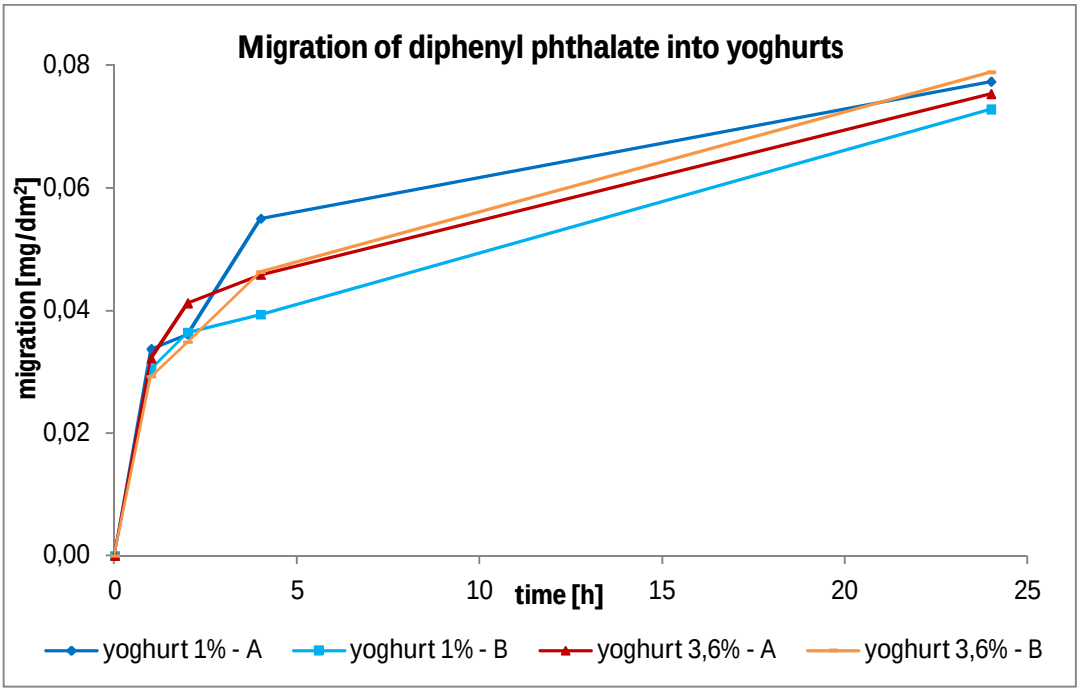

Figure 5.16: Migration of diphenyl phthalate into yoghurts (1% and 3,6% fat)

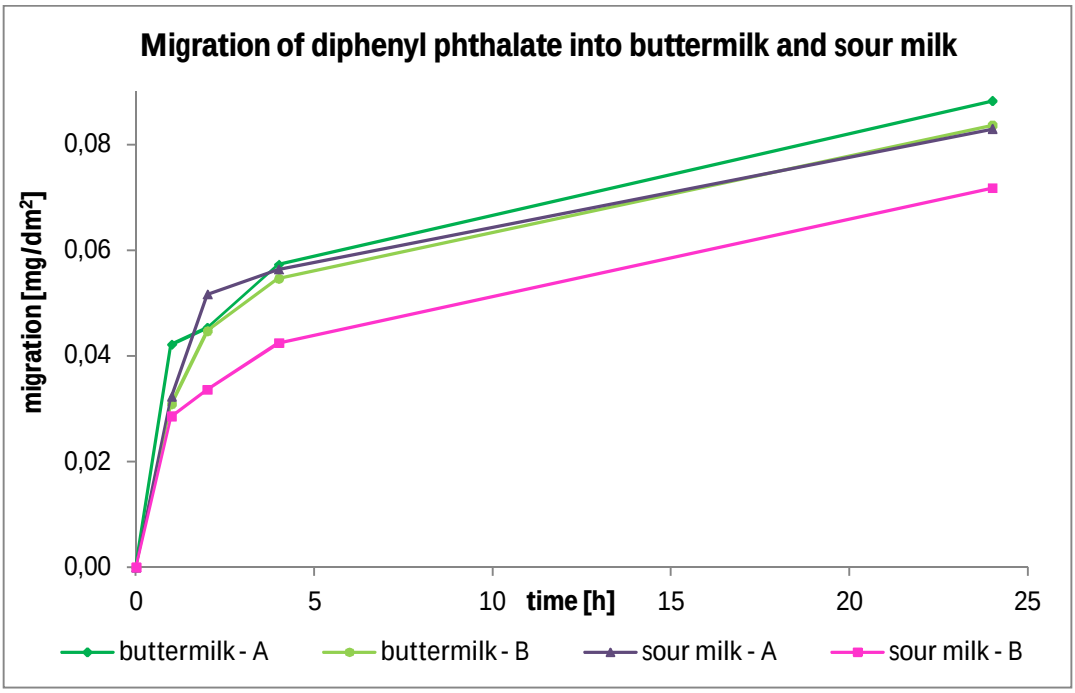

Figure 5.17: Migration of diphenyl phthalate into buttermilk (1% fat) and sour milk (3,5% fat)

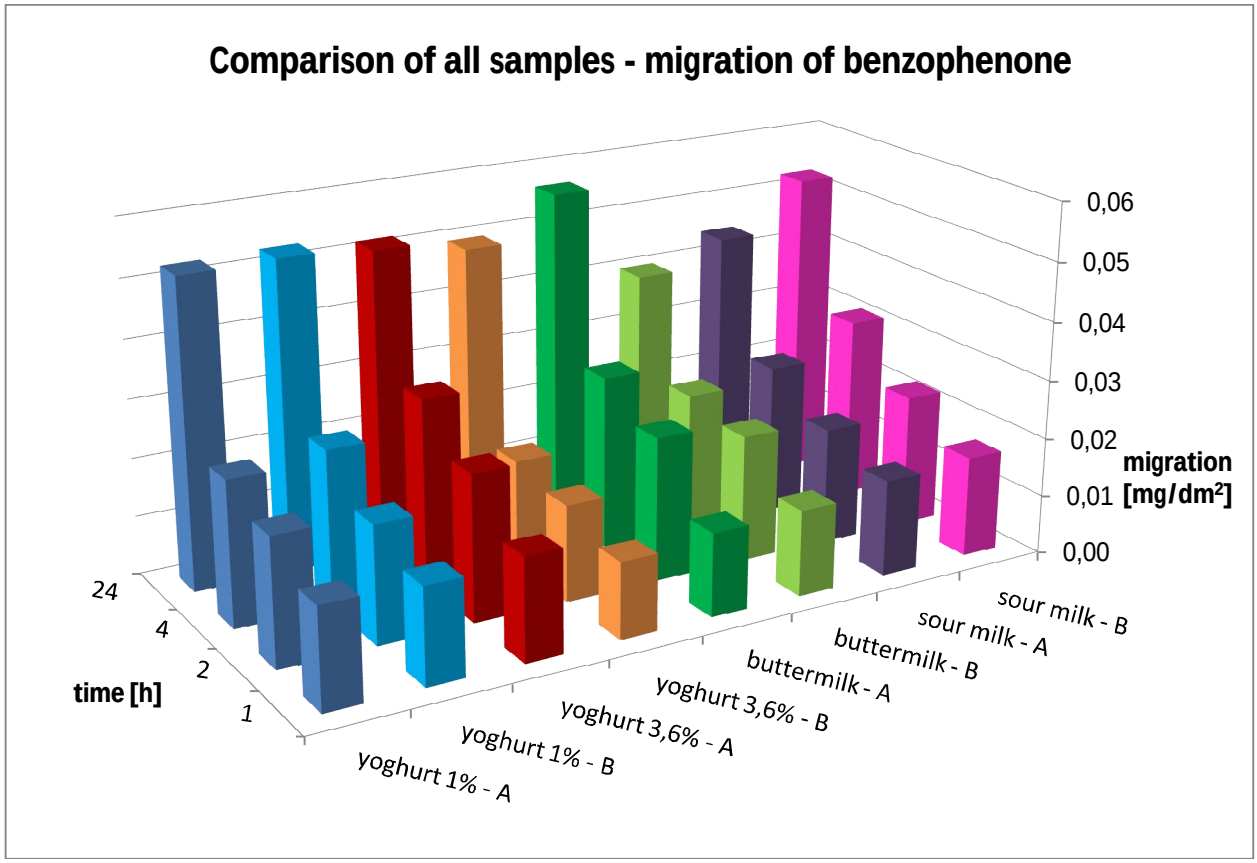

Figure 5.18: Comparison of all dairy products – migration of benzophenone

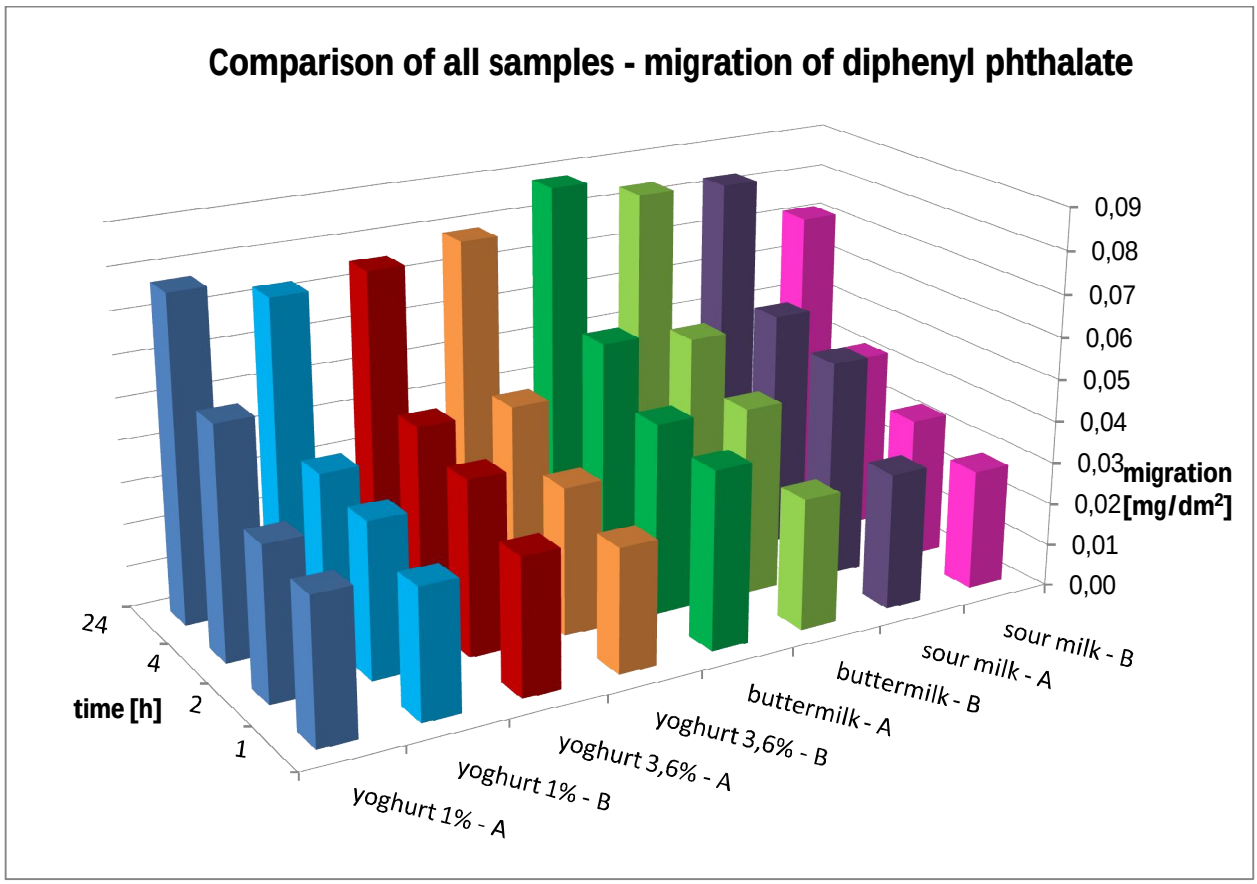

Figure 5.19: Comparison of all dairy products – migration of diphenyl phthalate

Before discussing these data it has to be stated that probably ageing effects of the test film B led to obviously incoherent results. This fact definitely influences the discussion. A comparison of the test films A and B was presented in chapter 4.1.2.
Regarding the migrating analytes one by one the following conclusions can be recognized from the above data:

After 24 hours migration of benzophenone into yoghurts was in the same range – no matter if low or high fat yoghurt. The pre-tests showed differing results, one study led to higher migration rates into the high fat yoghurt, the other one to higher results into the low fat yoghurt.

Migration of benzophenone into buttermilk and sour milk varied quite much. At first (until t = 1h) migration of BP into sour milk exceeded migration into buttermilk. Then migration into buttermilk increased more compared to sour milk; after 24 hours buttermilk A and sour milk B showed higher values than the other 2 samples. Again the pre-tests led to differing results, the first pre-test ended up with higher values for the buttermilk, in the second pre-test migration into buttermilk always exceeded migration into sour milk.

Migration of diphenyl phthalate into yoghurts was varying over time but did not end up with a distinct trend. Fat content of yoghurts did not seem to be influencing migration to a significant extent. The same result could be observed in the pre-tests. Migration of DPP into buttermilk exceeded migration into sour milk in the beginning but equalled for all samples at end of observation time especially as the standard deviations for sour milks were in the range of 15%. In the pre-tests migration into buttermilk was always higher than into sour milk, which could be found in the third study as well regarding the same products.

Summarizing it can be stated that migration of BP into the regarded products ended up in the same range with the yoghurts coming to very similar values whereas the more liquid samples were varying in the same range independently of the fat content. Migration of DPP varied even less, but a trend of higher migration into liquid samples and here into buttermilk – containing only 1% fat – could be observed.
This is a puzzling result as the phthalate is known to have a higher solubility in fats. In the present case it must be taken into account that the phthalate might have accumulated on the surface of the LLDPE test film and was maybe rather washed from the surface of the film than being migrated from the inside of the film.

5.3.3 Rheology

5.3.3.1 Rotational rheometry

5.3.3.1.1 Controlled shear rate (CSR)

In the controlled shear rate mode the principal flow behaviour was determined. As the selected samples were yielding and shear thinning gels an evaluation with the Herschel-Bulkley fit seemed appropriate.

The Herschel-Bulkley fit is defined as:

$$\tau = \tau_{HB} + b \cdot \gamma^{p}$$

With:

τ... shear stress [Pa]

τ_{HB} … flow point [Pa]

b…flow coefficient [Pas]

p… Herschel-Bulkley index, indicating shear thinning behaviour if p<1

Results of the controlled shear rate measurements are summarized in table 5.18; viscosity curves and flow curves are presented in figures 5.20 and 5.21.

The samples can be – at least roughly - distinguished by their viscosities and stresses. Yoghurts with higher fat content show higher viscosities than low fat yoghurts and the more liquid products buttermilk and sour milk. Buttermilk shows the lowest viscosities and stresses whereas low fat yoghurt and sour milk cannot be distinguished by this method.
As can be seen in Figure 5.20 all samples exhibit shear thinning behaviour but especially buttermilk ends up with shear thickening behaviour from shear rates of about 40 s^{-1}. An explanation may be that the gel like character of buttermilk origins from small flakes of butter suspended in the serum that is obtained in the buttering process. With higher shear rate these flakes accumulate to bigger agglomerates that are responsible for the shear thickening behaviour.

The other samples do not show this behaviour to such an extent with the gels formed by the casein networks exceeding the effect of accumulating fat globules because they are incorporated in the casein networks. However as can be learned from the Herschel-Bulkley indices (p_i) that are near or bigger than 1 all samples show differing flow behaviour at higher shear rates. Another reason for that could also be geometry effects like wall slip.

Transient effects can be recognized at low shear rates both in the viscosity curves and the flow curves. These effects were tried to be minimized by adjusting the measuring time but could not be averted completely. These effects were neglected because they were not valued as disturbing for the characterisation of the samples.

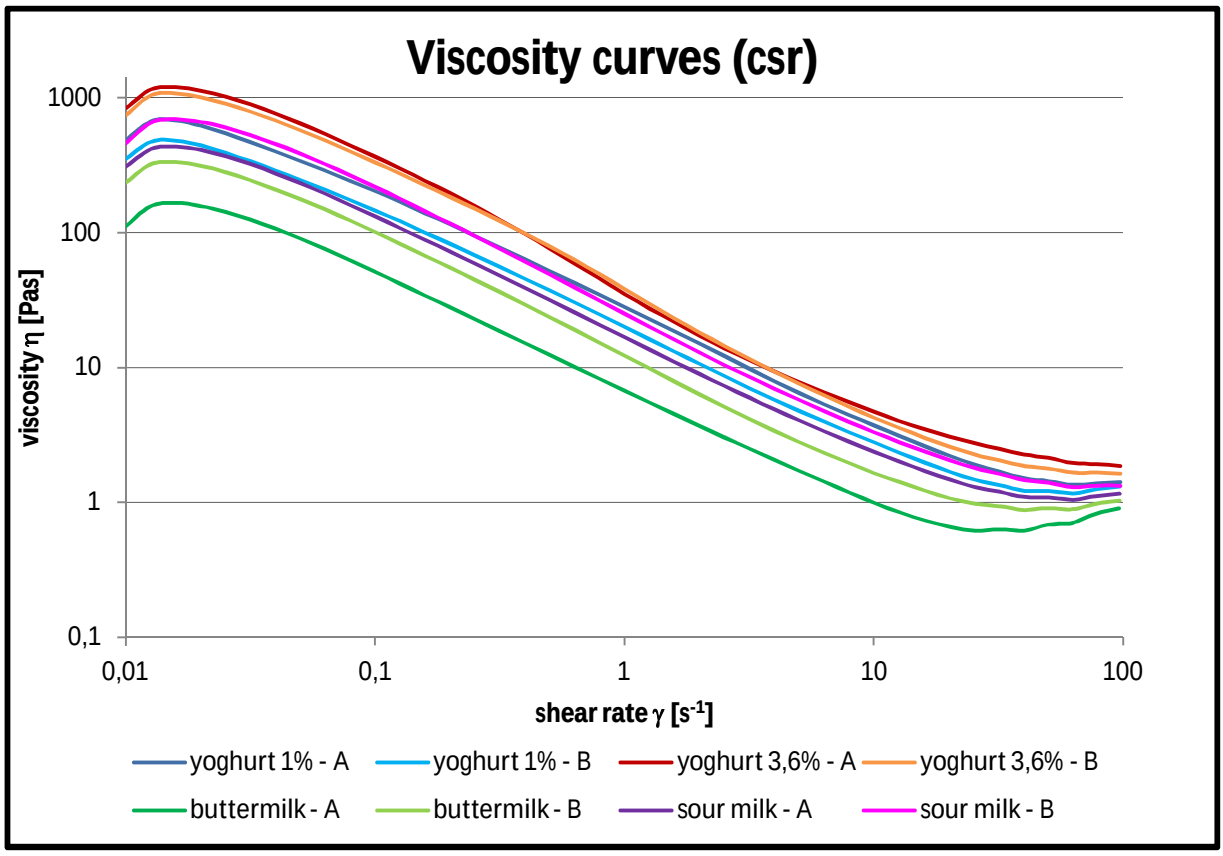

Figure 5.20: Viscosity curves of dairy products

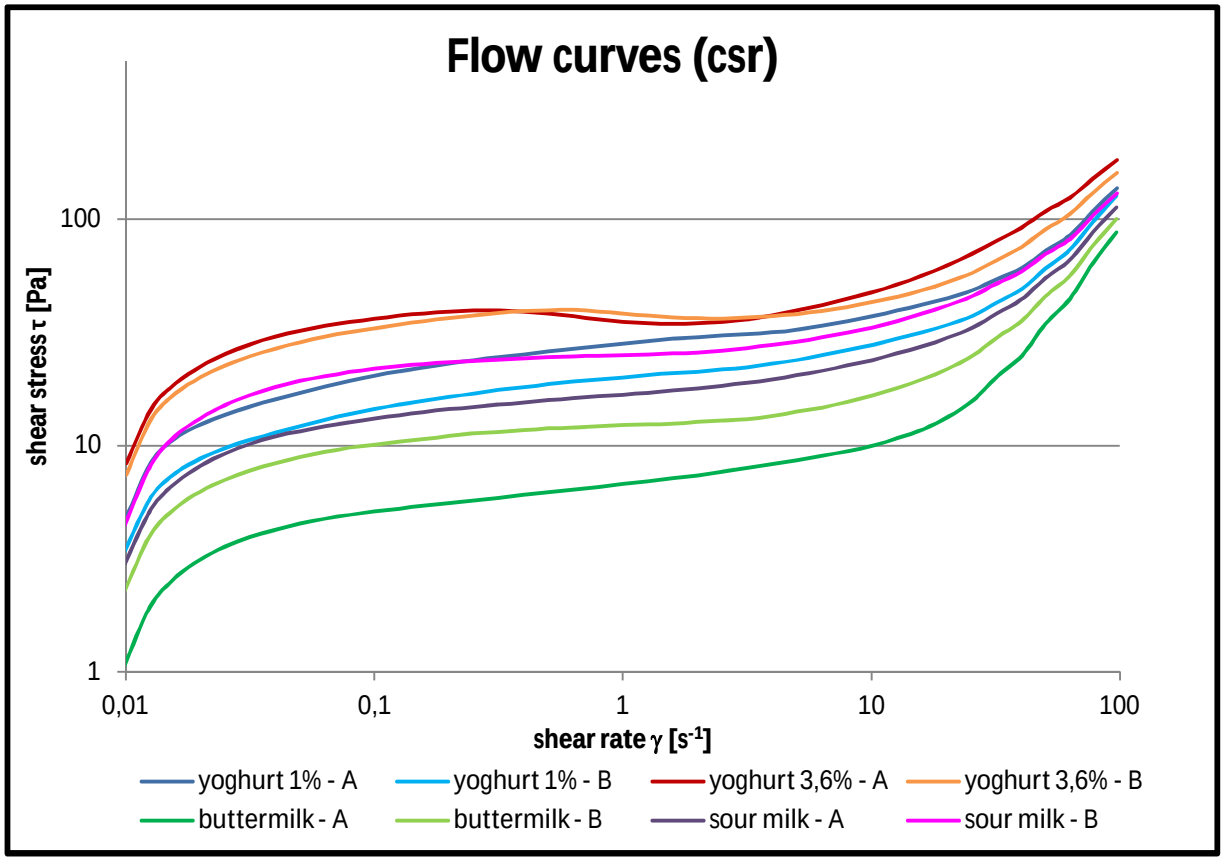

Figure 5.21: Flow curves of dairy products

5.3.3.1.2 Controlled shear stress (CSS)

Another possibility to determine the yield stress or flow point τ_0 is the measurement in the controlled shear stress (CSS) mode. The results of the determination of yield stresses (flow points) τ_0 obtained from the gamma-tau diagram are presented in table 5.18.

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No	Description	CSS	Herschel-Bulkley parameters (CSR)		
		τ_0 [Pa]	τ_{HB} [Pa]	b [Pas]	p [-]
1	Natural stirred yoghurt 1% fat - A	20,6 ± 1,1	26,6 ± 1,5	1,05 ± 0,14	0,922 ± 0,028
2	Natural stirred yoghurt 1% fat - B	18,4 ± 0,8	20,0 ± 1,3	0,82 ± 0,1	0,957 ± 0,025
3	Natural stirred yoghurt 3,6% fat - A	28,0 ± 1,6	28,2 ± 2,1	2,30 ± 0,28	0,882 ± 0,039
4	Natural stirred yoghurt 3,6% fat - B	32,5 ± 0,7	35,3 ± 3,5	0,58 ± 0,06	1,15 ± 0,03
5	Natural buttermilk 1% fat - A	5,0 ± 0,4	7,7 ± 0,4	0,064 ± 0,003	1,508 ± 0,01
6	Natural buttermilk 1% fat - B	10,6 ± 1,2	13,3 ± 2,0	0,229 ± 0,044	1,237 ±0,038
7	Sour milk 3,5% fat - A	12,5 ± 0,9	16,4 ± 1,1	0,66 ± 0,029	1,00 ±0,012
8	Sour milk 3,5% fat - B	16,2 ± 0,7	24,1 ± 1,4	1,08 ± 0,211	0,946 ± 0,057

Table 5.18: τ_0 and Herschel-Bulkley parameters of dairy products obtained by rotational rheometry (CSR and CSS)

The obtained data of τ_0 correlate well with the Herschel-Bulkley flow points τ_{HB} which can be evaluated as a positive control for both methods.

Again it can be seen that the samples containing more fat exhibit higher values of yield stresses; this is valid both for yoghurts and the liquid products. Again yoghurts show higher yield stresses than buttermilk or sour milk.

5.3.3.2 Oscillatory rheometry

5.3.3.2.1 Amplitude sweep

The results of the amplitude sweep are presented in table 5.19 and in figures 5.22 and5.23.

The data obtained from the amplitude sweep draw a complex picture of the samples and their fragile structures. As was anticipated low fat products showed a wider resistance towards irreversible structure destruction compared to the high fat products. This can be learned of the LVR values. This is because the casein networks having less fat globules built in the inner structure are tighter and therefore resist disruption to a larger amount. In contrast the high fat products gain elasticity by the incorporated fat globules, which is reflected by the higher values of G' and G'' compared to the low fat samples.

In addition there can be recognized a step within the values that has its origin in the difference of texture. The more solid yogurts exhibit higher values of G' and G'' compared to the more liquid buttermilk and sour milk samples.

The higher elasticity of the fatter products is also reflected by the higher flow points τ_F. It is remarkable that the values of G' and G'' at the crossover (the flow point) are very low compared to the values within the LVR, which means that the structure forming gel networks have to be disrupted thoroughly before they flow.

No	Description	LVR [%]	G'(γ = 1%) [Pa]	G''(γ = 1%) [Pa]	τ_F (G' = G'') [Pa]	G' = G'' [Pa]
1	Natural stirred yoghurt 1% fat - A	2,4 ± 0,15	211 ± 15	49 ± 3	14,7 ± 1,9	22,2 ± 1,7
2	Natural stirred yoghurt 1% fat - B	2,42 ± 0,35	268 ± 4	63 ± 1	19,8 ± 1,1	30,5 ± 0,4
3	Natural stirred yoghurt 3,6% fat - A	1,16 ± 0,41	341 ± 20	86 ± 6	17,4 ± 0,4	31,6 ± 1,2
4	Natural stirred yoghurt 3,6% fat - B	1,72 ± 0,31	393 ± 41	96 ± 10	24,0 ± 2,4	38,9 ± 4,4
5	Natural buttermilk 1% fat - A	2,97 ± 0,17	55 ± 2	12 ± 1	5,1 ± 0,3	6,0 ± 0,1
6	Natural buttermilk 1% fat - B	1,85 ± 0,38	123 ± 11	29 ± 3	8,8 ± 0,6	13,7 ± 1,1
7	Sour milk 3,5% fat - A	1,72 ± 0,33	182 ± 14	43 ± 4	14,1 ± 1,3	18,5 ± 2,2
8	Sour milk 3,5% fat - B	2,08 ± 0,2	160 ± 3	37± 1	11,3 ± 0,9	18,2 ± 0,4

Table 5.19: Results obtained from the amplitude sweep of dairy products

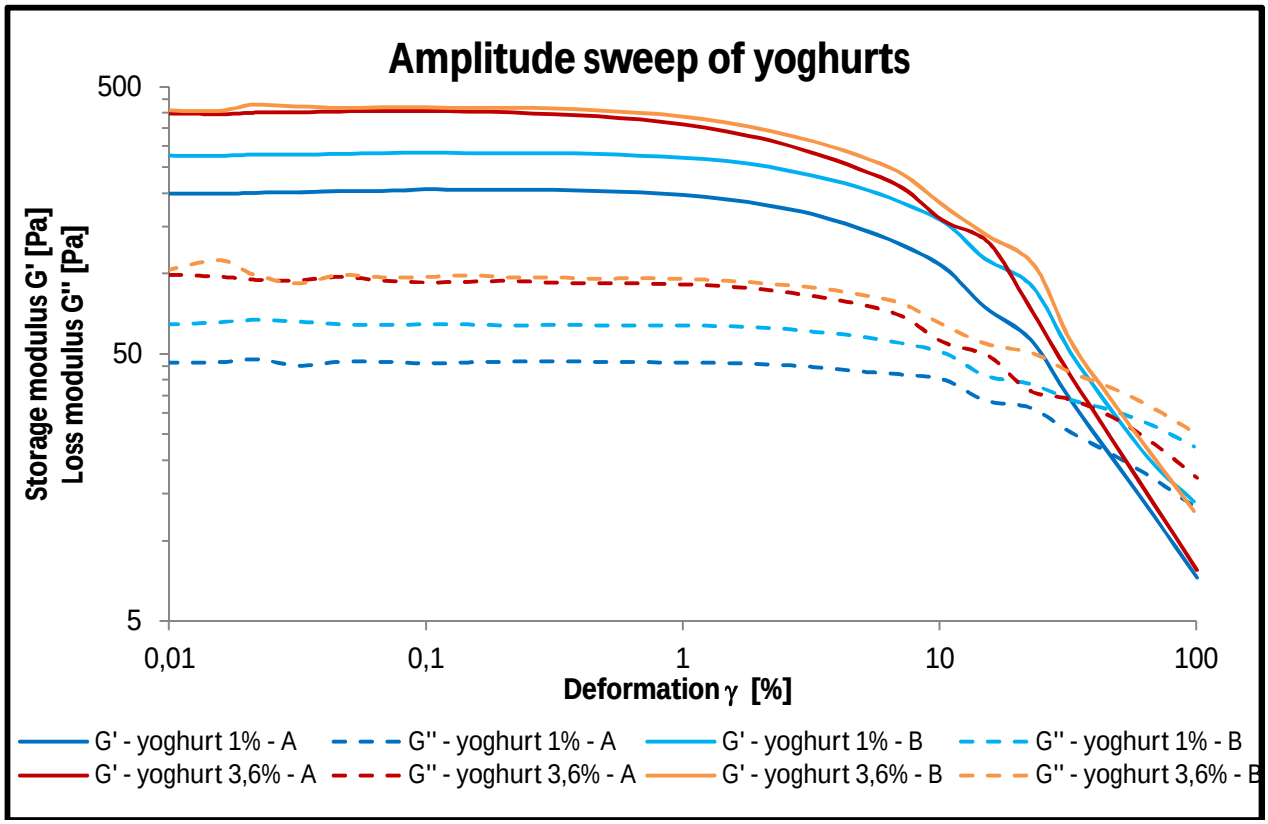

Figure 5.22: Amplitude sweeps of yoghurts

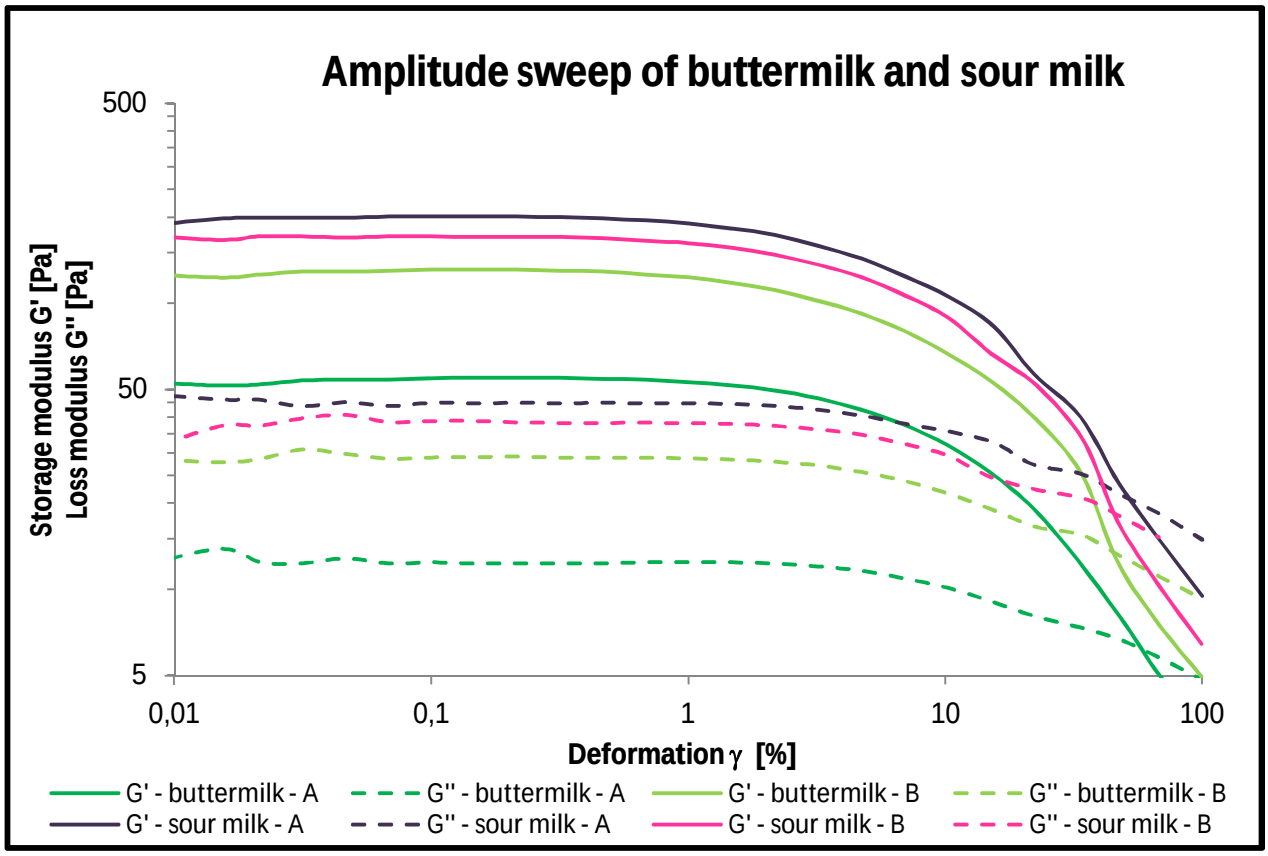

Figure 5.23: Amplitude sweeps of buttermilks and sour milks

5.3.3.2.2 Frequency sweep

The results of the frequency sweeps of dairy products are summarized in table 5.20 and in figures 5.24 and 5.25.

No	Description	Angular frequency ω = 100 rad/s			Angular frequency ω = 0,1 rad/s		
		G' [Pa]	G''[Pa]	tan δ	G' [Pa]	G'' [Pa]	tan δ
1	Natural stirred yoghurt 1% fat - A	275 ± 19	81 ± 3	0,30 ± 0,01	116 ± 6	30 ± 1	0,26 ± 0,01
2	Natural stirred yoghurt 1% fat - B	276 ± 13	80 ± 2	0,29 ± 0,01	115 ± 3	30 ± 1	0,26 ± 0,01
3	Natural stirred yoghurt 3,6% fat - A	497 ± 4	147 ± 1	0,29 ± 0,00	206 ± 1	59 ± 1	0,28 ± 0,00
4	Natural stirred yoghurt 3,6% fat - B	871 ± 6	246 ± 4	0,28 ± 0,00	360 ± 6	101 ± 3	0,28 ± 0,00
5	Natural buttermilk 1% fat - A	51 ± 4	21 ± 1	0,40 ± 0,03	24 ± 1	6 ± 0	0,25 ± 0,01
6	Natural buttermilk 1% fat - B	99 ± 6	34 ± 2	0,34 ± 0,00	39 ± 12	12 ± 1	0,34 ± 0,12
7	Sour milk 3,5% fat - A	195 ± 2	65 ± 2	0,33 ± 0,01	85 ± 2	23 ± 1	0,27 ± 0,00
8	Sour milk 3,5% fat - B	242 ± 26	77 ± 8	0,32 ± 0,00	107 ± 11	29 ± 3	0,27 ± 0,00

Table 5.20: Results obtained from the frequency sweep of dairy products

The data obtained from the frequency sweep reveal clearly distinct values of G' and G'' for each group of dairy products. The highest values of G' (and G'' respectively) were measured in high fat yoghurt followed by low fat yoghurt and sour milk while buttermilk exhibited the lowest values of G' and G''. There is also an order regarding either the "more solid" or the "more liquid" samples. Both with yoghurt and the liquid samples the higher the fat content the higher are G' and G''. By G' exceeding G'' in all samples, the gel character of the samples is confirmed. This is also backed by the values of tan δ that are in the range of 0,25 – 0,4 exhibiting the lower values at low frequencies. Values of tan δ equalling smaller than 1 are a characteristic of visco-elastic materials. The fact that all tan δ of the tested samples are in the same range is most likely because the gels of the tested samples origin from casein networks. The smaller values of tan δ at low frequencies might be a sign for a more stable gel network at long time rest. However the higher values of tan δ at high frequencies are likely to be a sign of measurement instabilities in the beginning of the measurement as the frequency sweep is usually started with high frequencies.

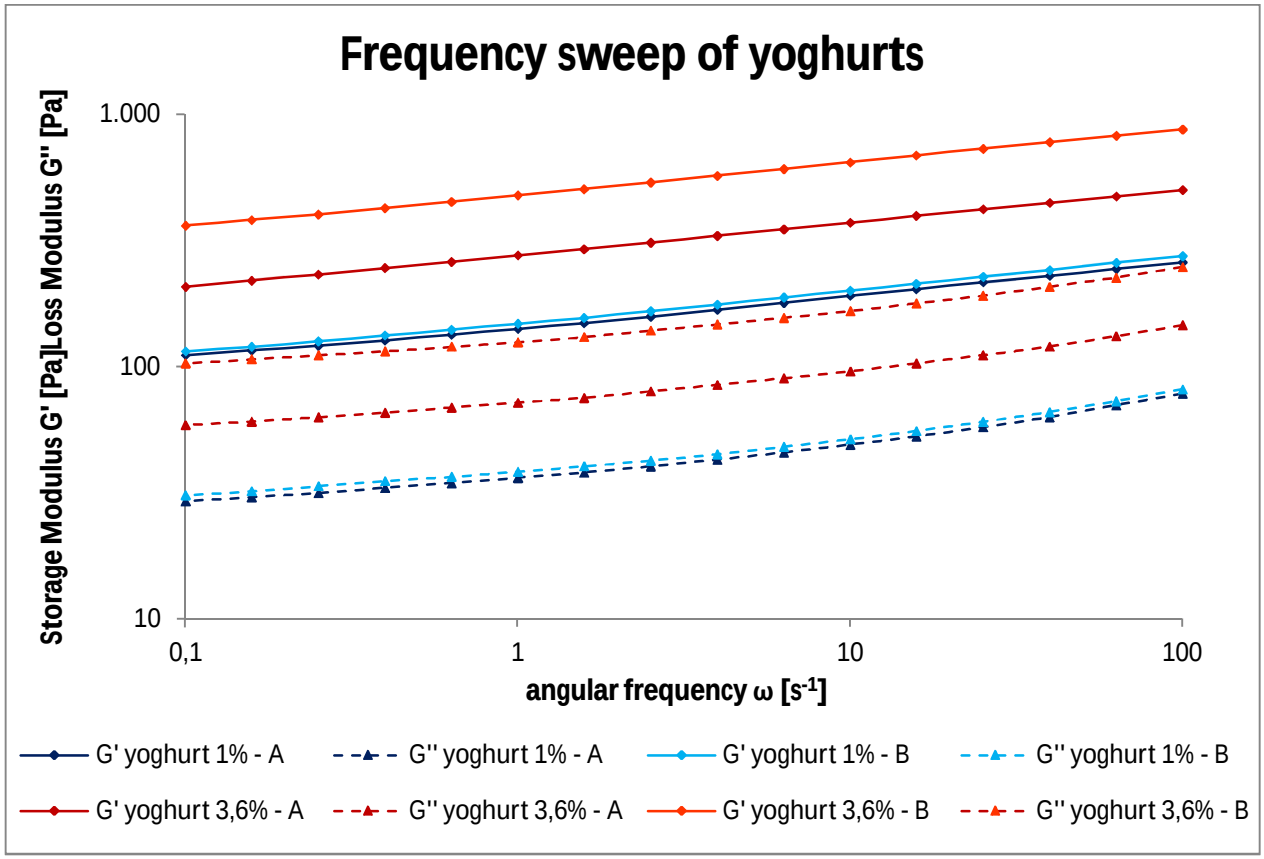

Figure 5.24: Frequency sweeps of yoghurts

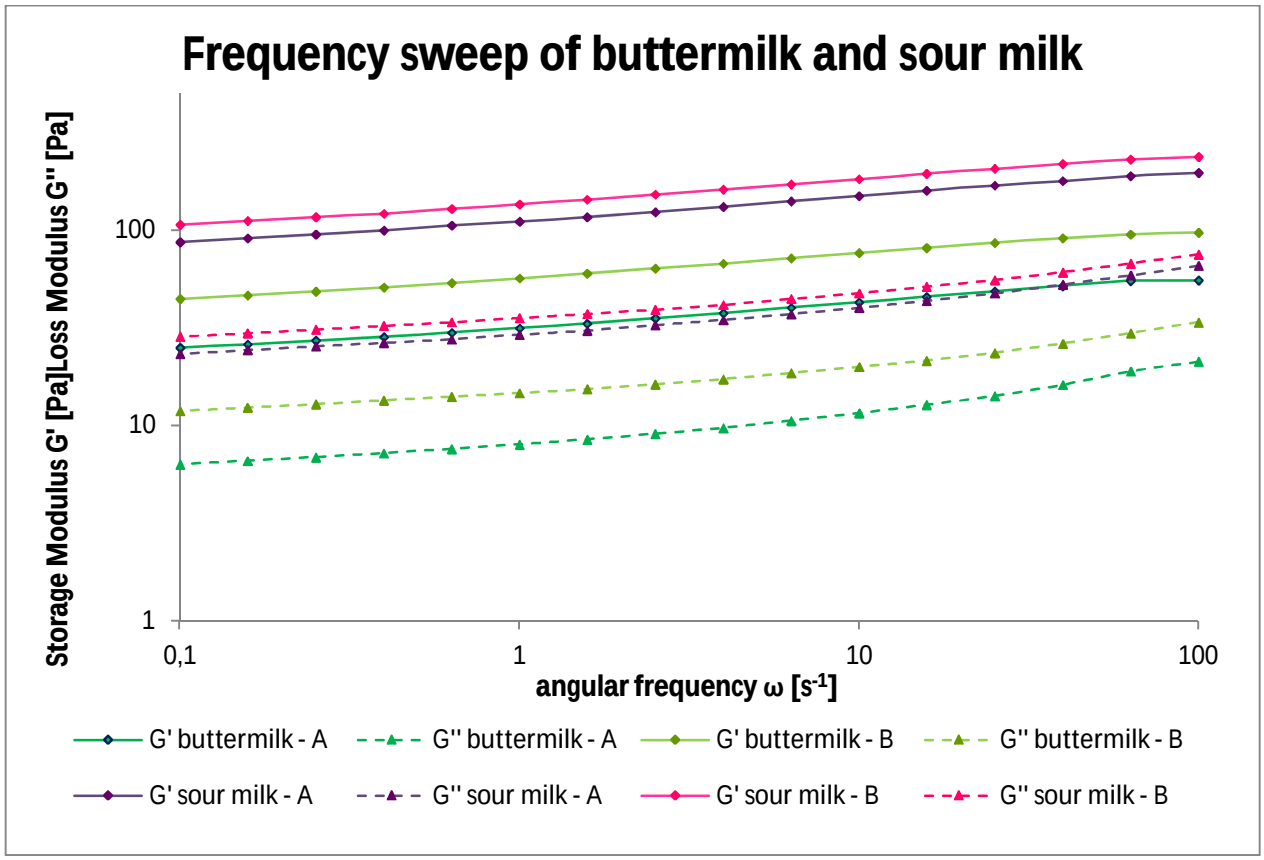

Figure 5.25: Frequency sweeps of buttermilks and sour milks

5.3.4 Discussion - Rheological properties of dairy products related to migration

Evaluating the whole set of results of dairy products leads to the following assumptions:

Although the rheological characterisation is an appropriate means to differentiate the samples in product groups a clear correlation to migration rates cannot be given. However, there seems to be a relationship between the migration of the regarded additives and the storage moduli G' of the food samples. The higher the value of G' the less migration takes place.

On the other hand the migration data obtained in this study deviate quite a lot to make a clear predication concerning a differentiation. In this study this might be caused by several facts. First of all the uncertainty about the LLDPE test film has to be mentioned. As already demonstrated the ratio of the migrating analytes benzophenone and diphenyl phthalate changed from ~ 2,5 over ~1 to < 1 (0,6 to 0,3) over the course of the three migration studies.

The products and chemicals used for these migration tests were not changed and the obtained data were coherent within each test series. So this led to the conclusion that the test film had changed somehow. Probable reasons for the different behaviour could be an ageing of the PE material in that way that the PE chains untangled and let the incorporated additives free. The additives could diffuse more easily to the surface of the film and the amount that was found in the samples originated only partly from the diffusion process but rather from washing off.

A third explanation for the weak relation of migration and rheology data can be found in the fact that the purchased samples not only varied in the fat content, which was part of the investigation, but also varied in contents of carbohydrates, protein and water. These were obviously too many parameters influencing both rheological properties and migration rates and therefore no direct correlation statement can be given at that time.

5.4 Modelled migration

The results of the modelled (computed) migration are presented in tables 5.21 and 5.22 and in figures 5.26 to 5.33.
The partition coefficient K was chosen at several levels as the real values were not known or determined. A partition coefficient K = 0 equals high solubility of the migrant in the food whereas K = 100 means low solubility of the migrant in the food.

Temperature [°C]	estimated diffusion coefficient of benzophenone [cm^2/s]	estimated diffusion coefficient of diphenyl phthalate [cm^2/s]
5	1,1 E-9	2,3 E-10
25	1,3 E-8	2,8 E-9
40	7,1 E-8	1,5 E-8
70	1,3 E-6	2,8 E-7

Table 5.21: Estimated (computed) diffusion coefficients of benzophenone and diphenyl phthalate in LDPE and LLDPE

Temperature	Partition coefficient K	migration time t	migration of benzophenone at migration time [mg/dm^2]	migration of diphenyl phthalate at migration time [mg/dm^2]
5°C (Film B)	0	24 h	0,42 (= 54,5%)	0,20 (= 20,6%)
	1	24 h	0,42 (= 54,2%)	0,20 (= 20,5%)
	10	24 h	0,40 (= 51,6%)	0,19 (= 20%)
	100	24 h	0,26 (= 33,4%)	0,15 (= 15,2%)
40°C (Film B)	0	10 d	0,77 (= 100%)	1,00 (= 100%)
	1	10 d	0,76 (= 98,9%)	0,95 (= 98,9%)
	10	10 d	0,69 (= 89,6%)	0.86 (= 89,7%)
	100	10 d	0,34 (= 44,1%)	0,43 (= 44,7%)
25°C (Film A)	0	22 d	0,67 (= 100%)	0,84 (= 100%)
	1	22 d	0,67 (= 99%)	0,83 (= 99%)
	10	22 d	0,61 (= 90,7%)	0,76 (= 90,8%)
	100	22 d	0,32 (= 47,4%)	0,40 (= 47,7%)
70°C (Film A)	0	25 h	0,67 (= 100%)	0,84 (= 100%)
	1	25 h	0,67 (= 99%)	0,83 (= 99%)
	10	25 h	0,61 (= 90,4%)	0,76 (= 90,6%)
	100	25 h	0,31 (= 46,6%)	0,39 (= 47,1%)

Table 5.22: Results of computed migration at different partition coefficients K

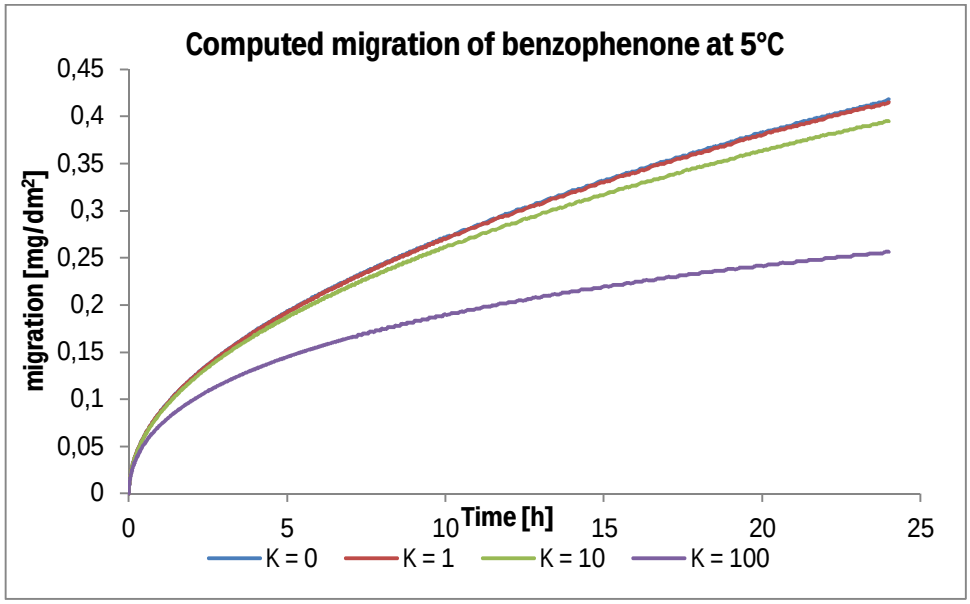

Figure 5.26: Computed migration of benzophenone at 5°C and various partition coefficients K (test film B)

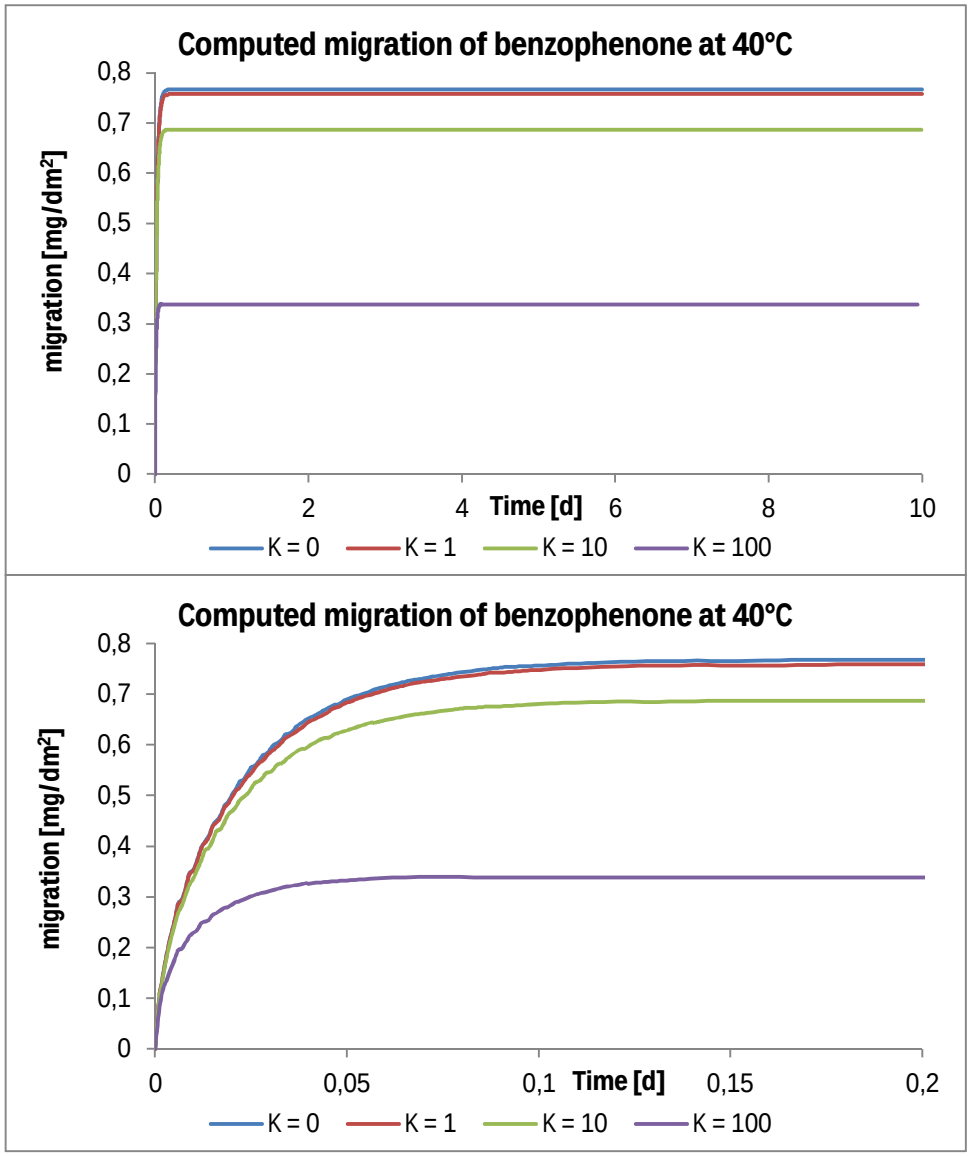

Figure 5.27: Computed migration of benzophenone at 40°C and various partition coefficients K (test film B)

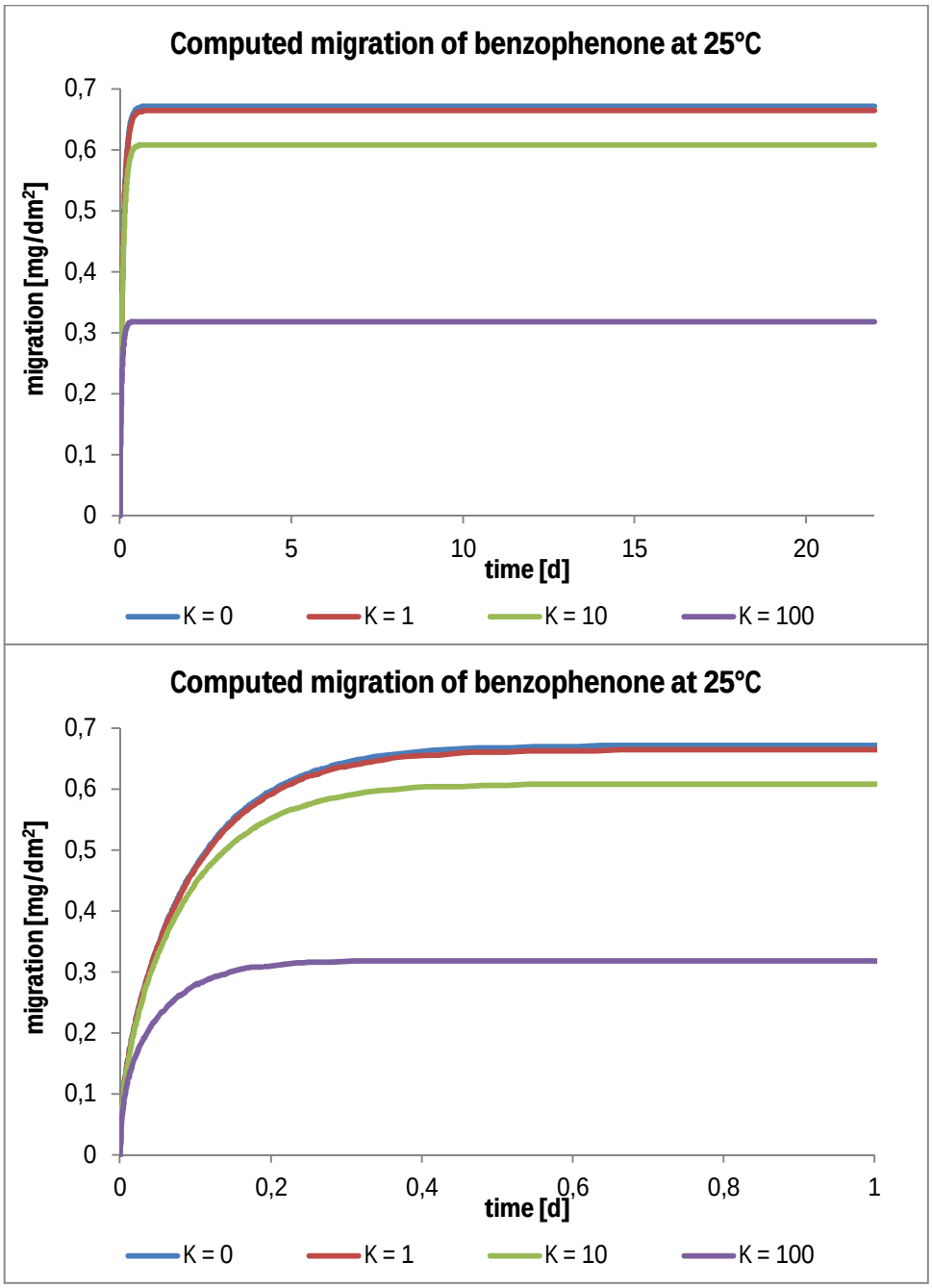

Figure 5.28: Computed migration of benzophenone at 25°C and various partition coefficients K (test film A)

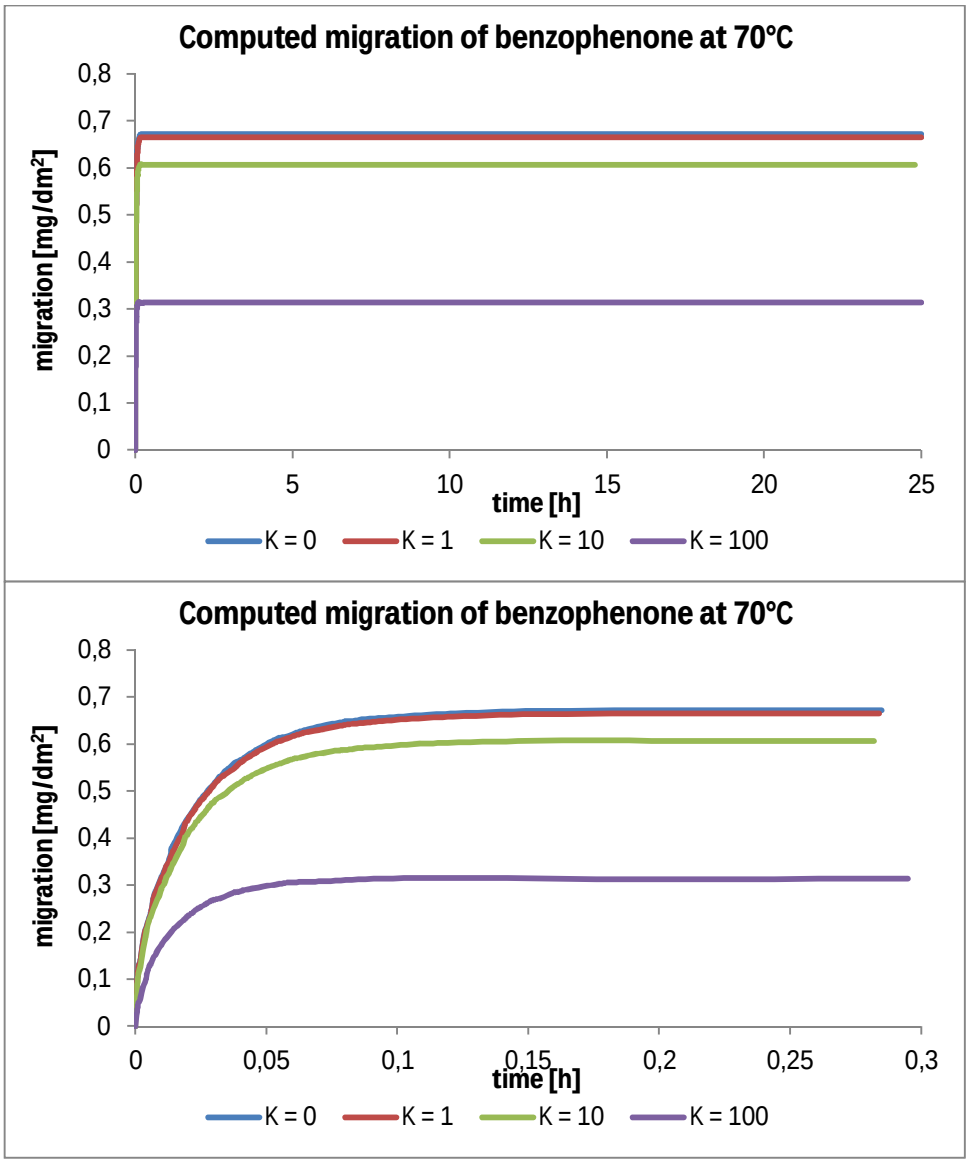

Figure 5.29: Computed migration of benzophenone at 70°C and various partition coefficients K (test film A)

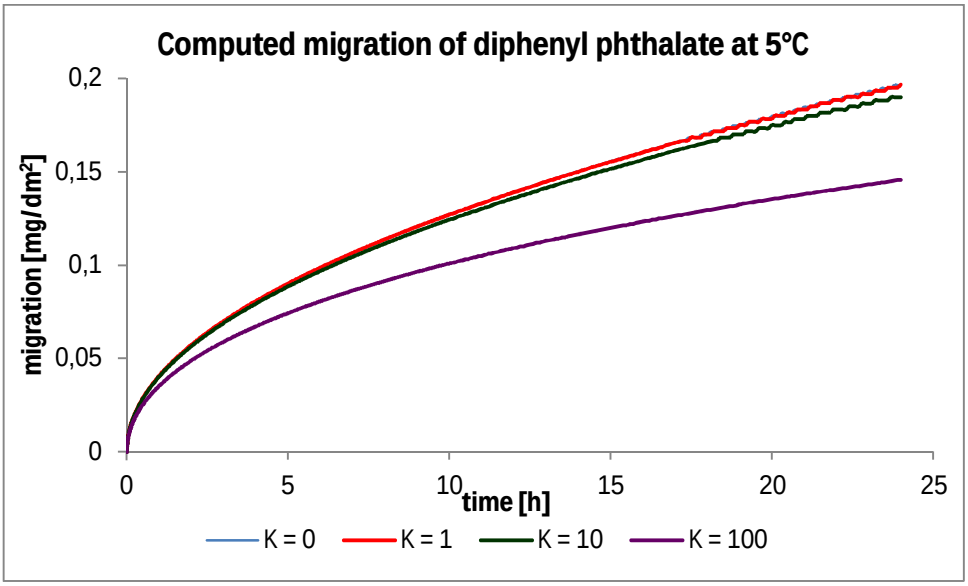

Figure 5.30: Computed migration of diphenyl phthalate at 5°C and various partition coefficients K (test film B)

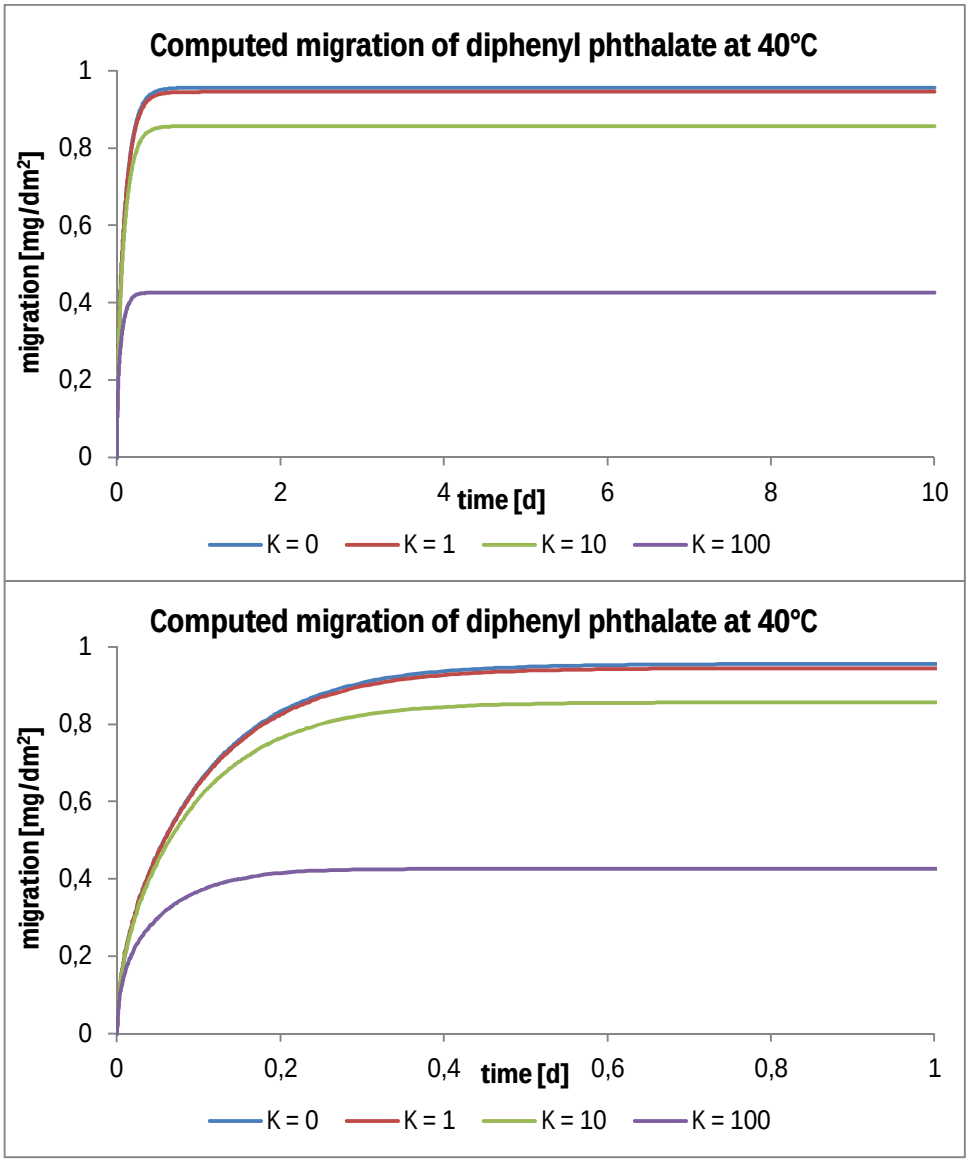

Figure 5.31: Computed migration of diphenyl phthalate at 40°C and various partition coefficients K (test film B)

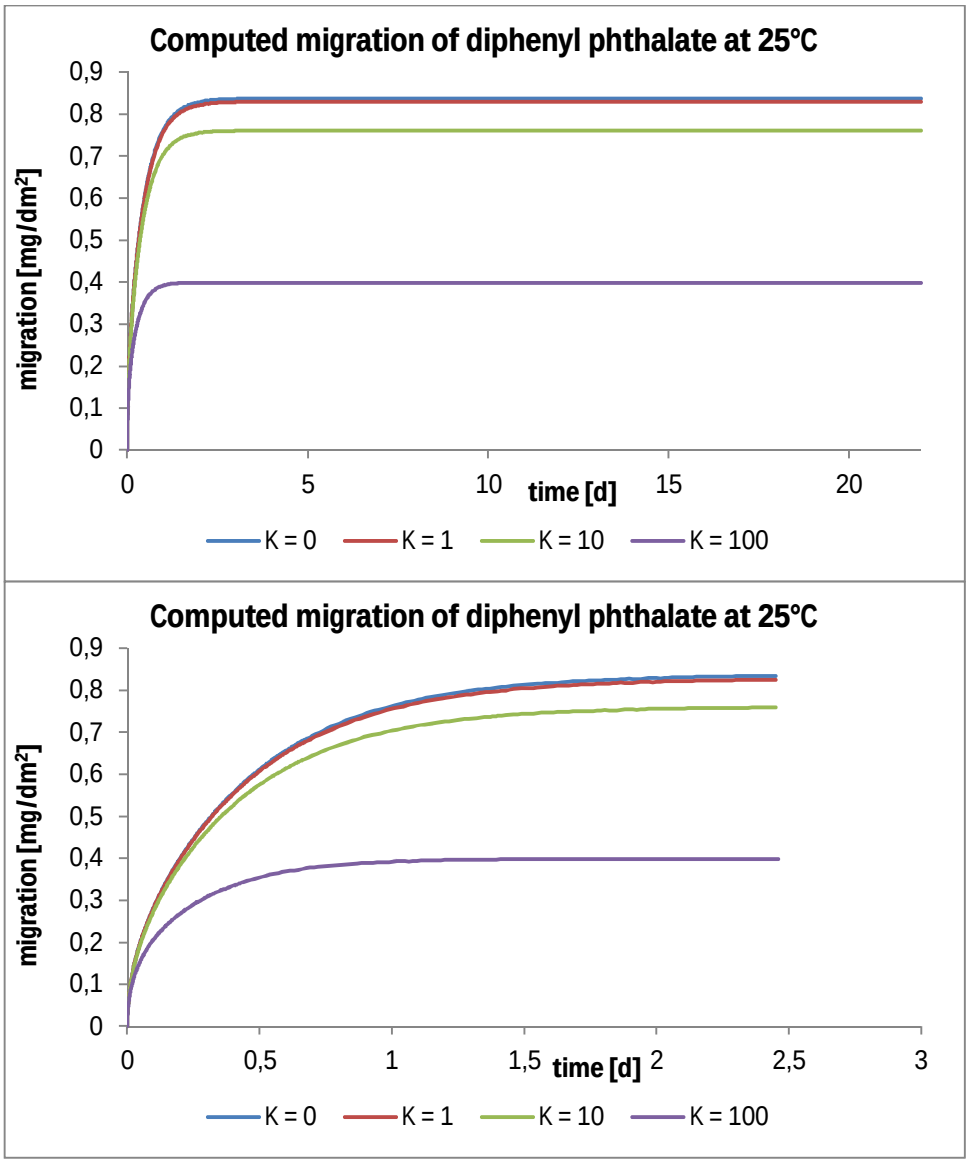

Figure 5.32: Computed migration of diphenyl phthalate at 25°C and various partition coefficients K (test film A)

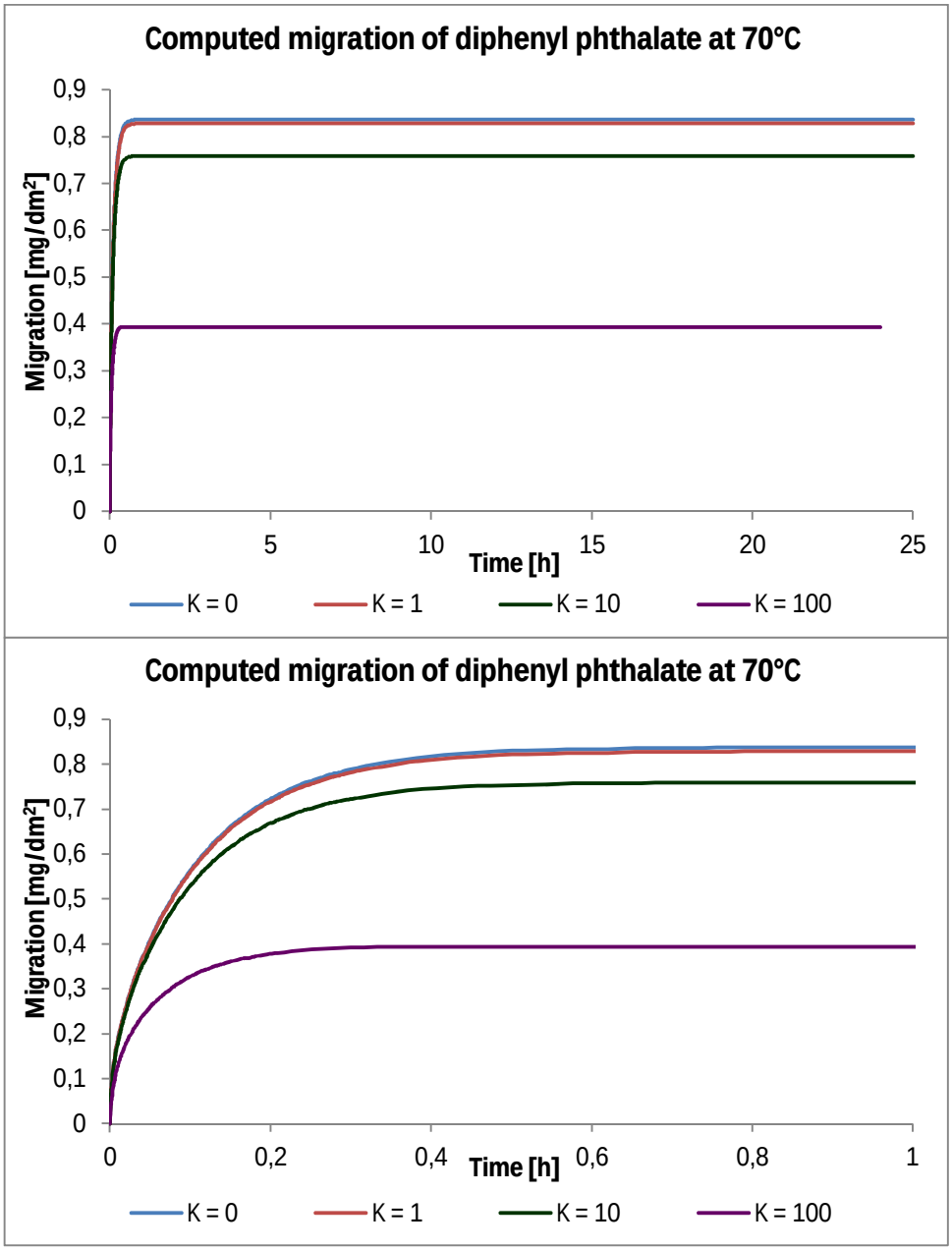

Figure 5.33: Computed migration of diphenyl phthalate at 70°C and various partition coefficients K (test film A)

As can be evaluated from the results both migrants (benzophenone and diphenyl phthalate) are predicted to reach equilibrium in dependency of the partition coefficients very quickly and long before the end of the migration time. This is the case at all temperatures apart from 5°C at which the migration time was set very short (according to the real test conditions). According to the modelling program the final amount of migrated compounds is hence dependent on the temperature and the partition coefficient between the polymer and the food. It can be noticed that although the diffusion coefficients of benzophenone and diphenyl phthalate differ by about a power of ten the eventual migration rates are comparable after the migration time. However benzophenone being the smaller molecule reaches the equilibrium levels within a shorter time compared to diphenyl phthalate.

The diffusion coefficients are mainly influenced by the molecular weight of the migrants besides of the temperature.

6 Discussion

To our knowledge this was the first study dealing with migration of additives from packaging materials into food in direct relation of structure related properties of the food. Consequently working on this thesis brought up several new interrelationships that were not expected to such an extent. Selecting the foods and test conditions aimed at a practical approach i.e. foods that are available in a supermarket. In due course very several different foods were observed and resulted in maybe more questions than answers.

As the examined foods were so different so in the following they shall be discussed separately. Besides as the foods were tested with two different films and applying different test conditions a direct comparison is difficult. However a comparison to the results obtained by Peter Volansky in (3) is possible and showed that migration values into the various foods were in comparable ranges with the earlier results.

6.1 Ketchup

Ketchup as a model food was chosen to obtain more information about a group of foods that consist to a high percentage of plant-originated particles and are often a main ingredient in spiced sauces accompanying foods.

The test conditions of the migration study (temperatures and migration under static/dynamic conditions) were chosen for several reasons and considerations.

The temperatures were to reflect different storage conditions. The higher temperature (70 °C) was also to reflect temperatures that can be reached easily in foods when heated or reheated especially in plastic dishes in a microwave oven.

As already mentioned in chapter 4 (Materials and Methods) the conditions “static” and “dynamic” were applied to mimic a static storage (as on a shelf) as well as a state in motion.

Various difficulties came up both with the migration tests and the rheological measurements. One the one hand it was realized that the selected samples shared several factors affecting the structure. Here these should be mentioned:

- amount and kind of the thickening agent
- kind of the thickening agent: natural or modified starch, kind of starch
- other thickening agents: xanthan gum, carrageen gum or others
- particle size and form of tomato particles
- ratio of particles compared to the remaining ingredients.

Especially the tests executed at 70 °C gave rise to some thoughts. Which reactions were promoted at this temperature? How changed the hydro-colloidal network of the carbohydrates due to possible re-agglutination and how far would this have an impact on the migration process?

These questions are interesting in particular as there was no opportunity to conduct rheological testing at 70 °C that could have helped to throw light on the differing migration behaviour especially in the case of benzophenone.

In terms of the migration testing that is well regulated it also ought to be considered that structure changes due to elevated temperatures might not be considered in the accelerated (worst case) migration testing

standards at higher temperatures. This should be taken into account for all new foods that are specially designed in respect to their structure in order to achieve a positive texture perception; these structural elements might not tolerate higher temperatures.

Bearing in mind that ketchups exhibit shear thinning behaviour and evaluating the results of the rheology tests it can be maintained that structure changes as for instance induced by shear stress can also lead to differences in migration. As could be shown in the viscosity curves (see figure 5.5) the tested samples showed shear-thinning to different extents. A conclusion of this finding is that migration into products in motion (under stress) is likely to differ to migration into the same product at rest because under stress the food structure is changed. So evaluating and predicting migration by modelling should also comprise structure changes due to applied stress as it is the case when the products are transported over a longer period.

To answer all these questions in this case – regarding ketchups – many more samples or samples with precise composition had to be investigated. Both ways were not intended at the beginning as it was a pronounced goal to investigate commercially available products.

6.2 Dry foods

Dry foods were selected to be investigated during this work because migration into dry foods had been neglected for a long time. Dry foods were supposed not to be very susceptible to migration because they are often not in direct contact with the packaging material and migration over the gas phase was not considered. This changed some years ago when high levels of migrated (volatile) compounds were detected in dry foods such as cake, pasta or rice (63) (64).

In this study wheat flours and sugar was investigated, flours being a food with a complex chemical composition as all contents of the grain are present (i.e. fat, protein, carbohydrates, vitamins and minerals) while sugar is a pure material containing nothing else but sucrose.

The selection of particle sizing as the food structure related technique in relation to migration gave interesting results.

Three major observations could be made with these two model foods (wheat flour and sugar).

1. Migration differed with particle size
2. Migration of benzophenone into flours resulted in oppositional in dependency on particle size compared to diphenyl phthalate: i.e. the smaller the particle size the more benzophenone migrated and the bigger the particle size the more diphenyl phthalate migrated
3. Migration exhibited a combined dependency on chemical composition and particle size: i.e. migration into flours of higher milling grade (type) that contained higher fat contents was higher.

Especially the high migration values found with powdered sugar let assume an interaction with the ambient humidity that forms a film of a water-sugar solution that facilitates the transition of compounds from a plastic film to the food. This capillary film could also promote an accelerated transport process (other than diffusion controlled) into the bulk, which should be subject of further investigations. This sugar solution film is also likely to induce different diffusion coefficients leading to higher migration rates.

The effect of humidity should also be considered when conducting migration testing using the food simulant Tenax™ that is the simulant to use in the case of dry foods. As was demonstrated by Barnkop

and Petersen humidity influences the uptake of volatile compounds as for instance benzophenone (62). The reliability of analysis has to be questioned. In addition it will have to be tested if Tenax™ really is the right approach to assess the migration into dry foods as it consists of a defined particle size distribution and polarity that might not be appropriate for all dry foods in the same way.

6.3 Dairy products

The chosen samples of dairy products represented a cross section on the variety on Austria's market.
Again some challenges accompanied this group of foods both in respect to the migration testing and to the rheology testing.
The trouble coming with the migration testing originated from the test film leading to incoherent migration values in the pre-tests. Driven by these inconsistencies SEM pictures were produced of both test films. They revealed big differences in the film surface, being more rough and irregular on the LLD-PE film used for the migration tests of dairy products and dry foods compared to the LD-PE film used for the migration tests of ketchups (cf. figures 4.1 and 4.2, chapter 4.1.2)

Although the test film appeared to be quite irregular the data of each associated set of analyses was coherent. In contrast it can also be seen as a hint to consider changes of packaging materials as well. Especially LLD-PE is assumed to be prone to faster structure changes as the polymer chains are entangled in a more loosen way compared to e.g. LD-PE or even PP.

In terms of rheology it was learnt that structure of dairy products is a very delicate system that has to be handled with the outmost care.

In this study a clear relationship between rheological parameters and migration could hardly be found, which might come from the irregularities derived of the test film. Dynamic (oscillatory) rheology is surely an appropriate means to characterise structural elements of dairy products. However, the contribution of each constitutional component (i.e. water content, fat content, protein composition) might be of further interest to research.

6.4 Comparison to computed (modelled) migration

The importance of modelled migration assessment is acknowledged. However a comparison to practically determined values can help to refine the modelling algorithms.

Figures 6.1 to 6.8 show the comparison of the simulated (modelled) migration at various partition coefficients and temperatures and the determined values of this thesis.

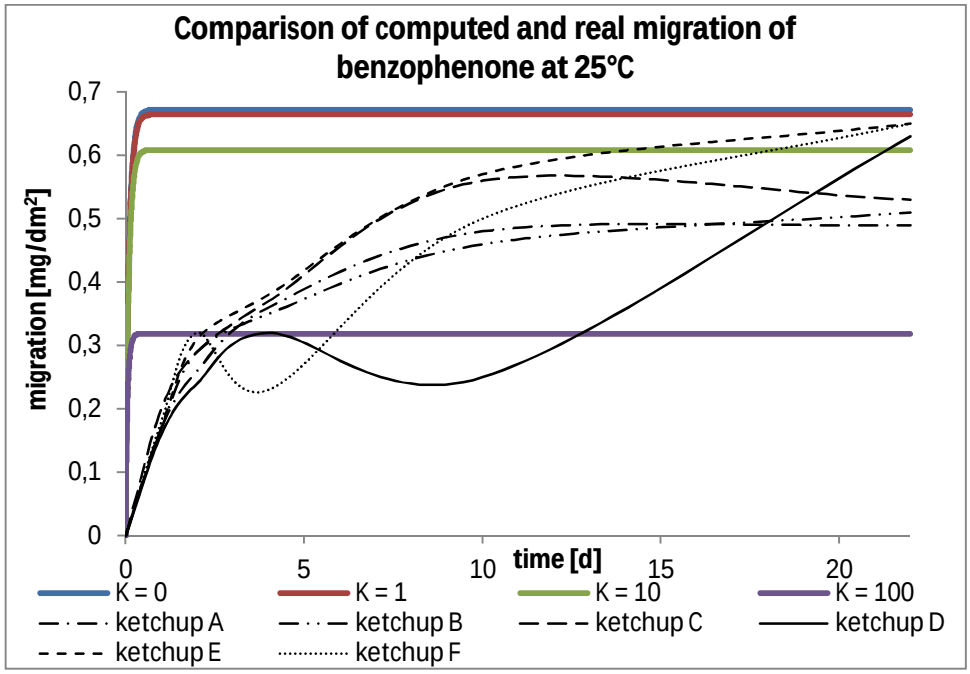

Figure 6.1: Comparison of computed and real migration (into ketchups) of benzophenone at 25°C

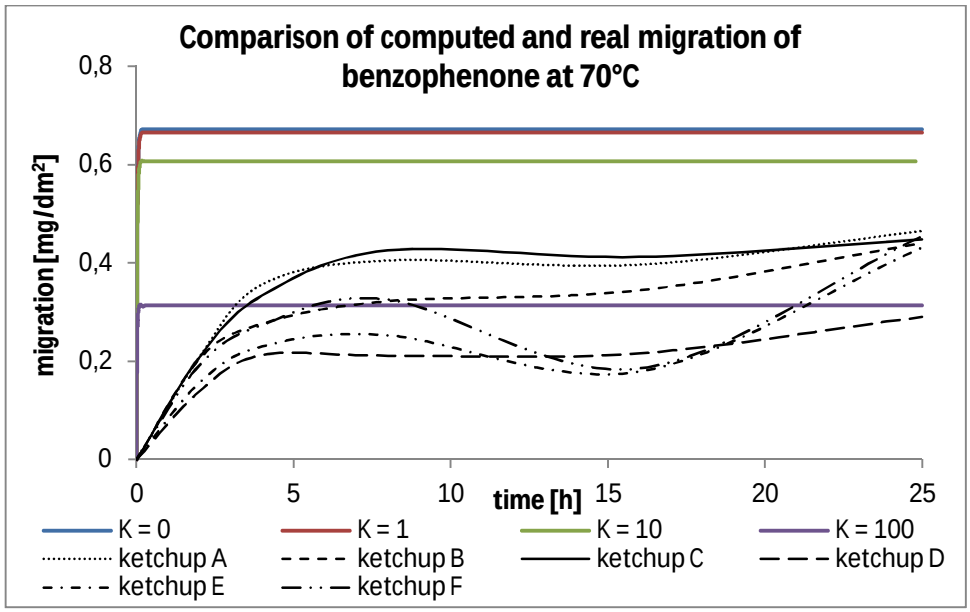

Figure 6.2: Comparison of computed and real migration (into ketchups) of benzophenone at 70°C

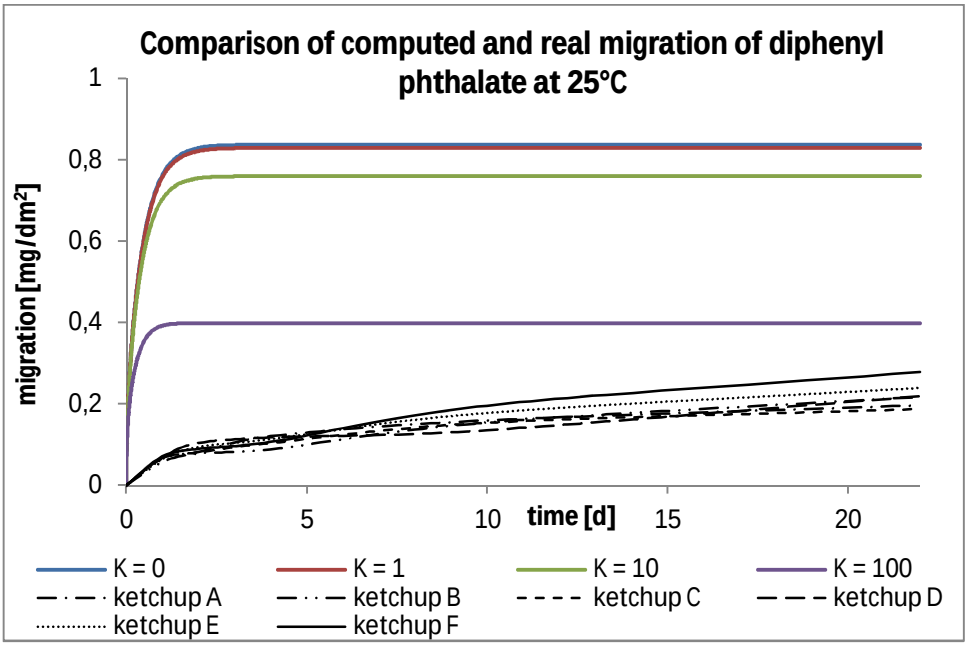

Figure 6.3: Comparison of computed and real migration (into ketchups) of diphenyl phthalate at 25°C

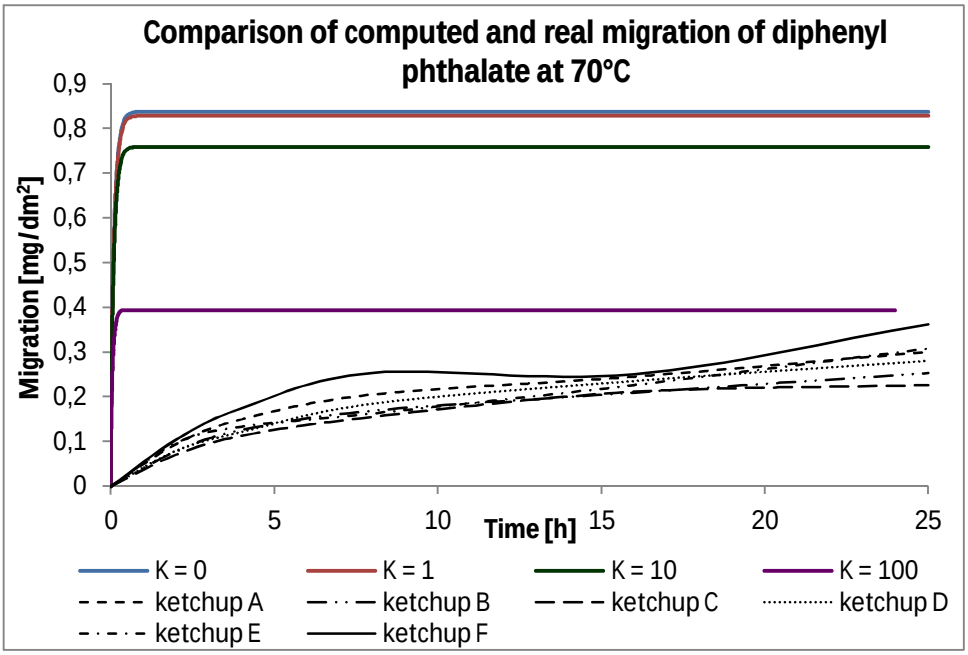

Figure 6.4: Comparison of computed and real migration (into ketchups) of diphenyl phthalate at 70°C

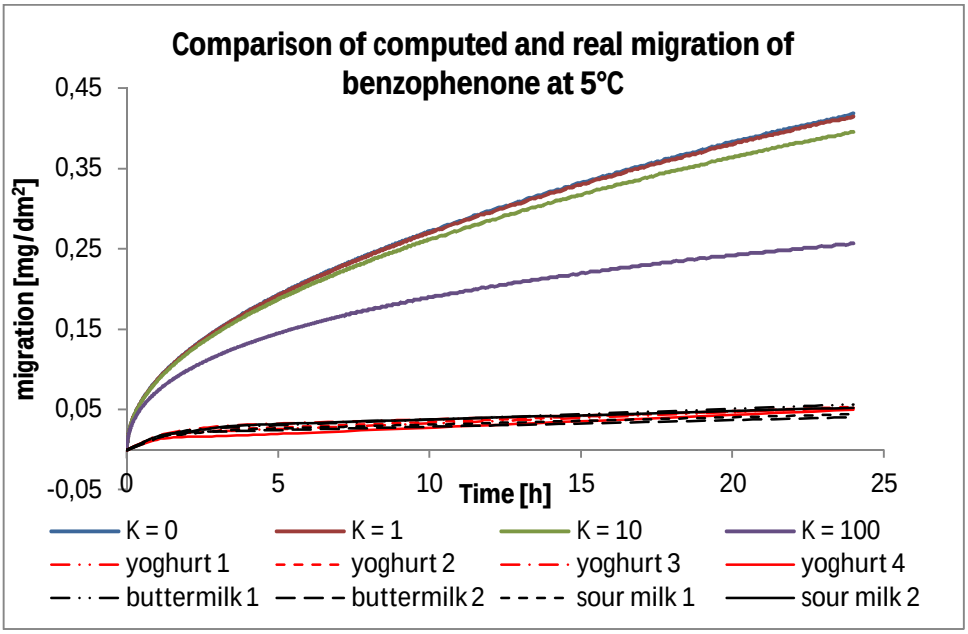

Figure 6.5: Comparison of computed and real migration (into yoghurts) of benzophenone at 5°C

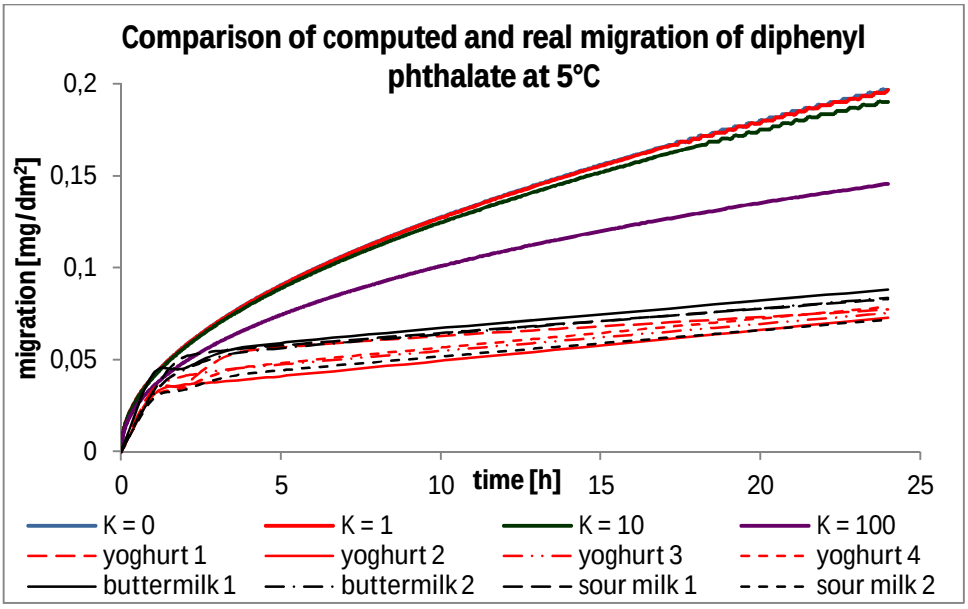

Figure 6.6: Comparison of computed and real migration (into yoghurts) of diphenyl phthalate at 5°C

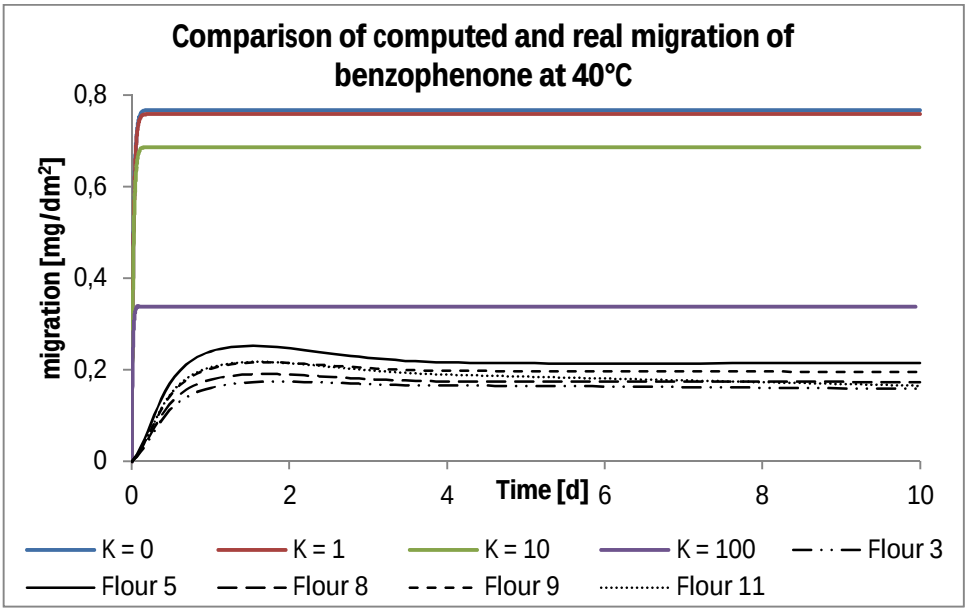

Figure 6.7: Comparison of computed and real migration (into flours) of benzophenone at 40°C

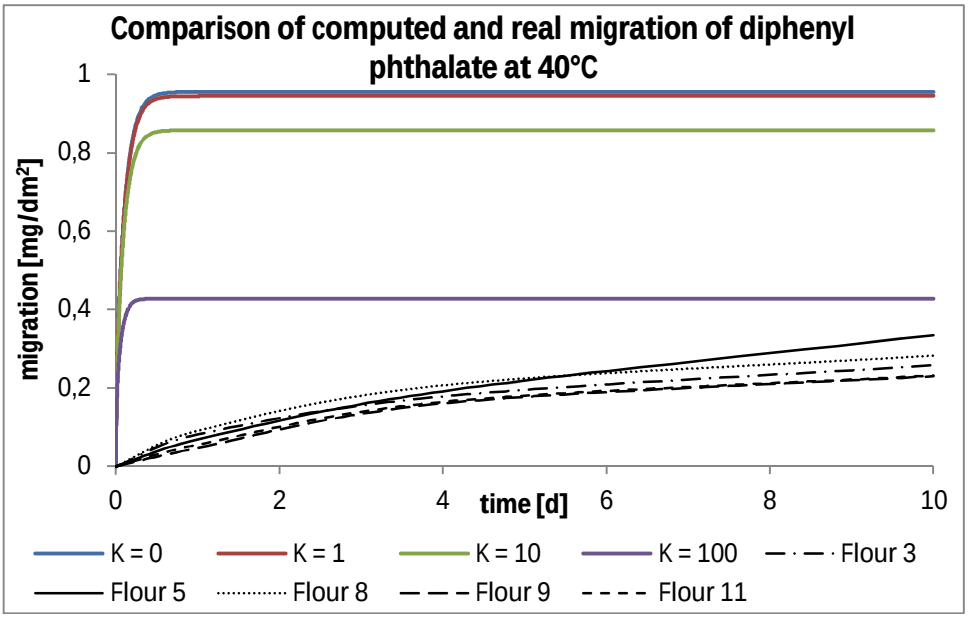

Figure 6.8: Comparison of computed and real migration (into flours) of diphenyl phthalate at 40°C

It can be easily seen that migration into real foodstuffs runs quite differently compared to the simulated migration. It can be recognized that the states of equilibrium are below the simulated equilibrium at the lowest assumed solubility of the migrants in the food under nearly all test conditions. Only in the case of migration at 25°C a comparable result was obtained.

The migration behaviour in the very beginning cannot be compared entirely as the first data points in the practical testing were only obtained after a time of 1 or 2 hours or even after 1 day in the case of the tests

at 25°C and 40°C respectively. Even taking that fact into account, the process of migration is known to be more complex than is respected by the applied modelling software. Interfacial effects like swelling of the polymer film or pore forming at the surface as it is obvious for dry foods are not considered in the used software.

6.5 Comparison to the FACET – approach

From 2008-2012 the EU– project FACET ("flavourings/additives/contact materials exposure task"; contract number: KBBE- 211686) was conducted within the 7th framework programme of the EU (65).

In this project migration was evaluated by the equilibrium constants $K_{P/F}$ (between packaging material and food) that are determined by the diffusion coefficients in the respective layers both packaging or contact material and food. Diffusion coefficients within the foods were valuated higher in liquid foods compared to semisolid or solid foods; this seems reasonable. Results obtained within the present thesis support this statement. A second approach was proposed classifying the foods according to their migration into "ethanol-water equivalents" (66) instead of the food simulants specified in the Regulation (EU) 10/2011. This approach sought to determine zones in which particular foods could be equalled a specified ethanol-water solution in terms of migration behaviour (66). This is a very interesting approach as it would simplify the food simulant procedures. The idea behind this approach is to assess the actual exposure risk to migrating compounds in a most realistic way.

In Regulation (EU) 10/2011 the food simulants A, C and D1 are ethanol-water solutions and meant to simulate foods of various fat contents (mainly). In the FACET project some foods were compared in terms of their migrating behaviour into the proposed food simulant and a particular ethanol-water solution. It could be demonstrated that there is still some scope left for improvement (66).

Results and thoughts transported in this thesis fit well into the approaches of the FACET project. On the one hand differences in solidity represented by the rheological properties of the selected foods led to differences in migration, although these differences were small. On the other hand it could also be shown that considering fat contents alone is insufficient.

6.6 Conclusion

In conclusion it has to be said that food structure obviously does have an influence on migration. The composition of the structural elements needed to be clearly investigated so that the impact of the complexity of foods in all their various realizations can be understood in respect to the topical issue of migration.

With respect to the regarded substances it is indispensable to consider the partly opposite migrating behaviour i.e. migration rate – velocity of transport to and within food, potential gradient – activity and susceptibility within food, size and chemical properties of migrating compounds – polarity and reactivity.

The temperature dependency of food structure elements should be investigated further and taken into account regarding the migration. Not only the transport process itself is temperature dependent, structure is as well.

In the case of dry foods surface effects should be investigated further, in particular the promotion of changes on the surface properties by ambient humidity that might lead to very different migration values than expected as for instance it could be demonstrated for sugar crystals.

The techniques applied in the practical work for this thesis are worth to be considered in the determination of food structure and structure related properties but surely had to be refined and combined with additional techniques especially microscopic ones.

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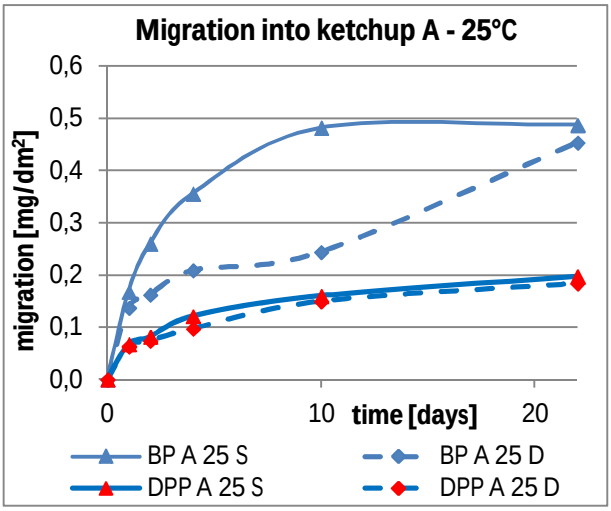
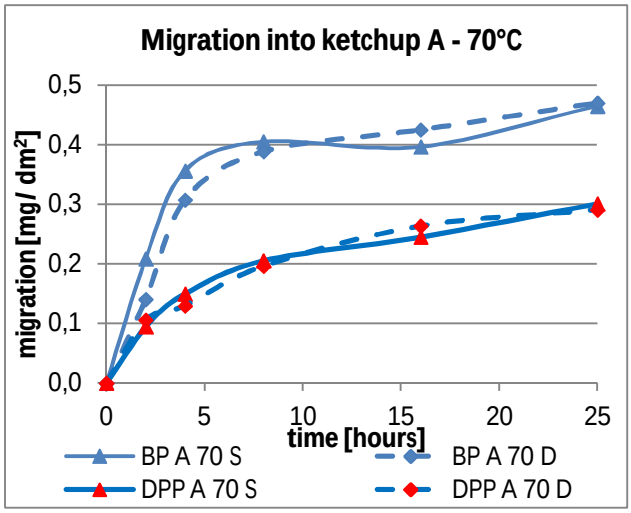
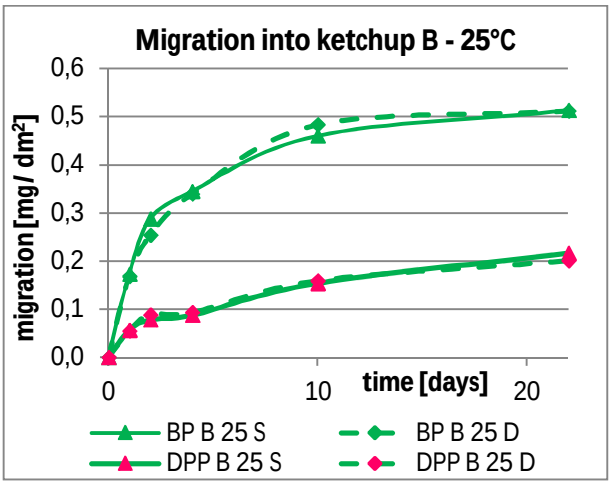
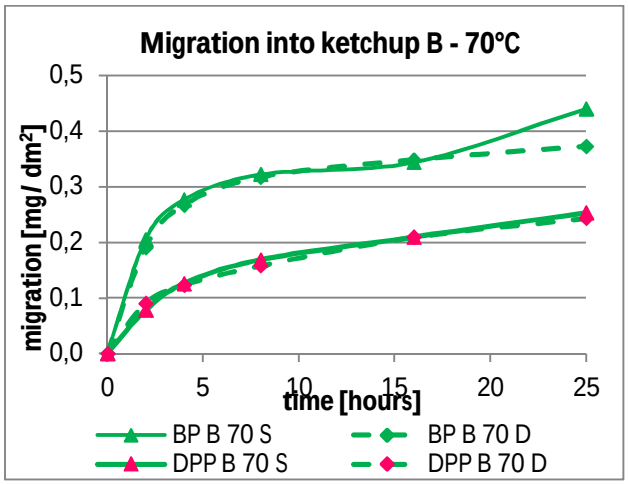
8 Appendix

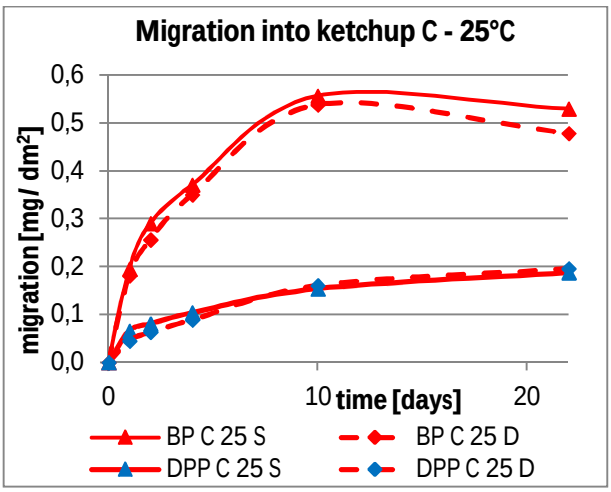
8.1 Migration curves of ketchups:

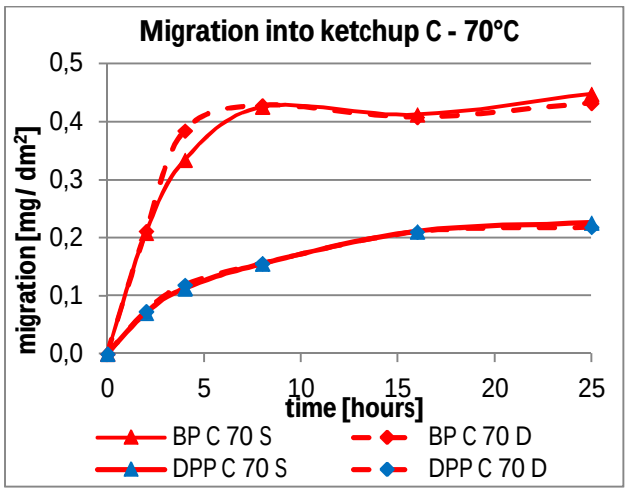


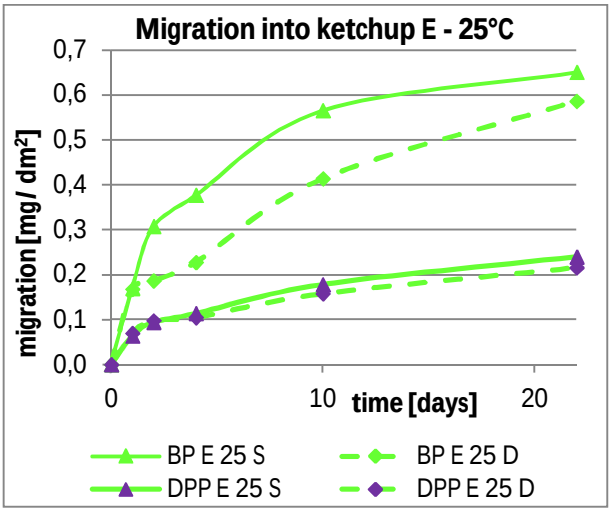


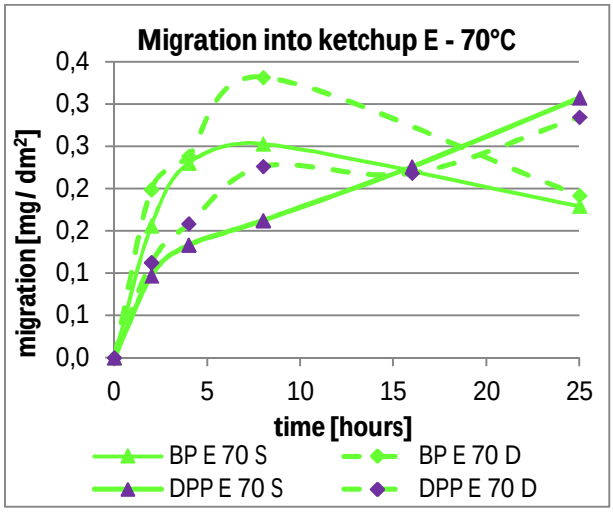


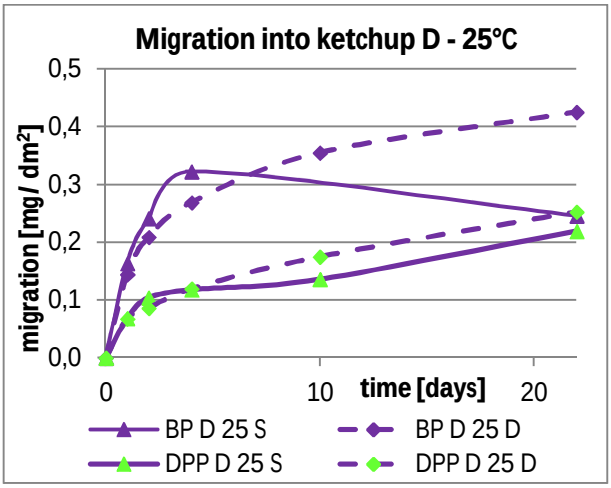


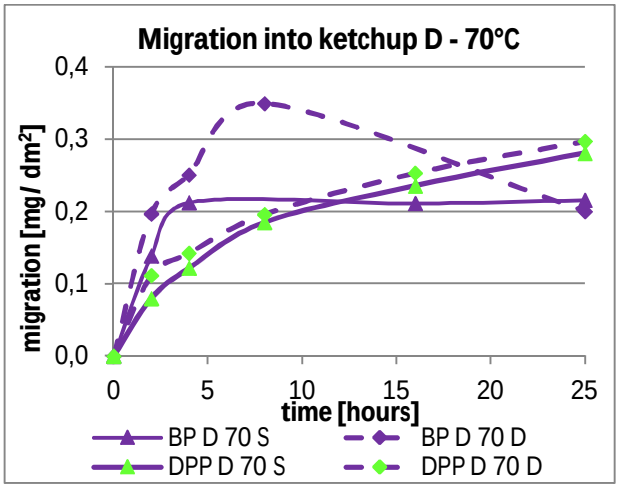


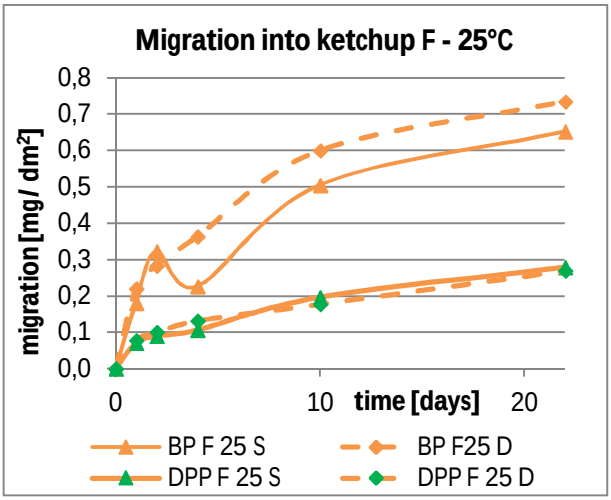


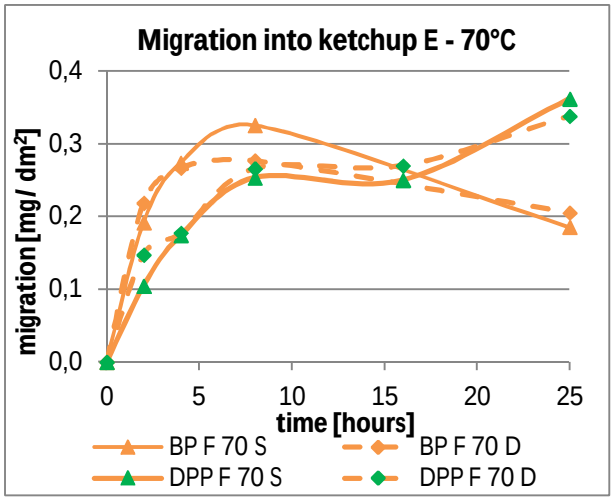

Migration into ketchup E - 25°C
migration [mg/ dm²]
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
0
10
20
time [days]
BP E 25 S
BP E 25 D
DPP E 25 S
DPP E 25 D


Migration into ketchup E - 70°C
migration [mg/ dm²]
0,4
0,3
0,3
0,2
0,2
0,1
0,1
0,0
0
5
10
15
20
25
time [hours]
BP E 70 S
BP E 70 D
DPP E 70 S
DPP E 70 D

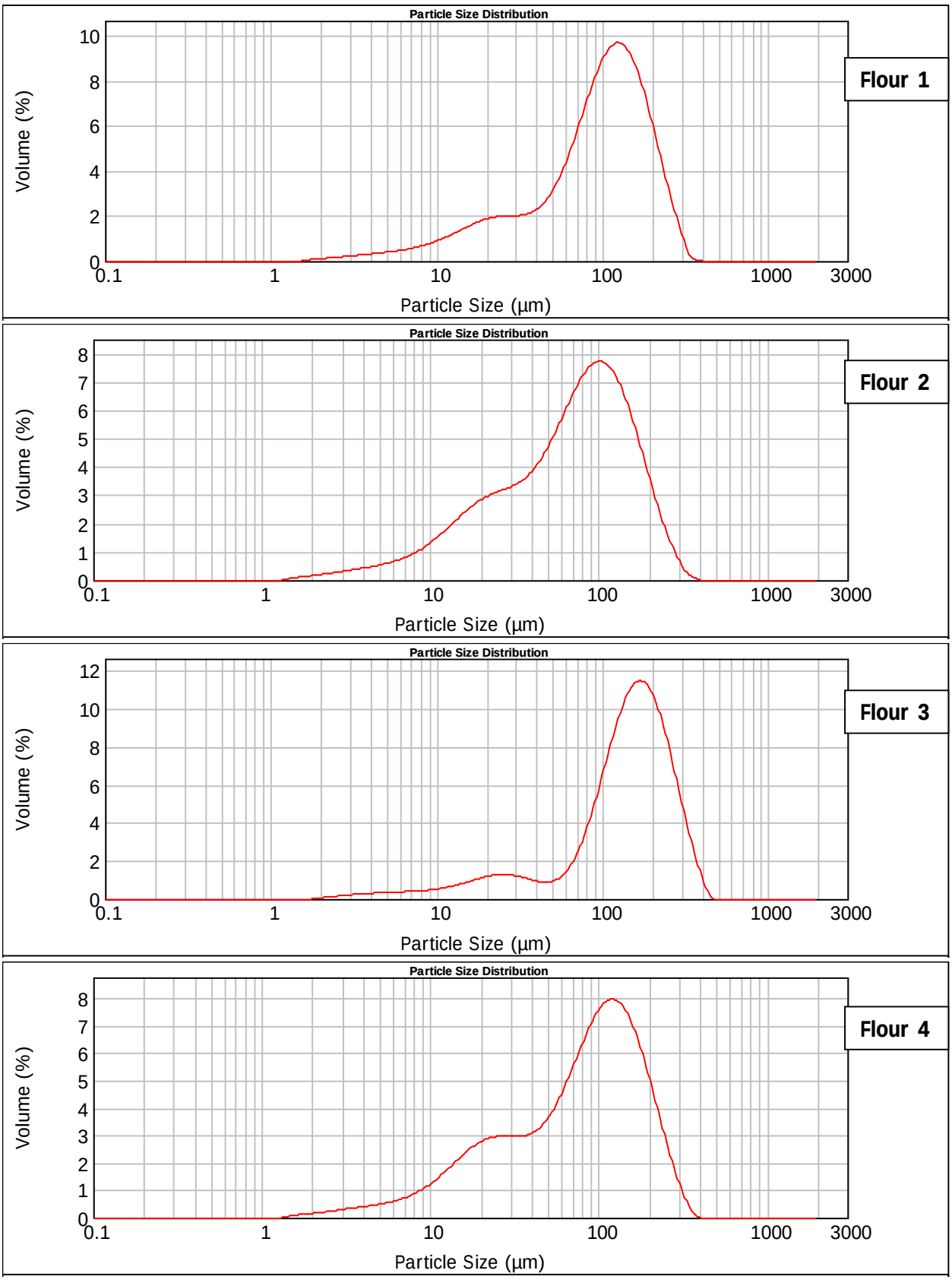

Migration into ketchup D - 25°C
migration [mg/ dm²]
0,5
0,4
0,3
0,2
0,1
0,0
0
10
20
time [days]
BP D 25 S
BP D 25 D
DPP D 25 S
DPP D 25 D

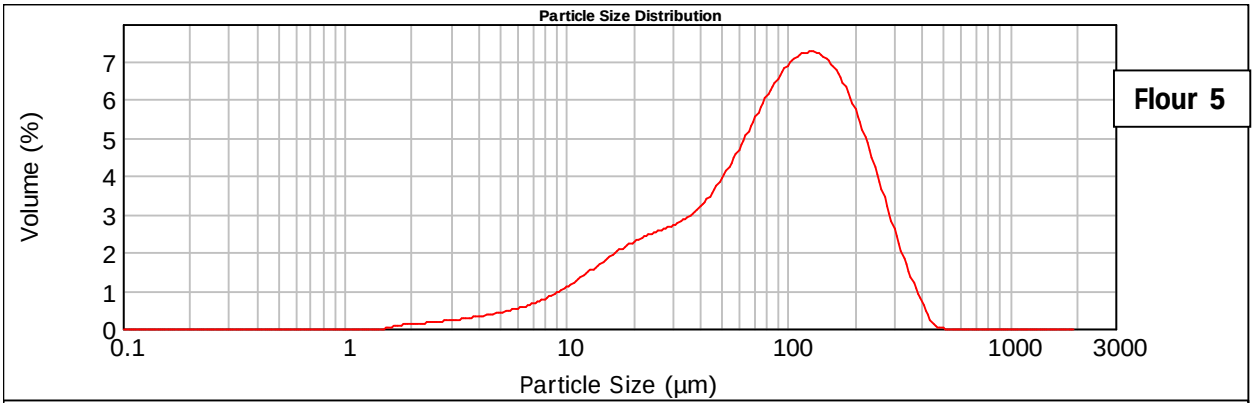

Migration into ketchup D - 70°C
migration [mg/ dm²]
0,4
0,3
0,2
0,1
0,0
0
5
10
15
20
25
time [hours]
BP D 70 S
BP D 70 D
DPP D 70 S
DPP D 70 D

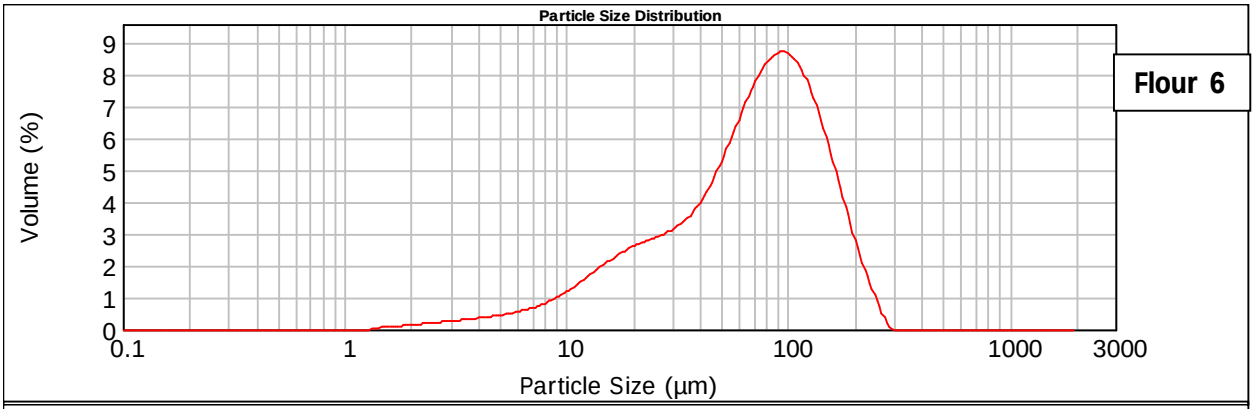

Migration into ketchup F - 25°C
migration [mg/ dm²]
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
0
10
20
time [days]
BP F 25 S
BP F25 D
DPP F 25 S
DPP F 25 D

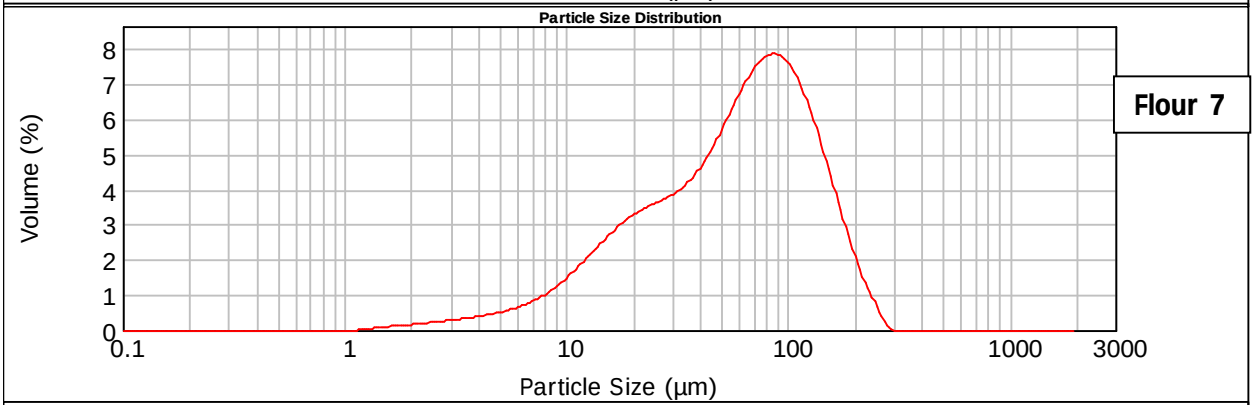

Migration into ketchup E - 70°C
migration [mg/ dm²]
0,4
0,3
0,2
0,1
0,0
0
5
10
15
20
25
time [hours]
BP F 70 S
BP F 70 D
DPP F 70 S
DPP F 70 D

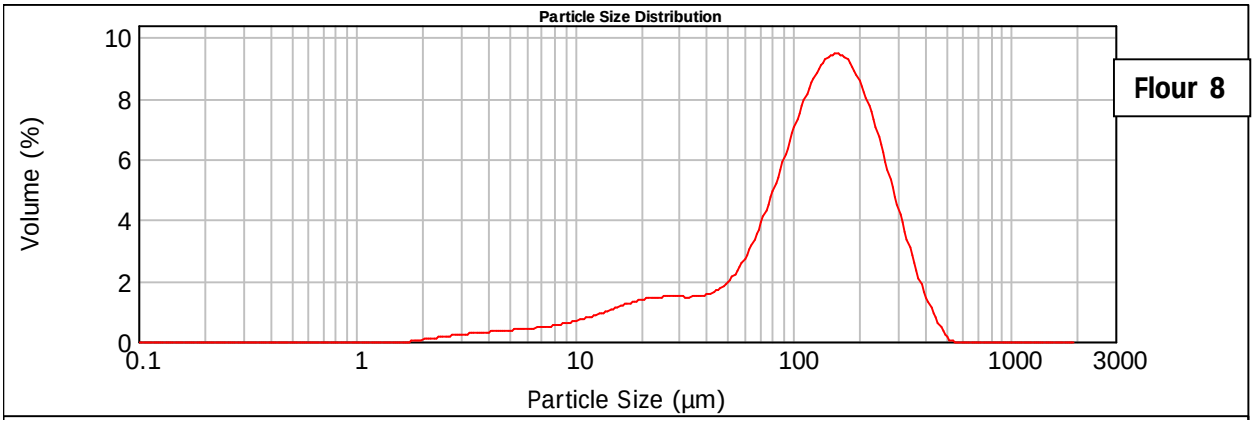
8.2 Particle size distributions of all examined flours

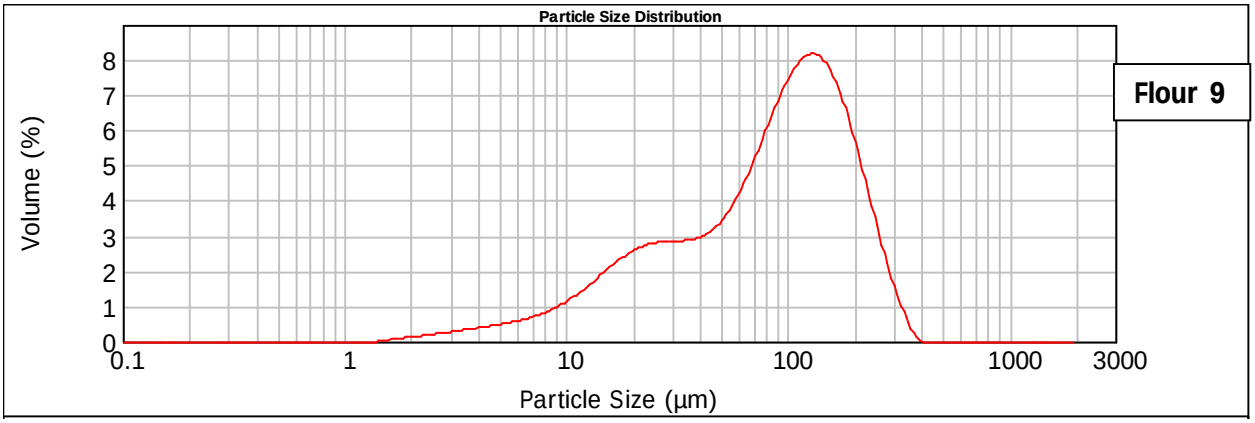


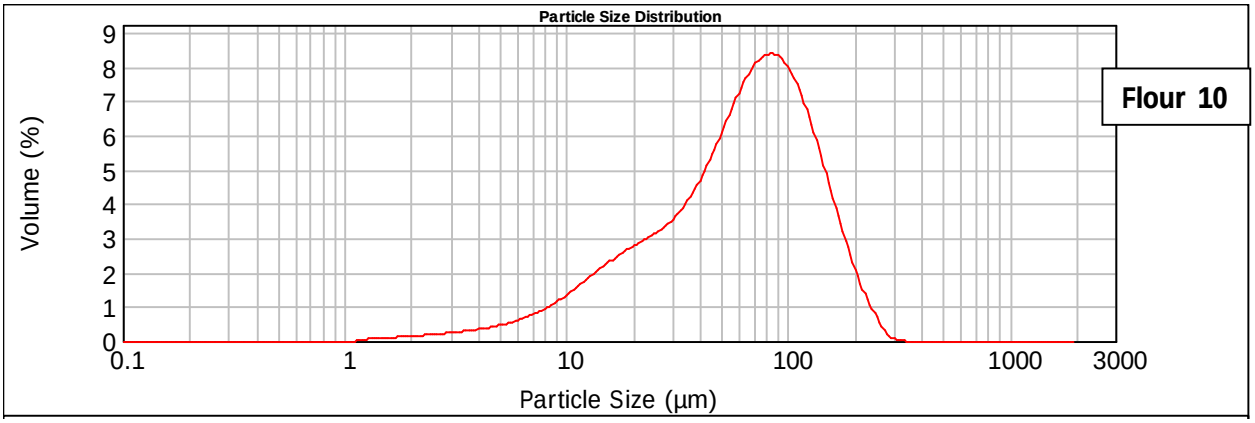

Particle Size Distribution
Volume (%)
0
1
2
3
4
5
6
7
0.1
1
10
100
1000
3000
Particle Size (µm)
Flour 5

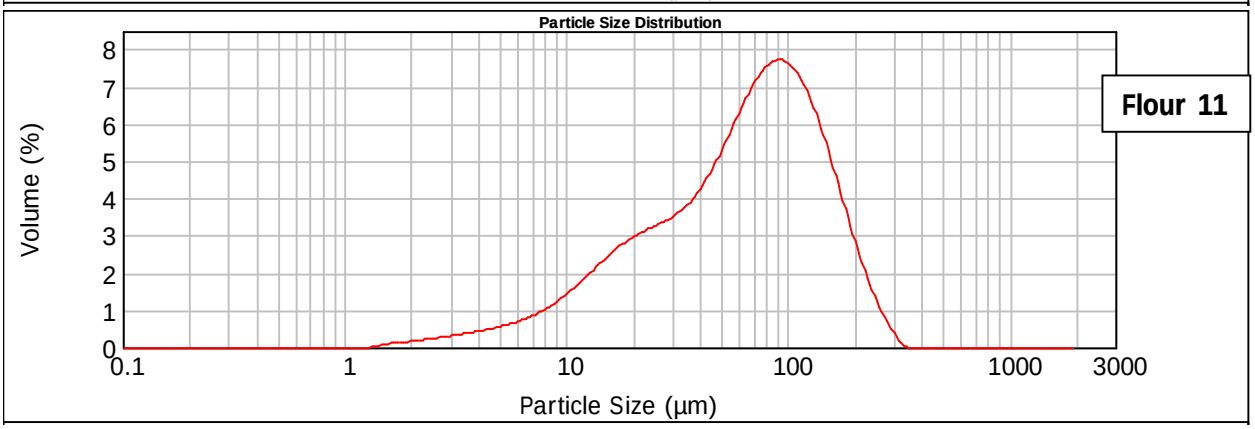

Particle Size Distribution
Volume (%)
0
1
2
3
4
5
6
7
8
9
0.1
1
10
100
1000
3000
Particle Size (µm)
Flour 6


Particle Size Distribution
Volume (%)
0
1
2
3
4
5
6
7
8
0.1
1
10
100
1000
3000
Particle Size (µm)
Flour 7


Particle Size Distribution
Volume (%)
0
2
4
6
8
10
0.1
1
10
100
1000
3000
Particle Size (µm)
Flour 8


Particle Size Distribution
Volume (%)
0
1
2
3
4
5
6
7
8
0.1
1
10
100
1000
3000
Particle Size (µm)
Flour 9


Particle Size Distribution
Volume (%)
0
1
2
3
4
5
6
7
8
9
0.1
1
10
100
1000
3000
Particle Size (µm)
Flour 10


Particle Size Distribution
Volume (%)
0
1
2
3
4
5
6
7
8
0.1
1
10
100
1000
3000
Particle Size (µm)
Flour 11

8.3 List of tables

8.4 List of figures

8.5 Abbreviations

% (v/v)	volumetric percentage
°Bx	Brix grade(s)
µg	micro gram(s)
µl	micro litre(s)
µm	micrometre(s)
A	Area
AFM	atomic force microscopy
AS	amplitude sweep
BBP	butyl-benzyl-phthalate
BP	benzophenone
cm	centimetre(s)
CSR	controlled shear rate
CSS	controlled shear stress
D	diffusion coefficient
d	day(s)
dm^2	square decimetre(s)
DPP	diphenylphthalate
EC	European Commission
EFSA	European Food Safety Agency
EU	European Union
FS	Frequency sweep
G’	storage modulus
G’’	loss modulus
h	hour(s)
HALS	(sterically) hindered amine light stabilizers

HDPE	High density poly ethylene
Hz	Hertz
IS	internal standard
K	partition coefficient
kg	kilogram(s)
LDPE	low density polyethylene
LDPE	Low density poly ethylene
LLDPE	linear low density polyethylene
LOAEL	lowest observed adverse effect level
LVR	linear visoelastic range
mg	milligram(s)
ml	milli litre(s)
NIAS	non-intentionally added substances
nm	nanometre(s)
NOAEL	no observed adverse effect level
OCT	optical coherence tomography
OML	overall migration limit
PAM	photo acoustic microscopy
PAT	photo acoustic tomography
PET	Poly ethylene glycol terephthalate
PP	Poly propylene
PPA	production process aids
PPPO	Poly(2,6-diphenyl-p-phenylene oxide)
PS	Poly styrene
PS-E	expanded poly styrene
PVC	Poly vinyl chloride
SEM	Scanning electron microscopy
SML	specific migration limit
UV	ultra-violette
WHC	water holding capacity [%]

Greek symbols:

δ	loss angle
$\tan \delta$	loss factor
η	apparent viscosity
η^*	complex viscosity
τ	shear stress
τ_0	flow point
τ_{HB}	Herschel-Bulkley-flow point
ω	angular frequency